Université du Québec
Institut National de la Recherche Scientifique
Centre Eau Terre Environnement

RÉCUPÉRATION PAR VOIE HYDROMÉTALLURGIQUE DES MÉTAUX À PARTIR DES DÉCHETS DE PILES MÉLANGÉES

Par

Kulchaya Tanong

Thèse présentée pour l'obtention
du grade de Philosophiae Doctor (Ph.D.)
en sciences de l'eau

Jury d'évaluation

Examinateur externe	Sébastien Sauvé Université de Montréal
Examinateur externe	Maria Elektorowicz Université Concordia
Examinateur interne	Mario Bergeron INRS-ETE
Codirecteur de recherche	Guy Mercier INRS-ETE
Directeur de recherche	Jean-François Blais INRS-ETE

AVANT-PROPOS

Cette étude présente les travaux réalisés afin de développer et d'optimiser un procédé de récupération des métaux à partir d'un mélange de déchets de piles par voie hydrométallurgique. Les résultats de ce projet de recherche ont mené à la rédaction d'un brevet et de six articles scientifiques. Cette thèse est divisée en deux parties.

La première partie présente la synthèse de ce projet de doctorat. Elle contient la revue de littérature en lien avec le projet et les principaux résultats obtenus.

La deuxième partie présente les six articles publiés, acceptés ou soumis dans des journaux internationaux:

Tanong K., J.F. Blais et G. Mercier (2014) Metal recycling technologies for battery waste. *Recent Patents on Engineering*, 8, 13-23.

Tanong K., L. Coudert, G. Mercier et J.F. Blais (2016) Recovery of metals from a mixture of various spent batteries by a hydrometallurgical process. *Journal of Environmental Management*, 181, 95-107.

Tanong K., L. Coudert, G. Mercier et J.F. Blais (2016) Study of the factors influencing the metals solubilisation from a mixture of waste batteries by response surface methodology. *Environmental Technology*, (article corrigé et retourné le 5 décembre 2016).

Tanong K., L.H. Tran, L. Coudert, G. Mercier et J.F. Blais (2016) Recovery of Zn from unsorted spent batteries using solvent extraction and electrodeposition. *Journal of Environmental Engineering* (article à soumettre en Janvier 2017).

Tanong K., L.H. Tran, , L. Coudert, G. Mercier et J.F. Blais (2016) Selective recovery of Cd (II), Mn(II) and Ni(II) from unsorted spent batteries using solvent extraction and electrodeposition. *Hydrometallurgy* (article à soumettre en Janvier 2017).

Tanong K., L.H. Tran, G. Mercier et J.F. Blais (2016) Recovery of Zn (II), Mn (II), Cd (II) and Ni (II) from unsorted spent batteries using solvent extraction, electrodeposition and precipitation methods. *Journal of Cleaner Production* (article soumis le 23 août 2016).

Demande de Brevet déposée au Canada

Blais J.F., G. Mercier, **K. Tanong**, L.H. Tran et L. Coudert (2015) *Method for recycling valuable metals from spent batteries*. Demande de brevet au Canada No. 2,915,371 (15 décembre 2015).

REMERCIEMENTS

Je tiens à remercier spécialement les professeurs Jean-François Blais et Guy Mercier, mes directeur et co-directeur de thèse, pour leur disponibilité en tout instant, leur soutien moral et l'encouragement qu'ils m'ont apporté durant mes études. Je remercie également les assistants de recherche et les associées de recherche Madame Myriam Chartier, Madame Nassima Kemache, Madame Lan Huong Tran et Madame Lucie Coudert pour leur aide et leurs conseils. Je remercie particulièrement l'associée de recherche Madame Lan Huong Tran pour son aide précieuse et ses conseils, surtout pour son soutien moral durant mes études. Je remercie aussi Madame Lucie Coudert pour sa disponibilité pour la correction de mes rapports et de mes publications. Je remercie également les professeurs Maria Elektorowicz, Sébastien Sauvé et Mario Bergeron d'avoir accepté d'évaluer ce travail. Je remercie Anne Carabin, Leila Ghorbel, Julien Mocellin, Alia Ben Ghacham, Oumar Dia, Louis-César Pasquier, Clémence Jouveau Du Breuil, Tengfei Xu, Vincent Taillard, Marie Le Pivert pour leur amitié et les moments de bonheur partagés avec eux. Je remercie tous les amis Thaïlandais au Québec et à l'Université Laval pour leur amitié et le bonheur partagés entre nous au Canada. Je remercie également toutes les équipes du laboratoire pour leur soutien et je leur souhaite bonne chance pour la suite. Enfin, j'aimerais aussi remercier tout particulièrement mon conjoint, Florent Pourcel ainsi que ma mère Rattana Tanong, mon père Aphichart Tanong, ma belle mère Marie-Dominique Pourcel, mon beau père Bernard Pourcel et ma belle soeur Camille Pourcel pour le soutien moral, l'aide et la disponibilité qu'ils m'ont apportés durant mes études. Je dois également remercier tous mes amis en Thaïlande, je souhaite vous revoir très bientôt.

RÉSUMÉ

Au Canada, près de 671 millions d'unités(Mu) de piles primaires (piles non rechargeables) ont été vendues en 2015, dont près de 173 Mu pour la province de Québec. Concernant les piles secondaires (piles rechargeables), des ventes de 22 Mu étaient attendues au Canada en 2015.

Actuellement, seulement 10% des piles usagées mises au rebut sont recyclées, les 90% restantes sont incinérées ou enfouies avec les déchets domestiques. Par conséquent, plusieurs milliers de tonnes de déchets sont envoyées chaque année vers des lieux d'élimination (sites d'enfouissement ou incinérateurs) en raison du manque de technologies innovantes et rentables permettant de les recycler.

Dans les procédés existants, le tri manuel limite considérablement le potentiel de recyclage des déchets de piles en raison des coûts élevés de main d'œuvre et du manque de technologies existantes. Le développement d'une nouvelle filière de traitement des déchets de piles sans tri manuel préalable est fortement encouragé d'un point de vue environnemental et économique. De plus, les métaux présents dans les déchets de piles sont des éléments inorganiques à haute valeur ajoutée.

Ce projet de recherche s'intéresse au recyclage et à la valorisation des métaux d'intérêt, tels que le zinc (Zn), le manganèse (Mn), le cadmium (Cd) et le nickel (Ni) présents dans les déchets de piles mélangées. Le mélange des piles usagées contient des piles alcalines, piles Zn-C, piles Ni-Cd, piles Ni-MH, piles Li-ion et piles Li-M. La proportion de chaque type de piles est estimée selon les quantités de piles usagées actuellement disponibles dans les sites de recyclage.

Une filière technologique de traitement a donc été mise au point afin de récupérer les métaux présents dans un mélange représentatif de déchets de piles. Les piles usagées ont d'abord été déchiquetées manuellement, puis tamisées et broyées afin d'obtenir une poudre fine homogène. Les métaux contenus dans cette poudre fine ont ensuite été solubilisés en présence d'un acide inorganique et d'un agent réducteur qui est utilisé pour favoriser la dissolution du Mn(IV). Plusieurs acides (organiques et inorganiques) ont été testés à 20 et 80°C et le meilleur rendement de solubilisation a été obtenu à 20°C avec l'acide sulfurique. L'optimisation des conditions opératoires telles que la concentration en acide, le ratio solide/liquide, le temps de résidence et le nombre d'étapes de lixiviation a été réalisée en utilisant le modèle Box-Behnken. Dans les conditions optimales (1,34 M H_2SO_4, ratio solide/liquide de 10%, temps de réaction de 45 min et 0,45 g de $Na_2S_2O_5$/g de poudre de piles), le lixiviat obtenu contenait du Mn (29 g/L), du Zn (21 g/L), du Cd (3,6 g/L), du Ni (4,5 g/L), du Co (0,3 g/L) et du Fe (0,7 g/L), ainsi que du Li à l'état de traces (< 0,08 g/L).

Après l'étape de solubilisation, le zinc a été récupéré sélectivement par extraction par solvant suivie d'une étape d'éléctrodéposition. La combinaison des deux méthodes a permis la récupération de 123 kg de Zn/t de poudre de piles avec une pureté de 99%. Un mélange consitué de 20% à 30% de Cyanex 272 (Acide di(2,4,4-triméthylpentyl)phosphinique) et de 2% de TBP (tributyl phosphate) a été utilisé comme solvant d'extraction. Le temps de réaction était de 10 min et le ratio phase organique/phase aqueuse (O/A) de 2/1 (v/v). Deux étapes d'extraction à 50°C ont été nécessaires pour maximiser la récupération du zinc. L'étape d'électrodéposition a été effectuée à un pH = 2 pendant 180 min en utilisant une densité de courant de 370 A/m^2.

La solution aqueuse appauvrie en zinc a ensuite été mélangée avec 30% de D2EHPA (acide di-(2-éthylhexyl) phosphorique) et 5% de TBP pour une co-extraction du cadmium et du manganèse. Ce solvant a été choisi pour cette étape à cause de sa grande capacité d'extraction à pH acide. L'étape d'extraction a été suivie par une éléctrodéposition pour récupérer sélectivement 34 kg de Cd/t de poudre de piles sous forme métallique pure à 98%. Le temps de réaction est moins long pour la solution synthétique (90 min) et plus élevé pour la solution réelle (240 min).

Après la récupération du cadmium par une électrodéposition sélective, le pH de la solution a été ajusté à 9 par ajout de NaOH et de Na_2CO_3 afin de précipiter le manganèse sous forme de carbonates. Une quantité de 550 kg/t de $MnCO_3$ a été récupérée avec une pureté de 94% après deux étapes de lavage avec de l'eau distillée.

Après avoir récupéré le Zn, le Mn et le Cd, les impuretés ont été éliminées à pH = 5,9 en utilisant du Cyanex 272 qui a une grande affinité pour le cobalt (ratio O/A = 0,5/1, une étape d'extraction, température = 50°C, temps de réaction = 10 min, 5% TBP). Une solution pure de $NiSO_4$ a été obtenue et après ajout de Na_2CO_3, le nickel a été récupéré sous forme de carbonates (36 kg Ni/t de poudres de piles) purs à 98% (pH = 9, deux étapes de lavage).

ABSTRACT

In Canada, nearly 671 million units of the primary batteries (non-rechargeable) were sold in 2015 and approximately 173 million units in the province of Quebec. Regarding to the secondary cells (rechargeable batteries), sales of 22 million units were expected in Canada in 2015.

Currently, only 10% of used batteries are recycled, the remaining 90% is incinerated or landfilled with the household waste. Consequently, thousands tons of wastes are sent to any available disposal sites each year (landfill or incineration) due to the lack of innovative and cost-effective recycling technologies.

Nowadays, manual sorting considerably limits the potential for waste batteries recycling because of the high labor costs and the lack of feasible technologies. The development of a new battery waste treatment system without manual sorting is strongly encouraged from an environmental and an economic perspective. Additionally, metals present in the waste batteries represent a high-value market.

This research focuses on the recycling and the recovery of metals of interest, such as zinc (Zn), manganese (Mn), cadmium (Cd) and nickel (Ni) present in the mixture of waste batteries. The mixture of waste batteries is mainly composed of alkaline batteries, Zn-C batteries, Ni-Cd, Ni-MH, Li-ion batteries and Li-M batteries. The proportion of each type of battery is estimated by the quantity of batteries currently available for recycling in the province of Quebec.

The waste batteries treatment system has been developed to recover the metals from a representative mixture of waste batteries in the present study. Spent batteries are first shredded manually, then sieved and milled to obtain a homogeneous fine powder. The metals contained in this fine powder were then solubilized in the presence of an inorganic acid and a reducing agent which is used to promote the dissolution of Mn(IV). Various types of acids (organic and inorganic) were tested at 20 and 80°C and the best yield of solubilization was obtained at 20°C with sulfuric acid. The optimization of operating conditions such as the acid concentration acid, the solid/liquid ratio, the residence time and the number of leaching stages was carried out by applying a Box-Behnken design. Under the optimal conditions (1.34 M H_2SO_4, solid/liquid ratio = 10%, 45 min of reaction time and 0.45 g $Na_2S_2O_5$/g of batteries powder), the leachate obtained mainly contained Mn (29 g/L), Zn (21 g/L), Cd (3.6 g/L), Ni (4.5 g/L), Co (0.3 g/L), Fe (0.7 g/L) as well as some traces of Li (<0.08 g/L).

After the solubilization step, the zinc has been selectively recovered by solvent extraction followed by an electroplating step. The combination of the two methods has enabled the recovery of 123 kg Zn/t of waste battery powder with a purity of 99%. A mixture of 20% to 30% of Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) and 2% TBP (tributyl phosphate) was used as the extractant solvent. The reaction time was fixed at 10 min and the organic/aqueous (O/A) ratio at 2/1. Two extraction steps at 50°C were required to maximize the zinc recovery. The electrodeposition step was carried out at pH = 2 for 180 min using a current density of 370 A/m^2.

The Zn-depleted aqueous solution was then mixed with 30% of D2EHPA (phosphoric acid dialkyl) and 5% of TBP to simultaneously extract the cadmium and the manganese. This solvent has been chosen for this step because of its high extraction capacity in acidic condition. After the extraction step, the electroplating was applied to selectively recover 34 kg Cd/t waste battery powder in a pure metallic form (98%). The electroplating reaction time is shorter for the synthetic solution (90 min) and higher for the real solution (240 min).

After removing cadmium from the solution by selectively electroplating, the pH of the solution was adjusted to 9 by an addition of NaOH and Na_2CO_3 to precipitate the manganese as carbonates. An amount of 550 kg/t of $MnCO_3$ was recovered with a purity of 94% after two washing steps with distilled water.

After Zn, Mn and Cd recoveries, the impurities were removed from the effluent at pH = 5.9 using 10% of Cyanex 272 that is selective for cobalt in the presence of nickel (O/A ratio = 0.5/1, one extraction step, temperature = 50°C, reaction time = 10 min and 5% TBP). A pure solution of $NiSO_4$ was obtained after the previous step. The nickel was precipitated with Na_2CO_3, $NiCO_3$ with (36 kg Ni/t of batteries powder) 98% purity (pH = 9, two washing steps) was finally obtained as a final product.

TABLE DES MATIÈRES

LISTE DES TABLEAUX

LISTE DES FIGURES

LISTE DES ÉQUATIONS

LISTE DES ABRÉVIATIONS

$(HR)_2$:	Solvant organique
$(NH_4)_2CO_3$:	Carbonate d’ammonium
$[M_{aq}]$:	Concentration des ions métalliques en phase aqueuse
$[M_{org}]$:	Concentration des ions métalliques dans la phase organique
AgCl:	Chlorure d’argent
$Ca(OH)_2$:	Hydroxyde de calcium
$CaCO_3$:	Carbonate de calcium
CaO:	Oxyde de calcium
CCME:	Conseil Canadien des Ministres de l’Environnement
$CdSO_4$:	Sulfate de cadmium
Cyanex 272:	Acide di (2,4,4-triméthylpentyl) phosphonique ($C_6H_{34}POOH$)
Cyanex 302:	Acide bis-(2,4,4 - triméthylpentyl) monothiophosphonique ($C_6H_{34}PSOH$)
Cyanex 921:	Oxyde Tri n octyl phosphinique (Mélange d’oxydes n octyl et n hexyl phosphinique)
Cyanex 923:	Oxyde tri alkyl phosphonique ($C_{24}H_{51}PO$)
D2EHPA:	Acide di (2-éthylhexyl) phosphorique
D_M:	Coefficient de distribution
D_{MA}:	Coefficients de distribution des métaux A
D_{MB}:	Coefficients de distribution des métaux B
FeS:	Sulfure de fer
H_2O_2:	Peroxyde d’oxygène
H_2S:	Sulfure d’hydrogène
H_2SO_4:	Acide sulfurique
HCl:	Acide chlorhydrique
INMETCO:	International Metals Reclamation Company
KOH:	Hydroxyde de potassium
L:	Ligand
LIX63:	5,8-diéthyl-7-hydroxy- dodécan-6-oxime
M:	Million d’unités
MDDELCC:	Ministère du Développement Durable, de l'Environnement et de la Lutte contre les Changements Climatiques
$Mg(OH)_2$:	Hydroxyde de magnésium
M^{m+}:	Ions métalliques dans la phase aqueuse
$MnCO_3$:	Carbonate de manganèse
MnO, Mn_2O_3, Mn_3O_4:	Oxydes de manganèse
MnO_2:	Dioxyde de manganèse
$MnSO_4$:	Sulfate de manganèse
$MR_2(HR)_{2n-2}$:	Espèce complexée (métal-organique)
Mt	Millions de tonnes métriques

Na_2CO_3:	Carbonate de sodium
Na_2S:	Sulfure de sodium
NaOH:	Hydroxyde de sodium
NH_4OH:	Hydroxyde d’ammonium
Ni-Cd:	Nickel - cadmium
$NiCO_3$:	Carbonate de nickel
Ni-MH:	Nickel - hydrure de métal
PA:	Polyamide
PEG :	Polyéthylène glycol
PVC:	Polyvinylchlorure
R:	Hydrocarbures à longue chaîne composant le solvant organique
RBRC:	Rechargeable Battery Recycling Corporation
RDD:	Résidus Domestiques Dangereux
rpm:	Rotations par minute
S/L:	Solide/liquide
S:	Concentration de ligand dans la phase organique
$ß_{A/B:}$	Facteur de séparation
TBP:	Tributyl phosphate
tm	Tonne métrique
Zn-C:	Zinc - carbone
ZnO:	Oxyde de zinc

PARTIE I: SYNTHÈSE

1 SYNTHESE

1.1 Introduction

Au cours des dernières décennies, les avancées technologiques ont entraîné une augmentation importante des quantités de déchets électroniques produits annuellement à travers le monde. Chaque année, plus de 50 millions de tonnes métriques (Mt) de déchets électroniques sont produits à travers le monde (Namias, 2013). Selon RIS international, une production de 15 327 tonnes (t) de déchets de piles avait été estimée pour le Canada en 2010 (RIS international, 2007). Ces déchets sont composés en moyenne de 50% de fer et d'acier, 21% de plastique, 13% de métaux non ferreux et 16% de divers constituants. Dans ces deux dernières catégories (métaux non ferreux et divers constitutants), des composés dangereux pour l'environnement sont présents, tels que l'arsenic (As), le cadmium (Cd), le chrome hexavalent (Cr(VI)), le mercure (Hg), le plomb (Pb) et le sélénium (Se). Une gestion inappropriée de ces déchets de piles peut entraîner une contamination des sols et des ressources en eau, suite à la dispersion de ces contaminants inorganiques dans la nature. Selon l'étude de l'Uniross, les piles secondaires ont 32 fois moins d'impact sur l'environnement que les piles primaires (Uniross, 2007), donc l'utilisation des piles secondaires doit être privilégiée pour protéger l'environnement.

La gestion des déchets de piles est devenue, au cours de ces dernières années, un défi environnemental et politique en raison des risques de lixiviation des métaux dans les sols et/ou dans les eaux souterraines lors de l'enfouissement. Diverses technologies de récupération et de recyclage de certains déchets de piles ont été développées et commercialisées dernièrement.

Cependant, le tri manuel des déchets de piles nécessaire pour l'application de ces technologies de traitement limite considérablement le potentiel de recyclage de ces déchets en raison des coûts élevés de main d'œuvre. Le développement de nouvelles filières de traitement des déchets de piles sans tri manuel préalable est fortement encouragé d'un point de vue environnemental et économique. En effet, les métaux présents dans les déchets de piles sont des éléments inorganiques à haute valeur; leur gisement étant de plus en plus rares et leur exploitation de plus en plus coûteuse.

L'objectif de ce doctorat est de développer une méthode de gestion adéquate des déchets de piles permettant de traiter simultanément l'ensemble des déchets de piles sans tri manuel au préalable et de récupérer les métaux à haute valeur sous une forme la plus pure possible pour les valoriser. La première partie de ce travail présente la revue de littérature, suivie par la méthodologie, ainsi que les résultats principaux. La deuxième partie est consacrée à la présentation des articles scientifiques issus de ces travaux de doctorat.

1.2 Revue de littérature

1.2.1 Contexte général

De nos jours, une grande variété de piles est commercialisée à travers le monde; parmi lesquelles, nous retrouvons (Friedli, 2005):

- *Les piles primaires ou non rechargeables*: les piles alcalines (Zn-MnO_2); les piles Zn-carbone; les piles oxyde de zinc; les piles lithium-dioxyde de manganèse; les piles bouton oxyde de zinc; les piles bouton oxyde d'argent;
- *Les piles secondaires ou rechargeables* (à partir d'une source d'électricité): les piles Ni-MH; les piles Li-ion; les piles Ni-Cd; les piles Li-polymère; les petites piles scellées au plomb-acide; les piles plomb-acide.

Aujourd'hui, il est impossible d'imaginer vivre sans piles. Elles sont la source d'énergie principale dans les appareils électroniques. Leur consommation augmente depuis des années avec la multiplication des produits électriques et électroniques. Dans les sections suivantes, seront discutées les caractéristiques importantes de chaque type de piles.

1.2.2 Types de piles

1.2.2.1 Piles Alcalines

Les piles alcalines représentent près de 10% des piles fabriquées à travers le monde. En Amérique du Nord, ces piles sont couramment utilisées et représentent près de 80% des piles commercialisées aux États-Unis et au Canada (Olivetti *et al.*, 2011).

Les piles alcalines sont composées d'une anode en zinc (Zn) et d'une cathode en dioxyde de manganèse (MnO_2) et graphite (carbone) (Almeida *et al.*, 2006). L'électrolyte est composé d'une solution très conductrice d'hydroxyde de potassium (KOH). Le Tableau 1.1 présente la composition générale des piles alcalines. Le processus de décharge des piles alcalines peut être décrit par les demi-réactions d'oxydo-réduction présentées aux Équations 1.1 et 1.2.

Demi-réaction de décharge à l'anode dans les piles alcalines:

Équation 1-1 $\mathbf{Zn_{(s)} + 2\ OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2\ e^-}$

Demi-réaction de décharge à la cathode dans les piles alcalines:

Équation 1-2 $\mathbf{MnO_{2(s)} + H_2O_{(l)} + e^- \rightarrow MnO(OH)_{(s)} + OH^-_{(aq)}}$

Tableau 1.1 Composition d’une pile alcaline Duracell AA (Almeida *et al.*, 2006)

Composition	Matériau	Poids sec moyen (g/pile)	Teneur en eau (%)
Enveloppe isolante	Acier	0,288	-
Isolant	Carton	0,060	6,4
Œillet plastique	Polyamide (PA)	0,215	1,4
Séparateur métallique	Acier	0,377	-
Collecteur anode	Laiton-étamé	0,438	-
Anode	Zn+ZnO+KOH	3,86	1,8 - 29
Séparateur	Papier	0,107	5,0
Cathode	MnO_2+C+KOH	11,9	8,0
Collecteur cathode	Acier	4,01	-
Feuille plastique	Polyvinylchlorure (PVC)	0,230	1,7
Total	-	23,5	-

1.2.2.2 Piles Zinc-Carbone

Les piles zinc-carbone (Zn-C) sont utilisées pour les appareils à faible consommation électrique comme les télécommandes, les lampes de poche, les horloges ou les radios à transistors (Sayilgana *et al.*, 2009). Les piles au Zn-C représentent 20% de l’ensemble des piles commercialisées au Royaume-Uni et 6% au Japon (Battery Association of Japan, 2011, The European Portable Battery Association, 2010). Les piles Zn-C sont des piles primaires. Leurs propriétés sont proches de celles des piles alcalines.

Les fractions fines de ces piles, qui contient les métaux sous forme d’oxyde, sont composées d’Al (0,03%), de Cr (0,01%), de Fe (0,52%), de K (4,74%), de Mn (30,1%), de Pb (0,01%), de Si (0,06%), de Ti (0,01%) et de Zn (19,1%) (Buzatu *et al.*, 2013b). Le processus de décharge est décrit aux Équations 1.3 et 1.4.

La demi-réaction de décharge à l’anode dans les piles Zn-C:

Équation 1-3 $\mathbf{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}$

La demi-réaction de décharge à la cathode dans les piles Zn-C:

Équation 1-4 $\mathbf{2\ MnO_{2(s)} + 2\ NH_4Cl + 2\ e^- \rightarrow Mn_2O_{3(s)} + 2\ NH_{3(g)} + H_2O_{(l)} + 2\ Cl^-_{(aq)}}$

1.2.2.3 Piles Nickel-hydrure de métal (Ni-MH)

Les piles Ni-MH sont couramment utilisées dans les véhicules électriques, en électronique (aspirateurs robotiques, voitures à contrôle à distance, etc.). Ce type de pile remplace les piles au cadmium qui sont plus toxiques.

En 2010, les piles Ni-MH représentaient 22% des piles vendues au Japon (Battery Association of Japan, 2011). En 2007, la vente de ces piles a été estimée à seulement 10% au Canada par RIS international (RIS international, 2007). Le Tableau 1.2 synthétise la composition des piles Ni-MH (Mantuano *et al.*, 2006).

Tableau 1.2 **Teneurs en métaux (%) mesurées dans les piles Ni-MH provenant de différentes entreprises (Mantuano *et al.*, 2006)**

Métal	Piles Ni-MH provenant de différentes entreprises			
	A	B	C	Moyenne
Al	0,81	0,94	0,85	0,90 ± 0,10
Cd	0,01	n.d.	n.d.	<0,01
Co	5,64	6,16	6,64	6,10 ± 0,70
Cu	0,02	-	-	0,02
Fe	0,09	0,06	0,15	0,10 ± 0,07
Li	0,05	0,07	0,10	0,07 ± 0,04
Mn	1,11	1,37	2,62	2,00 ± 1,00
Ni	46,8	52,8	47,9	49,0 ± 5,0
Pb	0,08	n.d.	n.d.	0,03 ± 0,07
Zn	1,56	0,01	1,13	1,00 ± 1,00

n.d: non détecté.

Le processus de décharge est décrit par les équations d'oxydo-réduction présentées aux Équations 1.5 et 1.6. Pendant la décharge, l'hydrogène est libéré à l'électrode négative et réagit avec les ions hydroxydes.

Les réactions de décharge à l'anode dans les piles Ni-MH:

Équation 1-5 $MH_{(s)} \rightarrow M_{(s)} + \frac{1}{2} H_{2\,(g)}$

Équation 1-6 $\frac{1}{2} H_{2\,(g)} + OH^{-}_{\ (aq)} \rightarrow H_2O_{\ (l)} + e^{-}$

La demi-réaction de décharge à la cathode dans les piles Ni-MH:

Équation 1-7 $NiOOH_{(s)} + H_2O_{(l)} + e^{-} \rightarrow Ni(OH)_{2(s)} + OH^{-}_{(aq)}$

1.2.2.4 Piles Lithium-Ion (Li-Co, Li-Mn ou Li-Ni)

Les piles Li-ion sont couramment utilisées dans les téléphones portables, les véhicules électriques, les ordinateurs, etc. (Li *et al.*, 2009). La production mondiale de ces piles a été estimée à environ 660 Mu en 2012 et les prédictions pour les années à venir sont en hausse (Cuthbertson, 2014).

Durant la décharge, les ions Li se déplacent de l'anode vers le métal actif constituant la cathode, ce phénomène fournit de l'énergie au circuit externe (Sloop *et al.*, 2007). Le processus de décharge de cette pile est décrit par les équations d'oxydo-réduction présentées aux Équations 1.8 et 1.9.

La demi-réaction de décharge à l'anode dans les piles Li-ion:

Équation 1-8 $\mathbf{Li_{(s)} \rightarrow Li^{+}_{(aq)} + e^{-}}$

La demi-réaction de décharge à la cathode dans les piles Li-ion:

Équation 1-9 $\mathbf{Li^{+}_{(aq)} + e^{-} + MnO_{2(s)} \rightarrow LiMnO_{2(s)}}$

1.2.2.5 Piles Nickel-Cadmium

Les piles nickel-cadmium (Ni-Cd) sont utilisées dans les outils électriques portatifs tels que le matériel de photographie, les lampes de poche, les éclairages de secours, etc. Au cours de ces dernières années, les ventes de piles Ni-Cd représentaient seulement 19,9% de l'ensemble des ventes de piles secondaires aux Canada (RIS international, 2007). Leur commercialisation et leur utilisation sont fortement restreintes du fait de la toxicité du Cd.

Les piles au Ni-Cd sont principalement composées de Cd (25%), Co (0,9%) et Ni (51%) (Nogueira *et al.*, 2004). Selon Huang *et al.* (2009), les constituants suivants peuvent être présents en plus faibles proportions: Co, Fe, Li, Mn et Zn. Le processus de décharge des piles Ni-Cd est décrit par les Équations 1.10 et 1.11.

La demi-réaction de décharge à l'anode dans les piles Ni-Cd:

Équation 1-10 $\mathbf{Cd_{(s)} + 2\ OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2\ e^-}$

La demi-réaction de décharge à la cathode dans les piles Ni-Cd:

Équation 1-11 $\mathbf{2\ NiOOH_{(s)} + 2\ H_2O_{(l)} + 2\ e^- \rightarrow 2\ Ni(OH)_{2(s)} + 2\ OH^-_{(aq)}}$

1.2.2.6 Piles Lithium-primaire

Les piles lithium-primaire sont principalement destinées aux applications nécessitant une longue durée de vie (GPI International, 2009). La distribution de ces piles représente seulement 0,1% des ventes au niveau du marché canadien (RIS international, 2007). Les piles au lithium-primaire sont généralement constituées de 0,8% Al, de moins de 0,1% Co, 0,1% Cu, 3,0% Fe, 5,5% Li, 37% Mn et 0,12% Ni (Granata *et al.*, 2012). Le processus de décharge des piles Li-primaire est décrit aux Équations 1.12 et 1.13 (Cook et Wagner, 2013).

La demi-réaction de décharge à l’anode dans les piles Li-primaires:

Équation 1-12 $\mathbf{x\ Li_{(s)} \rightarrow x\ Li^{2+}_{(aq)} + x\ e^-}$

La demi-réaction de décharge à la cathode dans les piles Li-primaires:

Équation 1-13 $\mathbf{2\ SOCl_{2\ (aq)} + 4\ e^- \rightarrow 4\ Cl^-_{(aq)} + SO_{2(g)} + S_{(s)}}$

1.2.3 Métaux présents dans les déchets de piles et leur toxicité

Le Tableau 1.3 indique les propriétés chimiques des métaux présents dans les déchets de piles, leur utilisation et leur toxicité.

1.2.4 Gestion des déchets de piles usagées à l’échelle mondiale

1.2.4.1 Cas de la France

La France suit le règlement de l’Union Européenne dans le cadre de la directive 2006/66/CE sur la gestion des piles en fin de vie. Les objectifs visent 1) à collecter plus de 45% de piles et d’accumulateurs en 2016; 2) à augmenter le rendement du recyclage: 65% pour les piles au Pb, 75% pour les piles Ni-Cd et 50% pour les autres accumulateurs; 3) et à éliminer les substances toxiques présentes dans les piles comme le Cd ou le Hg (Monier *et al.*, 2014).

Tableau 1.3 **Récapitulatif des propriétés chimiques des métaux, leur utilisation et leur toxicité**

Métal	Masse molaire (g/mol)	Forme la plus présente dans la nature	Utilisation	Toxicité
Cd	112,4	$CdCl^+$, $CdOH^+$, $CdCl_3^-$ et $CdCl_4^{2-}$	Les usines de fabrication des piles Ni-Cd, les revêtements, les pigments, les alliages, les plastiques, les fils téléphoniques, les huiles à moteur, etc. (Environnement Canada, 1999)	Dommages aux reins, nécrose et/ou disfonctionnement rénal, œdème pulmonaire, cancers des poumons ou de la prostate (Fowler, 2009)
Mn	54,94	Mn^{2+}, Mn^{3+}, Mn^{4+}, Mn^{6+} et Mn^{7+}	Les alliages, les aciers, les agents anti-corrosion (Housecroft *et al.*, 2010)	Troubles de développement intellectuel chez les enfants, troubles de la reproduction, malformations osseuses, ataxie et altérations du système nerveux central (WHO, 2001)
Ni	58,69	Ni^{2+}	Les aciers, les pièces de monnaie, les bijoux, les équipements dans la cuisine, les batteries, etc. (Housecroft, 2010)	Dermatites, asthme chronique, maladies cardiovasculaires ou rénales et cancers des poumons (Denkhaus *et al.*, 2002)
Zn	65,41	Zn^{2+}	Les aciers contre la corrosion, la production du laiton, les alliages, les toitures, les gouttières et les descentes d'eaux pluviales (International Zinc Association, 2010)	Dépression, léthargie, effets neurologiques, vomissements, irritation gastro-intestinale et cancers (Nriagu, 2007)

Dans le règlement français, la responsabilité du traitement des piles et des accumulateurs en fin de vie incombe aux producteurs. Ces derniers doivent donc déclarer les piles et les accumulateurs mis sur le marché ainsi que leurs procédés de collecte et de traitement des produits usagés. Les opérateurs de traitement doivent également déclarer les quantités de piles traitées.

La collecte des piles et des accumulateurs en fin de vie en France est majoritairement effectuée par deux éco-organismes: COREPILE et SCRELEC.

1.2.4.2 Cas de la Belgique

En Belgique, comme en France, la gestion des piles est régie par la directive 2006/66/CE. En 2012, les producteurs et les distributeurs devaient payer une cotisation fixe d'environ 657 $, ainsi qu'une contribution proportionnelle à la gestion des piles qu'ils ont produites (0,1628 $ par pile ou accumulateur produit) (Charette, 2014b). La cotisation à la collecte et au recyclage était gérée par BEBAT (Éco-organisme responsable de la gestion des déchets de piles). Les consommateurs peuvent déposer les piles dans les différents points de collecte, qui sont faciles à trouver sur le site internet de BEBAT. En 2014, la collecte des piles usagées par BEBAT a atteint 54,6%, ce qui a dépassé l'objectif européen fixé à 45% pour 2016 (BEBAT, 2016). Le traitement des déchets de piles est effectué par trois sociétés majeures en Belgique: CAMPINE SA, FMM-Fonderie et Manufacture de métaux S.A et ACCUREC S.A. Le procédé pyrométallurgique (procédé VARTA) et le procédé mécanique (procédé MA & CA) sont les principaux procédés utilisés pour traiter les piles usagées (Recybat, 2010).

1.2.4.3 Cas des États-Unis

Aux États-Unis, la gestion des piles grand public est différente dans chaque État. L'utilisation du Hg dans les piles alcalines, Zn-C et les piles à l'oxyde d'argent est interdite depuis 1993. Donc, les consommateurs peuvent jeter les piles alcalines achetées après 1993 avec les autres déchets résiduels (Charette, 2014b). Une association à but non lucratif nommée Call2Recycle collecte et traite les piles usagées gratuitement et particulièrement les piles secondaires. En 1996, *Battery Act* a mis en place les normes afin de gérer les piles Ni-Cd (Charette, 2014b). Il a été constaté que les piles Ni-Cd usagées accumulées sont transportées jusqu' à leur lieu de traitement par des camions de transport conventionnel et non par des camions de transport spécialisés (Charette, 2014b). En effet, les piles Ni-MH, Li-ion et Li-polymère ne sont pas considérées comme des matières dangereuses, sauf dans les États de la Californie et du New Jersey (Charette, 2014b). Les piles grand public sont ensuite traitées par l'entreprise Toxco et Kinsbursky Brother Inc.

1.2.4.4 Cas du Canada

Au Canada, le Conseil Canadien des Ministres de l'Environnement (CCME), a mis en œuvre le plan d'action pancanadien pour la responsabilité élargie des producteurs, il vise à renforcer la responsabilité des producteurs (Charette, 2014b). La gestion des déchets de piles est différente d'une province à une autre.

En Alberta, aucun programme ne s'applique systématiquement sur le recyclage des déchets de piles grand public (Charette, 2014b). Les piles usagées sont déposées dans différents points de collecte, puis récupérées par Call2Recycle. Dans cette province, il est interdit aux consommateurs de déposer les piles rechargeables parmi les matières résiduelles municipales. Au Manitoba, la responsabilité des producteurs impose des méthodes de récupération des piles grand public (Charette, 2014b). Ce sont les deux organismes Call2recycle et Recycle My Battery, qui s'occupent de la récupération et du traitement des déchets de piles.

Au Nouveau-Brunswick, la commission de gestion enviro-ressources du Nord-Ouest a mis en place un programme de recyclage de piles et instauré un service gratuit de récupération des déchets (Charette, 2014b).

En 2014, la composition des piles usagées recyclées au Canada a été estimée à 78,7% de piles alcalines, 2,2% de piles au lithium, 0,7% de piles Zn-C, 9,4% de piles Ni-Cd, 6,5% de piles Li-ion et 2,5% de piles Ni-MH (Klaassen et Lagourgue, 2015).

1.2.4.5 Cas du Québec

Les piles sont largement utilisées comme source d'énergie pour les équipements électriques en alimentation permanente ou en cas de secours. En 2012, près de 162 M de piles primaires ont été vendues uniquement au Québec, soit une consommation de 19,8 piles par habitant chaque année. Les ventes de piles au Québec sont en constante progression (+ 27 à + 35,5% en fonction du type de pile considéré). Par exemple, les ventes de piles au Zn-C ont augmenté de 19 M d'unités en 2004 à près de 44 M en 2007 et une hausse de 30% des ventes était attendue pour 2015 (basée sur des estimations) (Roberge, 2010a). Concernant les piles primaires au Li, les quantités vendues au cours de ces dernières années ont augmenté de 1,5 Mu en 2004 à près de 6,5 Mu en 2007, et une augmentation de 13% est prévue pour 2015 (basée sur des estimations) (Roberge, 2010a). La production de piles secondaires au Ni-Cd a connu une hausse de 3,8%

entre 2004 et 2007 mais une diminution de 67% est attendue pour 2015 (basée sur des estimations) en raison de l'interdiction de l'utilisation de ces piles en Europe et en Californie et en raison de leur remplacement par les piles Li-ion (Roberge, 2010a). Les Figures 1.1 et 1.2 montrent les quantités de piles primaires et secondaires vendues au Québec. Les données ont été citées à partir d'un document publié en 2010, en conséquence les quantités indiquées pour 2010 et 2015 sont basées sur des estimations.

Les quantités de piles commercialisées au Canada ont augmenté de 55% entre 2004 et 2007 et les prévisions pour le futur indiquent une augmentation importante des ventes dans les prochaines années. Concernant les piles primaires, une augmentation des ventes de 695 Mu en 2010 à 745 Mu en 2015 a été prévue. Concernant les piles secondaires, une baisse des ventes de 38 Mu en 2010 à près de 22 Mu en 2015 est attendue au Canada (Roberge, 2010a).

Les piles sont composées de métaux toxiques qui peuvent s'avérer problématiques lors de la gestion des déchets de piles. Les métaux contenus dans les piles sont le plus souvent présents sous une forme corrosive et réactive. Une fois libérés dans l'environnement, ils vont réagir et se recombiner selon différentes formes, les rendant encore plus difficiles à récupérer. Certaines de ces formes sont très facilement assimilables par les organismes vivants et peuvent parfois s'avérer très toxiques. Par conséquent, selon le règlement N°159, les piles sont considérées comme des Résidus Domestiques Dangereux (RDD) au Québec (Bourque, 2010). Une gestion efficace des piles usées est donc nécessaire en amont du traitement.

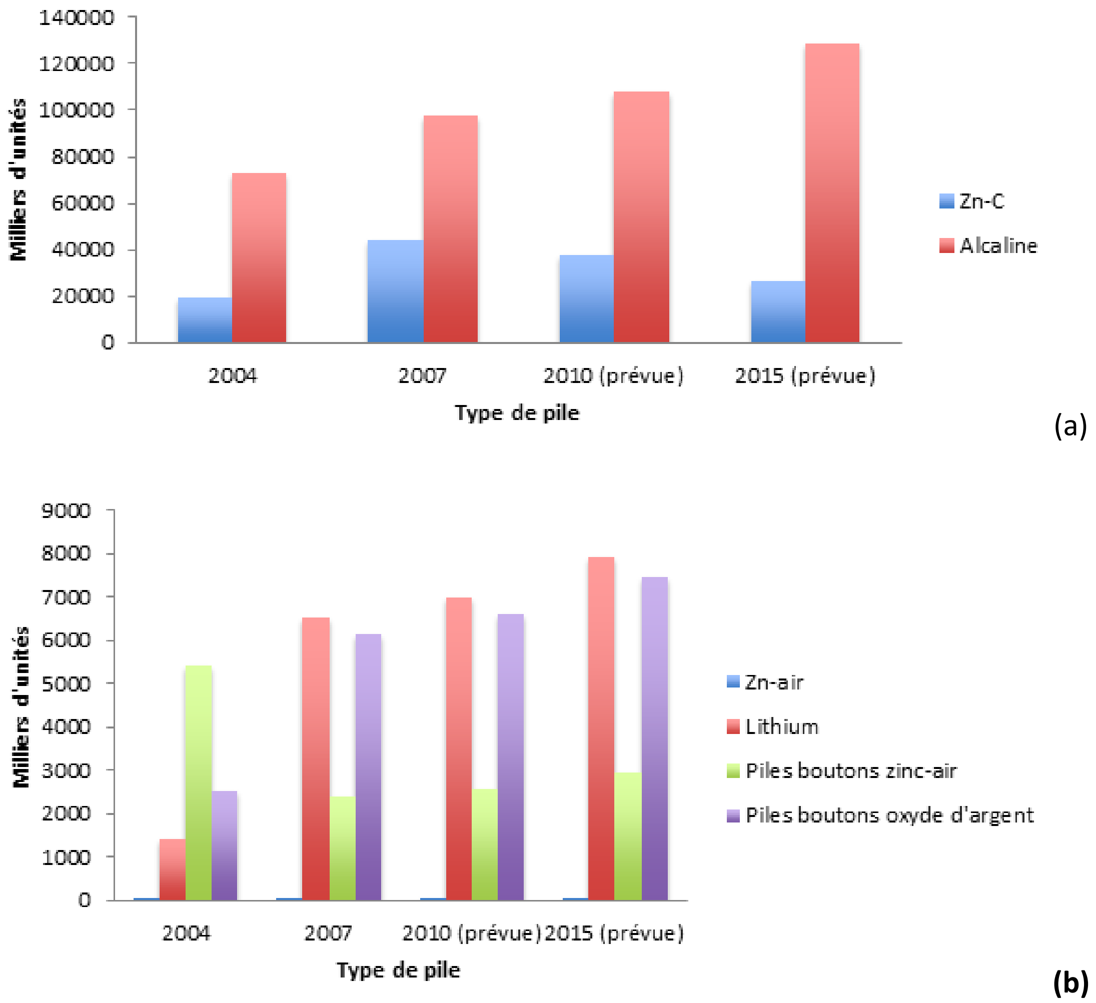


Figure 1.1 **Récapitulatif des vendues des piles primaire au Québec (J. Roberge, 2010a)**

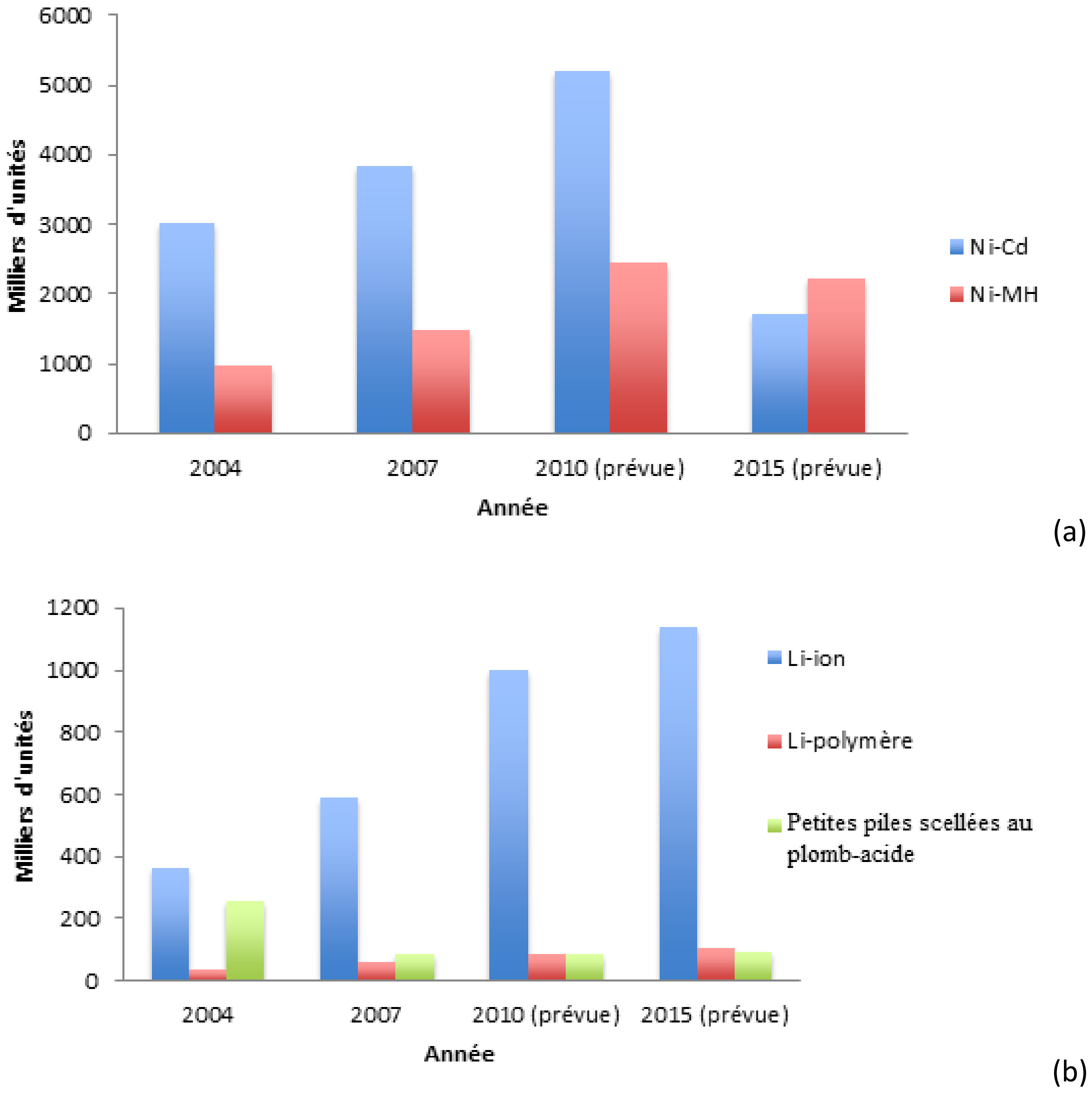


Figure 1.2 Récapitulatif des piles secondaires vendues au Québec (Roberge, 2010a)

1.2.4.6 Politique de gestion des matières résiduelles au Québec

Le plan d'action 2011-2015 mis en place dans la province de Québec vise à réduire les matières résiduelles, à améliorer leurs méthodes de gestion et à optimiser la performance des centres de tri des matières recyclables (Charette, 2014b). La politique en cours vise à impliquer davantage les producteurs et les utilisateurs dans la gestion des déchets. Ce programme permet de récupérer les matières résiduelles, de les éliminer et de financer des programmes de récupération et de mise en valeur (Charette, 2014b).

La mise en œuvre de la responsabilité élargie des producteurs a été démarrée par le MDDELCC (Ministère du Développement Durable, de l'Environnement et de la Lutte contre les Changements Climatiques) et Recyc-Québec (Charette, 2014b). Dans ce contexte, un programme gratuit de collecte de piles et de batteries, Appel à recycler, a été mis en place. Cet organisme à but non lucratif est financé par des éco-frais (0,004-0,24 $/unité de piles pour les piles primaires excepté les piles au lithium, 0,04-0,47 $/unité de piles pour les piles primaires (piles au lithium), 0,01-0,24 $/unité de piles pour les piles secondaires (MDDELCC, 2012)) perçus par les entreprises ayant l'obligation de collecter et de recycler les piles usagées (Call2Recycle, 2012). Cependant, seules les quantités de piles de moins de 5 kg sont acceptées (Charette, 2014b).

1.2.4.7 Récupération des piles au Québec

Au Québec, les piles usées sont collectées grâce à des points de dépôt et à des collectes municipales itinérantes. Les piles (rechargeables et non rechargeables) qui appartiennent à la filière des RDD sont collectées par des entreprises spécialisées comme Onyx, Clean Harbours, CRI Environment, Matrec, etc. Les piles non rechargeables sont traitées de manière sécuritaire par les entreprises telles que Stablex ou envoyées dans des sites d'enfouissement. Chez Stablex, les piles usagées sont stabilisées avant d'être solidifiées et enfouies de manière sécuritaire. Les piles rechargeables, quant-à-elles, sont collectées par le programme RBRC (Rechargeable Battery Recycling Corporation) avant d'être envoyées à Fort Érié en Ontario. Ces piles sont ensuite acheminées vers les installations d'International Metals Reclamation Company (INMETCO) en Pennsylvanie afin de récupérer les métaux présents dans ces piles usagées. En 2014, le taux de recyclage des piles primaires et des piles secondaires a été estimé à 1 740 492 kg et 550 769 kg, respectivement, au Canada (Klaassen et Lagourgue, 2015). Le taux de récupération est basé sur les quantités de piles mises sur le marché.

1.2.5 Procédés de traitement des déchets de piles

Au cours de ces dernières décennies, plusieurs procédés physiques, biologiques et/ou chimiques ont été développés afin de valoriser les métaux présents dans les déchets de piles usagées. Certains procédés de traitement des déchets de piles usagées ont été mis au point afin de gérer un ou plusieurs types de piles. Cependant, il n'existe pas à ce jour de procédé permettant de valoriser les métaux présents dans l'ensemble des déchets de piles mis au rebut de nos jours au Canada. La section suivante présente les procédés typiques utilisés pour traiter les déchets de piles avec quelques exemples de procédés appliqués à l'échelle laboratoire et/ou à l'échelle industrielle.

1.2.5.1 Procédés physiques

Les procédés physiques de traitement des déchets de piles usagées ne nécessitent pas l'utilisation de produits chimiques. Ils se basent sur l'exploitation des différentes propriétés physiques spécifiques des éléments métalliques présents telles que le poids spécifique, les propriétés magnétiques, la conductivité électrique, etc.

Plusieurs procédés physiques de traitement peuvent être utilisés afin de gérer les déchets de piles usagées et de valoriser les métaux qui y sont présents.

1.2.5.2 Procédés pyrométallurgiques

Le procédé est basé sur l'utilisation de températures élevées pour décontaminer ou traiter des matrices solides contenant des contaminants organiques et/ou inorganiques. Dans le cas des déchets de piles, plusieurs réactions peuvent avoir lieu au cours des procédés pyrométallurgiques tels que la décomposition des composés métalliques, la réduction d'un métal à partir de sa forme oxyde métallique, ou encore, l'évaporation des métaux ou de leurs composés.

Généralement, les procédés pyrométallurgiques sont réalisés dans des hauts fourneaux. Un mélange de castine (pierre calcaire), de coke et de fondant est utilisé. L'air est injecté au bas du four, ce qui entraîne la combustion complète du carbone en CO, ainsi qu'au-dessus du chargement. Après les réactions de réduction des oxydes métalliques, les métaux présents sous forme liquide sont récoltés par le bas du réacteur. Le mélange gazeux contenant les métaux est récolté puis refroidi par aspersion d'eau. Lors du refroidissement, les portions riches en métaux sont envoyées dans le condenseur ou à la raffinerie pour subir une étape de distillation et ce, en fonction de l'élément métallique présent.

1.2.5.3 Procédés biologiques

Les procédés de traitement biologique sont basés sur la capacité naturelle de certains microorganismes (bactéries et champignons) à transformer des composés métalliques solides en des formes solubles et extractibles. Des études ont mis en évidence que les bactéries acidophiles *Acidithiobacillus ferrooxidans* et *Sulfolobus sp.* peuvent s'avérer efficaces pour le recyclage des déchets de piles et de batteries (Pant *et al.*, 2012). Velgosova *et al.* (2013) ont étudié l'influence de l'acide sulfurique et des ions Fe^{3+} sur la biolixiviation du Cd présent dans les piles Ni-Cd usagées. Les résultats ont montré des rendements de biolixiviation atteignant 100% pour le Cd présent dans la cathode et 98% pour le Cd présent dans l'anode (Velgosova *et al.*, 2013). Les bactéries ferro-oxydantes utilisent le Fe(II) en solution comme source d'énergie. Le Cd ainsi oxydé est plus facilement solubilisé. Les coûts d'extraction par biolixiviation sont souvent plus faibles comparativement aux procédés chimiques mais les temps de réaction nécessaires sont plus longs (Ndlovu, 2008).

1.2.5.4 Procédés chimiques

Les procédés chimiques de lixiviation sont, quant à eux, basés sur l'utilisation de produits chimiques permettant la solubilisation des métaux contenus dans des déchets solides. De nos jours, les procédés hydrométallurgiques sont de plus en plus employés pour le traitement de déchets contenant des métaux.

Les procédés de lixiviation chimique développés au cours de ces dernières années génèrent des volumes importants d’effluents contenant des composés métalliques pouvant être valorisés. De nombreux modes de traitement chimique des effluents industriels contenant des métaux ont été développés. Parmi ces modes de traitement, les méthodes les plus répandues et les plus efficaces sont la précipitation-coagulation, l’adsorption sur résines échangeuses d’ions, l’électrodéposition ou l’extraction par solvant.

Dans le cadre de cette recherche, nous nous intéresserons uniquement aux technologies de traitement développées au cours de ces dernières qui sont applicables aux déchets de piles, et plus principalement aux piles qui alimentent les équipements électroniques.

1.2.5.5 Généralités sur les procédés de lixiviation

L’extraction des composés métalliques solubles présents dans un solide nécessite l’utilisation d’un solvant ou d’une solution de lixiviation appelée généralement « lixiviant ». Lors du traitement ou du recyclage de déchets, le composé métallique (hydroxyde, oxyde, carbonate, etc.) présent dans un déchet solide ou dans des boues est chimiquement solubilisé; produisant une solution concentrée en composés métalliques appelée « lixiviat ». Les métaux présents dans le lixiviat peuvent ensuite être récupérés par précipitation, par extraction au solvant ou par échange ionique, etc. Plusieurs facteurs peuvent influencer l’efficacité d’un procédé chimique de lixiviation, tels que les caractéristiques physico-chimiques du matériau à traiter, le type et la concentration de l’agent de lixiviation, la température, le temps de contact, etc.

1.2.5.6 Influence des paramètres sur la solubilisation des métaux

Lixiviation en présence d'agents complexants ou chélatants

Les agents complexants ou chélatants sont efficaces pour la solubilisation des métaux grâce à la formation de complexes ou de chélates solubles. Au cours de ces dernières années, de nombreuses études ont été réalisées afin d'évaluer l'efficacité de l'acide oxalique et de l'acide malique pour solubiliser les métaux sous forme de complexes solubles métaux-oxalates ou métaux-malates (Li *et al.*, 2012). Selon l'étude réalisée par Li *et al.* (2012), la plupart du Li présent dans les piles au Li peut être solubilisée en présence d'acide oxalique et de peroxyde d'hydrogène (catalyseur), alors que le Co ne se solubilise pas ou peu (Équation 1.14).

Équation 1-14 $4\ LiCoO_{2(s)} + 12\ C_4H_6O_{5(aq)} \rightarrow 4\ LiC_4H_5O_{5(aq)} + 4\ Co(C_4H_5O_5)_{2(aq)} + 6\ H_2O_{(l)} + O_{2(g)}$

D'après les résultats obtenus, seules la température et la concentration en ions oxalates impactent significativement l'efficacité du procédé alors que les autres facteurs ne sont pas influents. Les conditions optimales permettant d'obtenir le rendement le plus élevé (98% de $LiCoO_2$) sont une solution d'ions oxalates à 1 M, une température de 80°C, un temps de 120 min et un ratio solide/liquide (S/L) de 50 g/L.

Les ions ammonium peuvent former des complexes avec certains métaux tels que les ions Cu^{2+}, Cu^+ et Zn^{2+} (Bingol *et al.*, 2005) . La réaction de solubilisation mise en jeu lors de la solubilisation du Cu en présence d'hydroxyde d'ammonium (NH_4OH) et de carbonate d'ammonium ($(NH_4)_2CO_3$) est présentée à l'Équation 1.15 (Bingol *et al.*, 2005) .

Équation 1-15 $Cu_2(OH)_2CO_{3(s)} + 6\ NH_4OH_{(aq)} + (NH_4)_2CO_{3(aq)} \rightarrow 2\ Cu(NH_3)_4CO_{3(aq)} + 8\ H_2O_{(l)}$

Les résultats de cette étude montrent que la solubilisation du Cu augmente de 49% après 5 min de lixiviation à près de 80% après 240 min. Le meilleur rendement de solubilisation du Cu (98%) a été obtenu en présence de NH_4OH (5 M) et de $(NH_4)_2CO_3$ (0,3 M) après 120 min avec un ratio S/L fixé à 10% et une température fixée à 25°C sur des particules de taille < 450 µm.

Lixiviation en milieu basique

Certains hydroxydes et oxydes métalliques amphotériques (Zn, Sn, Pb, Al et Br) peuvent être solubilisés efficacement en milieu basique et plus particulièrement en présence d'hydroxyde de sodium (NaOH) (Équation 1.16). L'hydroxyde d'ammonium, quant à lui, peut être utilisé pour solubiliser certains métaux de transition (Co, Ni, etc.) présents dans les déchets solides sous forme d'hydroxydes (Équation 1.17).

Équation 1-16 $ZnO_{(s)} + 2\ NaOH_{(aq)} \rightarrow Na_2ZnO_{2(aq)} + H_2O_{(l)}$

Équation 1-17 $Ni(OH)_{2(s)} + NH_4OH_{(aq)} \rightarrow Ni(NH_3)_4(OH)_{2(aq)}$

Buzatu *et al.* (2013b) ont développé des procédés hydrométallurgiques pour le traitement des déchets de piles Zn-Mn, qui constituent 83% des déchets de piles mis au rebut. Les résultats de cette étude indiquent que près de 82% du Zn présent dans les piles Zn-C et 64% du Zn présent dans les piles alcalines peuvent être solubilisés en présence d'une solution alcaline ([NaOH] = 6 M) après 120 min de lixiviation.

Lixiviation en milieu acide

Les acides inorganiques (acide sulfurique, acide nitrique, acide chlorhydrique, etc.) et organiques (acide oxalique, acide citrique, acide tartarique, acide formique, etc.) ont été étudiés au cours de ces dernières années afin d'observer leur capacité à solubiliser les composés métalliques présents dans divers déchets solides, tels que le bois, le sol ou encore les déchets de piles. Selon l'étude réalisée par Li *et al.* (2012), les acides organiques peuvent être utilisés pour la solubilisation des métaux présents dans les déchets de piles. Les résultats obtenus sont présentés au Tableau 1.4. Li *et al.* (2005) ont étudié la solubilisation des métaux présents dans les piles Zn-MnO_2 en présence d'acide chlorhydrique. Les réactions de solubilisation mises en jeu sont présentées aux Équations 1.18 à 1.21. Les résultats obtenus par ces auteurs montrent que la solubilisation des métaux est augmentée (> 75%) avec l'augmentation de la concentration en acide chlorhydrique (HCl) et en présence de peroxyde d'oxygène (H_2O_2). De plus, les auteurs ont mis en évidence que l'utilisation d'un agent réducteur augmente de manière significative la solubilisation du Mn en raison de la transformation de MnO_2 en oxyde de manganèse (MnO), une forme plus soluble.

Équation 1-18 $MnO_{(s)} + 2\ H^{+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + H_2O_{(l)}$

Équation 1-19 $2\ MnOOH_{(s)} + 2\ H^{+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + MnO_{2(s)} + 2\ H_2O_{(l)}$

Équation 1-20 $ZnMn_2O_{4(s)} + 4\ H^{+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Mn^{2+}_{(aq)} + 2\ H_2O_{(l)} + MnO_{2(s)}$

Équation 1-21 $MnO_{2(s)} + 4\ HCl_{(aq)} \rightarrow Mn^{2+}_{(aq)} + 2Cl_2\uparrow_{(g)} + 2H_2O_{(l)}$

L'acide sulfurique (H_2SO_4), est l'acide le plus communément utilisé dans les procédés de lixiviation chimique afin de solubiliser les composés inorganiques, en raison de son faible coût et de son faible pouvoir corrosif. Des études ont mis en évidence que certains métaux présents dans les déchets de piles peuvent être solubilisés efficacement en présence d'acide sulfurique sous forme de sulfates comme l'indiquent les Équations 1.22 à 1.26.

Équation 1-22 $ZnO_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_2O_{(l)}$

Équation 1-23 $MnO_{(s)} + H_2SO_{4(aq)} \rightarrow MnSO_{4(aq)} + H_2O_{(l)}$

Équation 1-24 $Mn_2O_{3(s)} + H_2SO_{4(aq)} \rightarrow MnSO_{4(aq)} + MnO_{2(s)} + H_2O_{(l)}$

Équation 1-25 $Mn_3O_{4(s)} + 2\ H_2SO_{4(aq)} \rightarrow 2\ MnSO_{4(aq)} + MnO_{2(s)} + 2\ H_2O_{(l)}$

Équation 1-26 $MnO_{2(s)} + H_2SO_{4(aq)} \rightarrow MnSO_{4(aq)} + H_2O_{(l)} + \frac{1}{2}\ O_{2(g)}$

La lixiviation en présence d'acide sulfurique (0,7% (v/v)) permet de récupérer près de 100% du Zn sous forme de $ZnSO_4$ (sulfate de zinc) (de Souza *et al.*, 2001). Ces auteurs ont mis en évidence qu'une faible concentration en acide sulfurique (0,7% (v/v)) peut s'avérer efficace pour solubiliser ZnO (oxyde de zinc) et MnO (oxyde de manganèse) si la température et le temps de la réaction sont suffisament élevés (T = 50 °C et t = 180 min). Certain oxydes de manganèse (Mn_2O_3 et Mn_3O_4) ne sont que partiellement dissous car leur solubilité est faible (Biswas *et al.*, 2015b, de Souza *et al.*, 2001).

Lixiviation en milieu oxydant ou réducteur

La solubilisation de certains composés peut être influencée par leur état d'oxydation. En effet, le manganèse est plus soluble sous forme réduite, Mn(II), que sous sa forme oxydée, Mn(IV). Il est, par conséquent, plus facile de le solubiliser après réduction des ions Mn^{4+} en Mn^{2+} en présence d'un agent réducteur inorganique comme le métabisulfite (Mwema, 2002) ou des composés organiques tels que l'acide oxalique, l'acide citrique, l'acide tartarique, l'acide formique, le glucose, le lactose, le sucrose, la glycérine, le triéthanolamine et le thiosulfate (Biswas *et al.*, 2015b; Furlani *et al.*, 2009; Sayilgan *et al.*, 2009).

Le Tableau 1.4 présente un récapitulatif des différentes études de lixiviation chimique développées pour le traitement des déchets de piles. Les différentes études réalisées mettent en évidence que plusieurs paramètres incluant la nature et la concentration de l'agent de lixiviation, le ratio S/L, la température et le temps de rétention etc. peuvent influencer les performances de solubilisation des métaux présents dans les déchets de piles.

Influence de la concentration en agent de lixiviation

La solubilisation des métaux présents dans les déchets de piles est influencée par la nature du réactif sélectionné mais elle dépend également fortement de la concentration en agent de lixiviation dans le milieu. De nombreuses études ont mis en évidence qu'une augmentation de la concentration en agent de lixiviation favorise la solubilisation des métaux; notamment lorsque ces derniers sont présents dans le solide sous forme d'oxydes ou d'hydroxydes. Cependant, l'augmentation de la concentration en réactif entraîne une augmentation significative des coûts de traitement, ce qui n'est pas favorable à l'application de la technologie à échelle industrielle. Un exemple de l'effet de la concentration de l'agent de lixiviation a été réalisé par Veloso *et al*. (2005). Dans leurs résultats, les pourcentages de solubilisation du Zn et du Mn ont augmenté de 57,7% et 41,6% à 100% et 99%, respectivement, lors de l'augmentation de la concentration en H_2SO_4 de 1% (v/v) à 3% (Veloso *et al.*, 2005).

Tableau 1.4 **Performances de solubilisation des métaux présents dans divers déchets avec différents procédés de lixiviation chimique**

Types de piles	Élément	Réactif de lixiviation	Vitesse d'agitation (rpm)	T (°C)	Temps (min)	Concentration de réactif (M)	Ratio S/L	Extraction	Référence
Li-ion	Li, Co	Acide oxalique	300	80	120	1	50 g/L	98% $LiCoO_2$	(Sun *et al.*, 2012)
Zn-Mn	Zn, Mn	Acide sulfurique	200	60	60	2	100 g/L	96% Zn, 43% Mn	(Buzatu *et al.*, 2013a)
Zn-Mn	Zn, Mn	Hydroxyde de sodium	200	80	120	6	100 g/L	82% Zn	(Buzatu *et al.*, 2013b)
Ni-MH	Nd, Ce, Ni, Co, Mn et Zn	Acide sulfurique	500	50	120	2	100 g/L	>90% Ni, Co, Mn et Zn, >89% pour terres rares	(Meshram *et al.*, 2016)
Ni-Cd	Ni, Cd	Acide chlohydrique		40	100	12	150 g/L	95% Ni, Cd	(Fernandes *et al.*, 2012)
Ni-MH	Ni	Acide sulfurique	-	80 (1er lix.), 25 (2e lix.)	180 (1er lix.), 60 (2e lix.)	2 (1er lix.), 1 (2e lix.)	150 g/L	100% Mn, Co, Zn, 99% Ni et RE	(Innocenzi *et al.*, 2012)
Zn-C	Zn, Mn, Fe	Acide sulfurique + glucose	300	100	60	2	20 g/L	100% Zn et Mn, 80% Fe	(Biswas *et al.*, 2015b)

Influence de la température et du temps de rétention

La température est un paramètre qui influence les performances ainsi que les cinétiques de solubilisation des métaux (Veloso *et al.*, 2005). En effet, la température peut améliorer de façon significative l'efficacité de solubilisation des oxydes et/ou hydroxydes de métaux présents dans les déchets de piles. Toutefois, dans certains cas, une augmentation de la température n'a aucun effet sur l'efficacité de solubilisation des métaux. Zhu *et al.* (2012) ont mis en évidence que la température et le temps de rétention influencent significativement (p-value $< 0{,}05$) l'efficacité de récupération du Co et du Li. Veloso *et al*. (2005), quant à eux, ont étudié la récupération des métaux présents dans les piles alcalines en présence d'acide sulfurique. Selon leurs résultats, lorsque la température augmente de 45 à 55°C, la solubilisation de Zn et Mn n'est pas améliorée (Veloso *et al.*, 2005). Cependant, lorsque la température atteint près de 70°C, le rendement d'extraction du Zn augmente.

Plusieurs études ont constaté que l'augmentation du temps de réaction permet d'améliorer significativement le rendement de solubilisation des métaux présents dans les déchets de piles (Li *et al.*, 2011; Nayl *et al.*, 2014; Zhu *et al.*, 2012). En effet, la lixiviation des métaux se décompose en plusieurs étapes: l'hydrolyse, la diffusion, la nucléation, etc. (Nayl *et al.*, 2014). Cependant, lorsque la solution de lixiviation est saturée, le rendement de solubilisation des métaux demeure constant.

Influence du ratio S/L

Moradkhani *et al.* (2012) ont optimisé les paramètres de lixiviation du Cd présent dans les résidus de charbon filtre, et notamment le ratio S/L (solide/liquide). Des essais de lixiviation ont été réalisés avec des ratios S/L de 3, 5, 8 et 10%. Le meilleur rendement de solubilisation obtenu pour le Zn est de 95%, avec un ratio S/L fixé à 10%. Sun et Qiu (2012) ainsi que Li *et al.* (2010) ont obtenu des résultats de lixiviation similaires pour les déchets de piles Li-ion. En effet, ces auteurs ont observé une augmentation du rendement de solubilisation du Li présent dans les piles Li-ion avec l'augmentation du ratio liquide/solide. Ceci peut s'expliquer par le fait qu'en présence d'une plus grande quantité de solution de lixiviation, une plus grande quantité de protons peut réagir avec les particules métalliques et donc améliorer leur rendement de solubilisation. Buzatu *et al.* (2013), quant à eux, ont étudié la récupération du Zn et du Mn par lixiviation en présence d'acide sulfurique et de soude. Selon leurs résultats, les rendements de solubilisation ont augmenté de 91% à 92% pour le Zn et de 30% à 38% pour le Mn lors de la diminution du ratio S/L de 200 g/L à 50 g/L. En conclusion, le ratio S/L joue un rôle important sur les performances des procédés de lixiviation chimique.

1.2.6 Récupération et valorisation des métaux présents dans les effluents de lixiviation

1.2.6.1 Précipitation-coagulation

La précipitation est un phénomène complexe entraînant la formation de précipités métalliques insolubles. De manière générale, les composés inorganiques peuvent être précipités sous forme d'hydroxydes, de sulfures, de carbonates ou de phosphates.

Précipitation des métaux sous forme d'hydroxydes

Les composés métalliques sont couramment précipités sous formes d'hydroxydes par ajout d'agents alcalins tels que les hydroxydes de sodium (NaOH), de calcium ($Ca(OH)_2$), d'ammonium (NH_4OH) ou de magnésium ($Mg(OH)_2$) ou l'oxyde de calcium (CaO) (Blais *et al.*, 2008).

Plusieurs études de récupération sélective des métaux présents dans les effluents issus de la lixiviation chimique de déchets de piles ont été menées par précipitation-coagulation (Provazi *et al.*, 2011).

Provazzi *et al.* (2011) ont effectué une précipitation sélective des métaux issus des déchets de piles mélangées en présence et en absence de peroxyde d'hydrogène (H_2O_2). Une solution de NaOH à 2 M a été utilisée afin d'augmenter progressivement le pH de l'effluent à traiter et des échantillons ont été prélevés à pH 1,5 – 2,0 – 2,5 – 3,0 – 3,5 - 4,2 et 6,0. Lors de ces essais, les effluents ont été divisés en trois groupes: l'effluent concentré, l'effluent moyennement concentré et l'effluent faiblement concentré. Les essais réalisés sur l'effluent très concentré indiquent que le Mn est précipité à pH = 3,0 en l'absence de H_2O_2 (34%), tandis que la précipitation du Fe nécessite l'ajout de H_2O_2 pour obtenir de bons rendements de précipitation (77%) (Provazi *et al.*, 2011). Concernant l'effluent moyennement concentré, les auteurs ont mis en évidence que 38% du Cd, 77% du Ce, 44% du Co, 27% du La et 50% du Pb sont précipités à pH = 0,5, alors qu'à pH = 3, le Cr est majoritairement précipité (80%) et qu'à pH = 6, près de 40% du Cu et du Ti sont précipités (Provazi *et al.*, 2011). Selon ces résultats, la récupération des métaux par précipitation n'était pas sélective. Afin de récupérer les métaux de façon plus sélective, les auteurs ont effectué une extraction par solvant.

Précipitation des métaux sous forme de sulfures

Les métaux peuvent être précipités sous forme de sulfures en présence de composés sulfurés tels que le sulfure de sodium (Na_2S), l'hydrogénosulfure de sodium (NaHS), le sulfure d'hydrogène (H_2S) ou le sulfure de fer (FeS) (Blais *et al.*, 2008).

Les valeurs des pK_S des sulfures métalliques mettent en évidence que les sulfures de métaux sont moins solubles que les hydroxydes métalliques; indiquant qu'il est plus efficace de précipiter les métaux sous forme de sulfures. Tokuda *et al*. (2008) ont étudié la précipitation des métaux (Cu, Ni, Sn et Zn) présents dans les eaux usées en présence de H_2S. Ils ont mis en évidence que le Cu, le Ni et le Zn peuvent être précipités sélectivement à différentes valeurs du pH (pH = 1,5 pour le CuS, pH = 4,5 pour le ZnS, pH = 6,5-7,5 pour le NiS).

Précipitation des métaux sous forme de carbonates

Les composés métalliques peuvent être précipités sous formes de carbonates par ajout d'agents carbonatés tels que le carbonate de sodium (Na_2CO_3) ou le carbonate de calcium ($CaCO_3$) (Blais *et al.*, 2008). La majorité des carbonates métalliques possède une solubilité supérieure à celle des hydroxydes. Pakarinen et Paatero (2011) ont, quant à eux, étudié la précipitation sélective du Mn et du Fe à partir d'une solution contenant des ions sulfates. Le carbonate du calcium a été utilisé comme agent de précipitation. En effet, le Fe peut être précipité sélectivement aux alentours de pH = 6 en présence d'oxygène (Pakarinen *et al.*, 2011). Une solution pure contenant seulement des ions Mn^{2+} peut également être obtenue.

1.2.6.2 Échange ionique sur résine

L'échange ionique est un procédé de récupération des métaux très utilisé pour le traitement d'effluents industriels, basé sur la permutation des ions présents en solution avec les contre-ions (Na^+, K^+ ou H^+) présents sur les résines échangeuses d'ions. Les ions métalliques peuvent être extraits simultanément ou de façon sélective en fonction des spécificités des résines échangeuses d'ions utilisées.

Plusieurs résines cationiques ou chélatantes telles que la Dowex M-4195, la Dowex 50X, la Lewatit MonoPlus SP 112, l'Amberlite 200C, la Purolite C-100 MH, etc. peuvent être utilisées pour la récupération sélective des métaux présents dans les effluents issus du traitement des déchets de piles. Selon l'étude réalisée par Diniz *et al.* (2005), la résine chélatante Dowex M-4195 possédant un groupement bis-picolylamine peut être utilisée pour l'adsorption sélective d'ions métalliques présents dans des solutions acides contenant 48 mg/L de Co, 85 mg/L de Cu, 6 g/L de Fe, 48 mg/L de Mn, 100 Mg/L de Ni et 40 Mg/L de Pb. La résine Dowex permet l'adsorption de 24% du Co, de 99,8% du Cu, de 25% du Fe, de 91% du Ni, de 31% du Pb et de seulement de 1,3% du Mn (Diniz *et al.*, 2005).

1.2.6.3 Extraction par solvant

Par définition, le solvant est une substance qui a le pouvoir de former une solution homogène avec d'autres substances. À l'échelle industrielle, les solvants organiques qui contiennent un ou plusieurs atomes de carbone dans leur structure moléculaire, sont les plus utilisés. Ils ont la propriété d'être volatils et relativement inertes chimiquement (Bégin *et al.*, 2002). Les solvants jouent un rôle important dans le domaine de l'extraction (p.ex. industries chimique, pétrochimique, pharmaceutique et alimentaire etc.). Ils peuvent être polaires (un solvant qui est constitué de molécules présentant un moment dipolaire), apolaires (un solvant dont le moment dipolaire est nul), protiques (un solvant possédant au moins un atome d'hydrogène acide dans la molécule) et aprotiques (un solvant qui ne contient pas d'atome d'hydrogène acide).

À cause de leurs propriétés, les solvants organiques sont largement utilisés dans les procédés hydrométallurgiques concernant la récupération des métaux présents dans les lixiviats ou effluents (Bégin et Guerin, 2002). Le principe et les différents types de solvants seront discutés dans cette section.

Généralités sur le procédé

L’extraction liquide/liquide par solvant est une technique du traitement basée sur le transfert d’un composé métallique depuis une solution aqueuse vers une solution organique non miscible ou partiellement miscible. Au contact des deux phases, un équilibre de partage s’établit entre la concentration de l’ion métallique dans la phase aqueuse et sa concentration dans la phase organique. Cet équilibre est caractérisé par un coefficient de distribution. Normalement, les ions métalliques sont entourés par les molécules d’eau, donc ils ne sont pas dissous dans les solvants organiques non polaires. Par la suite, afin de réaliser l’extraction, les espèces hydratées doivent se transformer en espèces plus hydrophobes dans la phase organique par 1) la réaction entre les anions et les cations produisant des complexes non polaires; 2) la formation d’une paire d'ions; 3) le remplacement des molécules d'eau par les composés organiques (solvatation). De manière générale, il existe trois types de solvants commercialisés tels que 1) agents d’extraction échangeurs d’ions; 2) agents de solvatation; 3) agents chélateurs.

Agent d’extraction échangeur d’ions

Généralement, il y a deux types d’agents d’extraction échangeurs d’ions: les échangeurs d’ions acides et les échangeurs d’ions basiques. Dans le cas d’une extraction par échange d’anions, des groupements fonctionnels tels que les amines primaires, secondaires ou tertiaires échangent leurs contres ions contre des anions à extraire. Le processus général d’extraction du métal par cet extractant est présenté par l’Équation 1.27:

Équation 1-27 $CoCl_4^{2-} + 2\ R_3NH^+Cl^- \Leftrightarrow (R_3(NH))_2CoCl_4 + 2\ Cl^-$

Où:

R: Hydrocarbures à longue chaîne composant le solvant organique

L'échangeur cationique contient des groupements fonctionnels négatifs attirant les cations. Il est normalement utilisé en milieu acide. Les ions hydrogène qui occupent les sites actifs sur les groupements fonctionnels peuvent être remplacés par les cations métalliques à travers le mécanisme d'échange ionique. Ces agents d'extraction incluant les carboxylates, les sulfonates, les phosphates etc., sont les solvants organiques les plus connus. Le mécanisme d'extraction de ce type de solvant est décrit à l'Équation 1.28:

Équation 1-28 $Zn^{2+} + 2\ (RH)_2 \Leftrightarrow ZnR_2(RH)_2 + 2\ H^+$

Où:

$(HR)_2$: Solvant organique;

$MR_2(HR)_{2n-2}$: Espèce complexée (métal-organique).

Agent d'extraction solvatatant

Dans le mécanisme de ce type d'extraction, le solvant réagit comme une base de Lewis. Ainsi, un doublet électronique libre présent sur le groupe actif réagit avec le composant à extraire. Le produit de l'extraction correspond à un complexe neutre entre un ion métallique et un ligand.

Les solvants organiques les plus connus dans ce type d’extraction sont le TBP (tributyl phosphate), le Cyanex 923 (Oxyde tri alkyl phosphonique), le Cyanex 921 (Oxyde Tri n octyl phosphinique), etc. Le TBP est largement utilisé pour récupérer les terres rares à partir de solutions d’acide de chlorure et de nitrate (Xie *et al.*, 2014). Selon l’étude de Peppard *et al.* (1957), rapportée par Xie *et al.* (2014), l’extraction du lanthane par le TBP est plus efficace en présence d’acide nitrique qu’en présence d’acide chlorhydrique (Peppard *et al.*, 1957; Xie *et al.*, 2014). Généralement, le TBP peut réagir comme modificateur de phase combiné avec les autres types de solvants afin d’éviter la formation de l’interphase pendant l’extraction (Barnard, 2010; Owusu, 1998; Vahidi *et al.*, 2009). Le Cyanex 923 est largement utilisé dans les procédés hydrométallurgiques car il est très sélectif pour le Cd (Gupta *et al.*, 2001). Le mécanisme d’extraction du métal par le Cyanex 923 peut être décrit par l’Équation 1.29 ci-dessous:

Équation 1-29 $$x\, M^{m+}{}_{(aq)} + y\, H^{+}{}_{(aq)} + z\, Cl^{-}{}_{(aq)} + n\, S_{(org)} \Leftrightarrow (H_yM_xCl_z)^{m+y-z}\, nS_{(org)}$$

Où:

M^{m+}: Ions métalliques dans la phase aqueuse;

H^{+}: Quantité d'acide en phase aqueuse;

Cl^{-}: Ions chlorure en phase aqueuse;

S: Concentration de ligand dans la phase organique.

Agents d'extraction chélateurs

Le mécanisme de ce type d'extraction est relié à la formation d'un complexe $M(H_2O)L$, où la molécule d'eau dans la couche externe est remplacée par le ligand (L) du solvant organique pour former un complexe (ML) (Chauhan *et al.*, 2015). Le mécanisme de la réaction peut être décrit par l'Équation 1.30:

Équation 1-30 $$\mathbf{M(H_2O)^{a+}_{n} + L^{b-} \Leftrightarrow M(H_2O)^{a+}_{n} \ldots\ldots L^{b-} \Leftrightarrow M(H_2O)^{a+}_{n-1} \ldots\ldots L^{b-} + H_2O \Leftrightarrow mL\ (H_2O)^{a-b}_{n-1}}$$

Où:

M: Métal;

L: Ligand.

Les solvants comme le D2EHPA (Acide di (2-éthylhexyl) phosphorique) ou Cyanex 272 (Acide di (2,4,4-triméthylpentyl) phosphonique) sont les plus connus dans le domaine de l'extraction des métaux avec une propriété très sélective et ils peuvent réagir comme des ligands organiques polydentés et comme donneurs d'électrons. C'est le cas de la molécule d'oxygène dans le groupement fonctionnel (-POOH) du Cyanex 272 et du D2EHPA qui est donneur d'électron et qui peut complexer les métaux et les transférer dans la phase organique.

L'optimisation du procédé de séparation des métaux par extraction par solvant doit considérer: 1) une séparation la plus pure possible; 2) un coût le plus bas possible.

Pour atteindre l'objectif précédent, comprendre le comportement du soluté dans la phase aqueuse et la phase organique est primordial.

Paramètres importants dans le procédé d'extraction par solvant

Les deux paramètres (coefficient de distribution (Équation 1-31) et facteur de séparation (Équation 1-32)) sont largement utilisés afin de déterminer la performance d'extraction et la sélectivité du solvant organique.

Coefficient de distribution (Owusu, 1998):

Équation 1-31 $\mathbf{D = [M_{org}]/[M_{aq}]}$

Où:

$D_{M:}$	Coefficient de distribution;
$[M_{org}]$:	Concentration des ions métalliques dans la phase organique;
[Maq]:	Concentration des ions métalliques en phase aqueuse.

Facteur de séparation (β) (Habashi, 1999):

Équation 1-32 $\boldsymbol{\beta = D_{MA}/D_{MB}}$

Où:

$ß_{A/B:}$	Facteur de séparation;
D_{MA} et $D_{MB:}$	Coefficients de distribution des métaux A et B, respectivement.

Provazi *et al.* (2011) ont mis en évidence que l'extraction par solvant est une technique de séparation des métaux plus efficace que le traitement par précipitation-coagulation. Par exemple, plus de 99% du Ti peut être extrait avec un pH compris entre 1,5 et 2,0. À un pH de 2,5, près de 99% du Zn est extrait alors qu'à pH = 3,0, près de 85% du Ni est récupéré. À pH = 3,5, le Cd et le La sont récupérés avec des rendements atteignant près de 80%. Le Fe et le Ce, quant à eux, sont extraits à pH neutre. D'après l'étude réalisée par Provazi *et al.* (2011), il est possible de séparer sélectivement certains métaux en présence de Cyanex 272 en fixant le pH de la solution à différentes valeurs. En effet, les résultats obtenus indiquent que les solutions de sulfates suivantes peuvent être récupérées: à pH = 2,5 pour le Zn; à pH= 3,0 pour le Ni; à pH = 3,5 pour le Cd et le La; à pH = 7,0 pour le Ce, le Co, le Cr, le Fe et le Mn (Provazi *et al.*, 2011). Selon la revue de littérature effectuée, le Ni ne pourrait pas être extrait à pH = 3,0 et le Cd est généralement extrait avant le Ni (Cytec, 2008c). Ceci est en désaccord avec les résultats obtenus par Provazi *et al.* (2011) qui ont récupéré le Cd et le Co à pH = 5,5 – 5,9 avant le Ni.

L'efficacité d'extraction des ions métalliques en présence de D2EHPA est fonction du métal considéré et peut être classée selon l'ordre décroissant suivant: Fe(III) > Zn(II) > Ca(II) > Cu(II) > Mg(II) > Co(II) > Ni(II). Nan *et al.* (2006) ont étudié les performances de l'extraction par solvant en présence d'Acorga M5640 et de Cyanex 272 afin de récupérer le Co, le Cu et le Ni. L'extraction par solvant en présence d'Acorga M5640 permet d'extraire près de 98,5% du Cu à un pH de 1,5-1,7. Cependant, les ions métalliques Co^{2+} et Ni^{2+} sont également co-extraits avec les ions Cu^{2+} en raison de leur grande concentration dans la même solution. Le Tableau 1.5 présente les résultats de plusieurs études ayant utilisé l'extraction par solvant comme technologie pour récupérer sélectivement les ions métalliques présents dans des effluents contaminés.

Tableau 1.5 Récapitulatif des pH d'équilibre et des pourcentages d'extraction obtenus pour différents ions métalliques en présence des différents solvants organiques

Type de solvant	**Groupe fonctionnel**	**Vitesse (rpm)**	**Concentration de solvant**	**Temps (min)**	**T (°C)**	**pH**	**Sélectivité**	**Extraction (%)**	**Références**
D2EHPA	Acide Di-Phosphorique	200	20% (v/v) D2EHPA	30	25	2,5 – 3 et 3,5	Zn>Mn>Ni	pH 2 = 100% Zn pH 3,5 = 95% Mn et 10% Ni	(Innocenzi *et al.*, 2012)
Cyanex 272	Acide Bis-Phosphinique	200	25% (v/v) D2EHPA	30	22	2–2,5 et 7	Zn>Mn>Ni	pH 2 = 100% Zn pH > 2 = Co précipité avec Mn pH 7 = 100% Mn	(Innocenzi *et al.*, 2012)
Cyanex 272	Acide Bis-Phosphinique	n.c	0,5 M	20	50	6	Co>Ni	90% Co, insignificatif extraction du Ni	(Cholico-Gonzalez *et al.*, 2015)
D2EHPA+Cyanex 302 (Acide bis-(2,4,4 -triméthylpentyl) monothiophosphonique)	Acide Di-Phosphorique et Acide phosphonique		0,15 M D2EHPA + 0,45 M Cyanex 302	10	25, 40 et 50	3	Cd>NI	100% Cd, 3% Ni	(Babakhani *et al.*, 2014)
LIX63 (5,8-diethyl-7-hydroxy-dodecan-6-oxime)/Versatic 10/nonyl-4PC	Oxime/ Neodecanoïque	800	-	0,5 ; 1, 1,5 ; 2 ; 3 ; 5 et 10	30	4	Ni>Co>Mn >Ca=Mg	90% Co et Ni, 8% Mn, 0% Ca et Mg	(Hutton-Ashkenny *et al.*, 2015)

1.2.6.4 Electrodéposition

Les métaux présents en solution peuvent être récupérés à l'aide d'un procédé électrochimique, à savoir l'électrodéposition. Dans les industries minières et métallurgiques, la récupération des métaux toxiques (Cu, Cr, Ni, Cd, etc.) ou des métaux valorisables (Ag, Au, Pt, etc.) est souvent effectuée par électrodéposition (Freeman, 1997). Étant donné que l'électrodéposition est une méthode de traitement qui ne nécessite pas l'utilisation de produits chimiques et qu'aucune boue n'est générée, cette technologie est dite « verte ». L'électrodéposition consiste en l'application d'un courant entre des électrodes (anodes et cathodes) favorisant l'apparition d'un dépôt métallique à la surface de la cathode par réduction cathodique (Équation 1.33). Le transfert des électrons dans la solution électrolytique est assuré grâce à l'oxydation des molécules d'eau en oxygène gazeux (Équation 1.34) (Chen, 2004) dans le cas où le contre-ion possède un potentiel d'oxydation standard plus bas que celui de H_2O par rapport à l'électrode d'hydrogène.

Équation 1-33 $\mathbf{M^{z+}_{(aq)} + z\,e^- \rightarrow M_{(s)}}$

Équation 1-34 $\mathbf{2\,H_2O_{(l)} \rightarrow O_{2(g)} + 4\,H^+_{(aq)} + 4\,e^-}$

Plusieurs paramètres tels que les conductivités de la solution et du dépôt formé à la cathode, le pH ou le transfert des électrons dans la solution sont autant de paramètres qui peuvent influencer l'efficacité d'enlèvement du métal et la qualité du dépôt formé. L'électrodéposition est une technologie qui ne nécessite pas l'utilisation de produit chimique et dont les coûts en électricité sont parfois faibles. Le plus fréquemment, l'électrodéposition est utilisée en industrie pour la production du Cu et du Zn. De plus, cette technologie a l'avantage d'être sécuritaire (Racz *et al.*, 2013).

Il existe un procédé d'électrodéposition permettant de récupérer le Zn (0,1 mol/L) et le Mn (0,06 mol/L) présents dans les effluents issus de la lixiviation chimique (HCl et H_2O_2) des piles Zn-C usagées. L'acide borique est utilisé afin d'empêcher la formation de dihydrogène, H_2. Le polyéthylène glycol (PEG), quant à lui, est utilisé afin d'améliorer la qualité du dépôt (homogène) et l'efficacité de déposition du Zn et de Zn-Mn sur la surface de l'électrode. Dans les conditions optimales (densité de courant = -10 mA/cm^2), le Zn est co-déposé avec du Mn (impuretés de 2%).

Le Tableau 1.6 présente un récapitulatif des procédés électrochimiques développés au cours de ces dernières années pour purifier les effluents contaminés et ainsi récupérer les métaux présents dans les effluents.

Tableau 1.6 **Récapitulatif des procédés électrochimiques développés pour la récupération de certains métaux présents en solution**

Électrode	**Densité de courant (mA/cm^2)**	**pH**	**Vitesse de rotation**	**Temps (min)**	**Temp. (°C)**	**Récupération (%)**	**Référence**
Électrode de travail = acier doux Électrode de référence = Ag/AgCl Contre-électrode = acier inoxydable	10 – 20 et 30	2,15	n.c.*	15 – 30 et 60	25	72% pour Mn et Zn	(Brito *et al.*, 2012)
Anode = Pb Cathode = acier inoxydable	45	n.c.	n.c.	360	n.c.	75% pour Zn	(Guillaume *et al.*, 2008)
Anode = Pb Cathode = Al	18 – 25 et 40	n.c.	n.c.	1 080	25	99,9% pour Cd	(Moradkhani *et al.*, 2012)
Électrode de travail = plaque de cuivre ou électrode de charbon, Électrode de référence = électrode au calomel saturée Contre-électrode = électrode de Pt-écran	1,75	n.c.	0 – 100 et 200	n.c.	60	99% pour Cd, 0,51% pour Ni, 0,05% pour Co	(Yang, 2003)
Cathode = feuille d'aluminium Anode = feuille de platine	0,35	n.c	0,90 L/min	300	n.c	100% Cd (97% pureté)	(Hazotte *et al.*, 2015)

** n.c. : non communiqué.*

1.3 Hypothèse, originalité et objectifs spécifiques

1.3.1 Hypothèse

Les procédés de traitement et de valorisation des déchets de piles développés à ce jour nécessitent, au préalable, un tri manuel des piles en fonction de leur composition. L'hypothèse générale de ce projet de doctorat est qu'il est possible de développer un procédé de traitement efficace et économiquement viable, permettant la valorisation des métaux présents dans l'ensemble des piles usagées mis au rebut annuellement. Une sous-hypothèse de ce projet de recherche est qu'il est possible de récupérer sélectivement les métaux valorisables (Mn, Ni et Zn) présents dans les lixiviats issus du traitement des déchets de piles non triées par extraction par solvant suivie de l'électrodéposition et de la précipitation et ce, de manière efficace et rentable.

1.3.2 Originalité du projet

Les piles sont des produits de consommation de la vie de tous les jours dont les applications sont très nombreuses et variées. De nos jours, il existe une grande variété de piles parmi lesquelles nous pouvons citer les piles alcalines, les piles Ni-MH, les piles Zn-C, les piles Ni-Cd, les piles Li-ion et les piles Li-M. Les piles sont très utiles dans la vie de tous les jours, mais la présence de métaux en de fortes concentrations peut s'avérer problématique lors de la gestion des déchets de piles. Bien sûr, il existe plusieurs types de piles qui peuvent être rechargées et réutilisées mais la majorité des piles produites à ce jour, ne peuvent être rechargées et doivent donc être gérées de manière sécuritaire étant donné que ces déchets sont considérés comme des matières dangereuses en raison de leurs compositions en éléments métalliques. L'enfouissement est le mode de gestion le plus utilisé au Québec pour gérer les déchets électroniques comme les piles. Cependant, ce mode de gestion n'est pas idéal en raison des risques de lixiviation des métaux présents dans les piles usagées dans les sites d'enfouissement et des risques pour la santé humaine, pour la faune et la flore liés à la toxicité de la majorité des métaux présents dans les piles. Récemment, plusieurs procédés de traitement des déchets de piles ont été développés afin de recycler les métaux présents dans ces déchets et de les réutiliser pour la fabrication de nouveaux produits tels que les piles, les batteries, etc. Cependant, la plupart des procédés développés à ce jour, ne permettent de gérer qu'un seul type de piles usagées, nécessitant au préalable une étape de tri pour séparer les piles en fonction de leurs compositions. Le tri des piles usagées doit être réalisé manuellement étant donné qu'aucune méthode permettant de le faire automatiquement n'existe à ce jour. Ce tri manuel requiert beaucoup de temps, augmentant de manière significative les coûts de gestion de ces déchets.

L'originalité de ce projet de doctorat est donc de développer un procédé de valorisation des déchets de piles qui soit efficace, économiquement viable et applicable à l'ensemble des piles usagées mises au rebut. Au cours de ces dernières années, quelques technologies ont été développées afin de traiter simultanément certains déchets de piles afin de récupérer les métaux valorisables présents dans ces déchets de piles. Parmi les technologies développées, les procédés hydrométallurgiques sont les plus couramment utilisés de nos jours. Le Tableau 1.7 illustre l'originalité de ce projet de recherche. Les procédés existants tels que le procédé BATENUS (Frohlich *et al.*, 1995), utilisent des résines échangeuses d'ions et un solvant organique pour séparer de manière sélective les métaux. Le procédé développé en laboratoire par Provazi *et al.* (2011) utilise l'extractant Cyanex 272 à différents pH, suivis par l'électrodéposition afin de séparer des métaux sélectivement. Par rapport aux procédés existants, notre procédé est moins complexe et plus efficace. Les rendements sont plus élevés et la récupération des métaux est plus sélective. Le Tableau 1.7 compare le procédé utilisé dans cette étude aux procédés existants. L'avantage de notre procédé réside dans l'utilisation de deux solvants d'extraction sélective des métaux et dans les rendements de récupération très élevés.

Tableau 1.7 Comparaison des technologies existantes avec le procédé à l'étude

	Procédés utilisés dans cette étude	**Procédé BATENUS (Frohlich *et al.*, 1995)**	**Procédé développé par (Provazi *et al.*, 2011)**	**Brevet US 2,827,710 (Farouk, 2003)**
Types de piles	Alcaline, Zn-C, Ni-MH, Ni-Cd, Li-ion, Li-M	Zn-C, Alcalines, Lithium et Ni-Cd	Zn-C, Alcaline, Ni-Cd, Ni-MH et Li-ion	Zn-C, Alcalines, Ni-Cd, Ni-MH
Lixiviation	H_2SO_4 (1,34 M) + $Na_2S_2O_5$	H_2SO_4 dilué	H_2SO_4	$H_2SO_4 + H_2O_2 + Fe^{2+}$
Enlèvement du Fe	Extraction par solvant + lavage sélectif	Séparation magnétique	Séparation magnétique	Séparation magnétique
Récupération des métaux	Extraction par solvant (Cyanex 272) + électrodéposition + précipitation = Zn, Ni, Co	Résine échangeuse d'ions sélective = Hg, Cu, Ni et Cd	Extraction par solvant + électrodéposition + précipitation (Cyanex 272) = Zn, Mn, Ni et Cd	Électrodéposition (Zn, MnO_2)
	Extraction par solvant (D2EHPA) + électrodéposition (Mn+Cd)	Extraction par solvant = Zn		Électrodéposition (Ni, Cd)

1.3.3 Objectifs spécifiques

L'objectif principal de ce projet de recherche est de développer une filière technologique efficace et économique permettant la récupération des métaux valorisables présents dans l'ensemble des déchets mixtes (non-triés) de piles.

Les objectifs spécifiques associés à ce projet peuvent être définis de la manière suivante:

- Réalisation de l'échantillonnage, du tri, de la désactivation et du démantèlement des déchets de piles;
- Préparation et caractérisation des poudres métalliques (anodes et cathodes) issues du broyage de chaque type de piles;
- Élaboration d'un mélange de poudres métalliques représentatif de la composition actuelle des déchets mixtes de piles mis au rebut chaque année;
- Étude du potentiel de divers agents de lixiviation pour la solubilisation sélective ou totale des métaux présents dans les déchets mixtes de piles;
- Sélection et optimisation d'une filière de lixiviation des métaux présents dans les déchets mixtes de piles;
- Étude des performances de diverses techniques hydrométallurgiques (précipitation, extraction par solvant, électrodéposition) pour la récupération sélective des métaux présents dans les lixiviats issus du traitement des déchets mixtes de piles;

- Étude technico-économique de la filière d’extraction et de récupération des métaux présents dans les déchets mixtes de piles développée au cours de ce projet de doctorat.

1.4 Matériel et méthodes

Ce chapitre présente les méthodes de préparation, d'échantillonnage, de caractérisation et de décontamination des mélanges de piles. Une brève description de la méthodologie et des plans d'expériences utilisés pour l'optimisation des paramètres opératoires de solubilisation des métaux, ainsi que les différentes technologies pour la récupération des métaux présents dans les eaux des procédés sont également exposées.

1.4.1 Échantillonnage, tri et désactivation des déchets de piles

Les différents types de piles utilisés au cours de ce projet (piles alcalines ($ZnMnO_2$), piles zinc-carbone (Zn-C), piles au lithium (Li-M), piles nickel-cadmium (Ni-Cd), piles nickel-hydrure métallique (Ni-MH) et piles lithium-ion (Li-ion)) ont été récupérés dans les sites de tri et les éco-centres de la ville de Québec (Canada). Dans un premier temps, les déchets de piles ont été triés manuellement et séparés en fonction de leurs types. Les piles (Li-M et Ni-MH) usagées ont ensuite été désactivées en présence d'azote liquide (pour empêcher leur explosion lors du contact avec l'air), rendues plus inertes avant d'être écrasées.

1.4.2 Démantèlement et préparation des poudres métalliques pour chaque type de piles

Les piles usagées ont ensuite été démantelées manuellement à l'aide d'une pince coupante; la fraction grossière (contenant des composantes en plastique, des morceaux de papier, etc.) a ensuite été retirée. Les piles Ni-MH et les piles au Li ont été congelées à -80°C dans de l'azote liquide avant d'être démantelées à l'aide d'une scie électrique afin d'éviter toute réaction violente ou toute explosion au contact de l'air. Les résidus de piles séparés ont été écrasés manuellement afin d'obtenir des poudres homogènes avant d'être séchés à 60°C pendant 24 h (Mantuano *et al.*, 2006). Les poudres de résidus de piles ont ensuite été digérées dans l'acide pour déterminer les teneurs en métaux présentes dans chacun des types de piles.

1.4.3 Préparation d'un mélange de poudres métalliques

Un mélange (5 kg) de poudre de piles représentatif de la composition moyenne des déchets de piles mis au rebut chaque année au Québec a été préparé. La composition moyenne des déchets de piles mis au rebut chaque année est de 68% de piles alcalines ($ZnMnO_2$), 15% de piles zinc-carbone (Zn-C), 0,8% de piles lithium métallique (Li-M), 14% de piles nickel-cadmium (Ni-Cd), 1,6% de piles nickel-hydrure de métal (Ni-MH), 0,28% de piles lithium-ion (Li-ion) (RIS international, 2007). Cette distribution de déchet de piles mis au rebut a été utilisée pour préparer le mélange utilisé pour les essais expérimentaux.

1.4.4 Étude des performances de divers agents de lixiviation pour la solubilisation des métaux présents dans les piles usagées

Une étude comparative des perfomances de solubilisation des métaux présents dans le mélange de piles en présence de plusieurs agents de lixiviation a été réalisée dans les mêmes conditions opératoires (ratio S/L, température et temps de réaction) pour une solubilisation sélective ou totale des métaux présents dans le mélange de poudres métalliques.

Les solvants étudiés sont:

- Solution de chlorure de sodium ([NaCl] = 1,0 et 4,0 M);
- Solution d'acide sulfurique ([H_2SO_4] = 0,5 et 2,0 M) (Senanayake *et al.*, 2010);
- Solution d'acide chlorhydrique ([HCl] = 0,5 et 2,0 M);
- Solution d'acide oxalique ([$C_2H_2O_4$] = 0,5 et 1,0 M);
- Solution d'acide acétique ([$C_2H_4O_2$] = 0,5 et 2,0 M);
- Solution de soude ([NaOH] = 0,5 et 2,0 M) (Senanayake *et al.*, 2010, Shin *et al.*, 2009);
- Solution de chlorure d'ammonium ([NH_4Cl] = 1,0 et 4,0 M) (Oishi *et al.*, 2008);
- Solution d'acide éthylènediaminetétraacétique ([EDTA] = 0,25 et 0,5 M (pH 4-5)) (Vatistas *et al.*, 2001).

Les paramètres et les conditions opératoires de cette partie sont présentés au Chapitre 3.

1.4.5 Sélection et optimisation d'une filière de lixiviation acide des métaux présents dans les déchets de piles

Cette étape d'optimisation a été réalisée à partir des résultats des essais de lixiviation précédents, en utilisant l'agent de lixiviation ayant donné les meilleurs rendements de solubilisation. L'optimisation des paramètres opératoires a été réalisée en se basant sur l'utilisation des plans d'expériences de type Box Behnken. Les paramètres opératoires étudiés sont le ratio solide/liquide (S/L), la concentration en agent de lixiviation et en agent réducteur, le temps de réaction et le nombre d'étapes de lixiviation. Dans le cadre des plans d'expériences de type Box Behnken, l'erreur pure (ou erreur expérimentale) est évaluée à partir de cinq réplicats (points expérimentaux) qui sont réalisés au centre du domaine expérimental; et ce, pour chaque série d'expériences. Afin de déterminer l'influence de plusieurs facteurs sur les performances de solubilisation des métaux présents dans le mélange de poudres métalliques et d'identifier les conditions optimales, différentes séries d'expérimentations ont été réalisées à l'aide du logiciel Design Expert 8.0:

- La première série d'expériences a été réalisée afin d'évaluer l'influence de quatre facteurs différents sur les performances du procédé de lixiviation, à savoir: le ratio S/L, la concentration en acide sulfurique, le nombre d'étapes de lixiviation et le temps de lixiviation;
- La deuxième série d'expériences a été réalisée afin d'étudier l'influence de quatre autres facteurs sur les performances du procédé de lixiviation, à savoir: la concentration en $Na_2S_2O_5$, la concentration en acide sulfurique~~,~~ la masse de NaCl, le nombre d'étapes de lixiviation. Pour cette série d'expériences, le ratio S/L et le temps de rétention ont été fixés à 10% et 30 min, respectivement;
- La troisième série d'expériences a été réalisée afin d'étudier l'influence de quatre facteurs différents sur les performances du procédé de lixiviation, à savoir: le ratio S/L, la concentration en H_2SO_4, la concentration en $Na_2S_2O_5$ et le temps de lixiviation. Dans la troisième série d'essais, le nombre d'étapes de lixiviation a été fixé à $n = 1$.

Le métabisulfite de sodium a été utilisé comme agent réducteur afin d'optimiser l'extraction des métaux et notamment du manganèse par réduction des composés Mn(IV) en Mn(II).

Les différentes séries d'expérimentations ont été réalisées à température ambiante dans des erlenmeyers à chicanes. Les solutions de lixiviation ont été préparées en ajoutant le volume requis d'acide sulfurique (H_2SO_4, 98%, Fisherbrand, Canada) pour obtenir la concentration souhaitée ainsi que la quantité requise de métabilsulfite de sodium ($Na_2S_2O_5$, LaboMat, Canada) requise pour obtenir la valeur indiquée par la matrice expérimentale.

La variation de chaque paramètre pour l'optimisation des conditions opératoires pour la lixiviation des métaux est présentée en détails dans les Chapitres 3 et 4. Enfin, les conditions opératoires optimales ont été testées en triplicats et les résultats obtenus ont été comparés à la théorie (rendements de solubilisation prédits par le logiciel).

1.4.6 Récupération des métaux présents dans les effluents

1.4.6.1 Essais de récupération des métaux par précipitation sélective en présence de NaOH

Le dispositif des essais de précipitation sélective est illustré par la Figure 1.3. Le pH de la solution a été augmenté progressivement par ajout d'une solution de NaOH. Un échantillon de 1 mL a été prélevé pour les pH suivants: 1,5 - 2,0 - 3,0 - 4,0 - 5,0 et 6,0, 7,0 - 8,0 - 9,0 - 10 - 11 et 12. Le volume total des prélèvements ne doit pas dépasser 10% du volume total initial pour que les résultats soient significatifs. Le pH et le POR des différents échantillons ont été mesurés juste après le prélèvement.

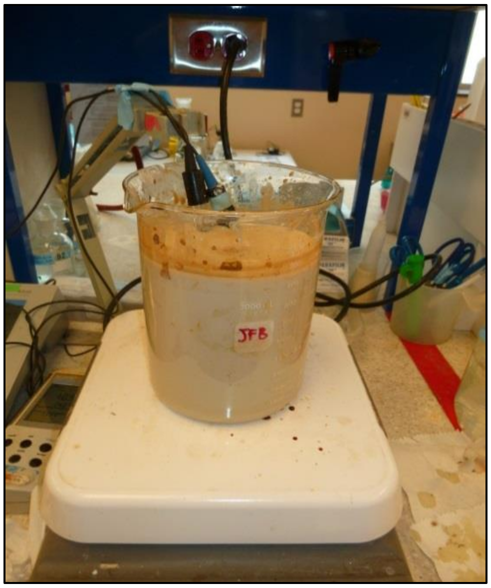


Figure 1.3 **Montage de précipitation sélective des métaux sous forme d'hydroxydes**

1.4.6.2 Essais de récupération des métaux par précipitation sélective en présence de Na_2CO_3

Une solution de NaOH a été utilisée pour ajuster le pH de la solution jusqu'à 4,0 puis le Na_2CO_3 (bicarbonate de sodium) a été ajouté pour ajuster le pH de la solution jusqu'à pH 10. L'utilisation de Na_2CO_3 permet de précipiter les métaux de manière sélective sous forme de carbonates. Des prélèvements de 1 mL ont été effectués progressivement entre pH = 1,5 et pH = 10. Le pH et le POR de chaque échantillon ont été mesurés.

1.4.6.3 Précipitation sélective du Fe sous forme d'hydroxydes en présence de NaOH après oxydation en présence de H_2O_2

Les courbes de solubilités des hydroxydes métalliques, ainsi que différentes études, ont mis en évidence que la précipitation des ions ferriques (Fe^{3+}) sous forme d'hydroxydes se fait à des pH allant de 2,0 à 3,5; alors que celle des ions ferreux (Fe^{2+}) se fait à des pH compris entre 3,0 et 7,0. La précipitation sélective du Fe peut être réalisée en ajoutant du NaOH jusqu'à pH = 3,5 après oxydation des ions ferreux en ions ferriques en présence de peroxyde d'hydrogène. Plusieurs quantités de H_2O_2 ont été testées afin d'évaluer la capacité d'oxydation des ions ferreux présents en solution:

- La quantité stœchiométrique;
- + 25% de la quantité stoechiométrique;
- + 100% de la quantité stoechiométrique.

Une solution de NaOH a été ajoutée progressivement pour augmenter le pH de la solution jusqu'à 3,5 et 4,0. La quantité de H_2O_2 requise a ensuite été ajoutée progressivement tout en contrôlant le pH de la solution et en ajoutant une solution de NaOH pour maintenir le pH de la solution entre 3,5 et 4,0. Un prélèvement de 1 mL a été réalisé après décantation pendant 1 nuit. Une vérification du pH du surnageant a été effectuée après 1 h et 24 h.

1.4.6.4 Procédé d’extraction par solvant

Des volumes de 50 mL de lixiviat et 100 mL de solution organique ont été introduits et mélangés dans un bécher de 200 mL (Figure 1.4a). Les deux solutions ont été mélangées sous agitation magnétique. Le pH a été contrôlé en ajoutant le NaOH pendant l’extraction. Enfin, les phases aqueuses et organiques ont été séparées par gravité et un échantillon a été prélevé dans la phase aqueuse (Figure 1.4b).

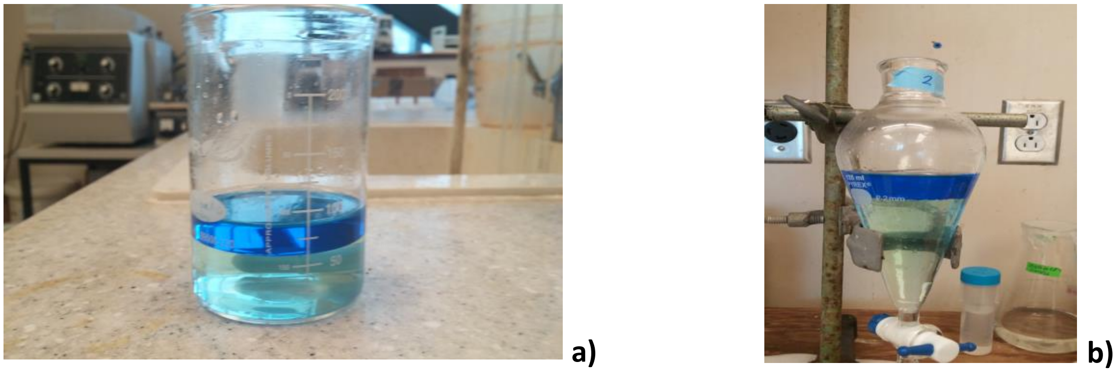


Figure 1.4 Photographie du montage du procédé d’extraction par solvant : a) étape d’extraction, b) étape de séparation par décantation

Les rendements de récupération des métaux ont été calculés par différence entre la teneur en métaux dans la solution aqueuse après extraction et la solution aqueuse d’origine.

Un plus grand volume de lixiviat et de solution organique a été utilisé dans un bécher de 2 000 mL afin de valider le procédé optimisé.

1.4.6.4.1 Récupération du Zn par solvant organique CYANEX 272 suivie par un procédé d'électrodéposition dans une solution synthétique

Une solution synthétique a été préparée et utilisée au début afin d'optimiser les conditions opératoires d'extraction. Ces conditions opératoires optimales sont ensuite appliquées à la solution réelle. Pour préparer la solution synthétique, les concentrations des métaux dans les présents dans le lixiviation issus des essais réalisés dans les conditions optimales de lixiviation ont été considérées (Chapitre 4). Les masses des différents sulfates métalliques correspondantes ont été pesées et introduites dans un volume précis d'une solution acide afin d'obtenir les concentrations visées. Les sulfates métalliques ont ensuite été dissous dans une solution acide. Le pH de la solution (pH < 2) est ajusté par ajout d'acide sulfurique.

La récupération et la séparation sélective du Zn ont été réalisées grâce au solvant Cyanex 272 (Cytec Canada Inc., Niagara Falls, ON, Canada). Le schéma général du procédé d'extraction est présenté à la Figure 1.5.

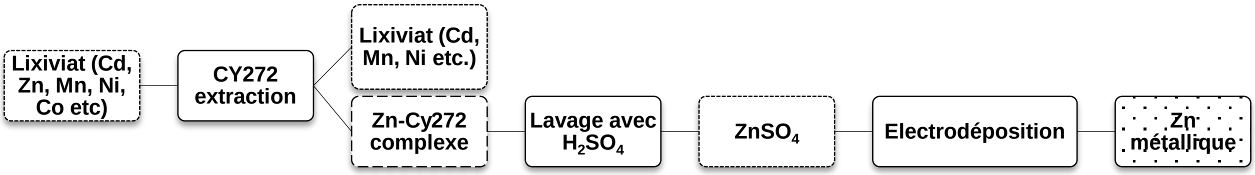


Figure 1.5 **Schéma simplifié du procédé de récupération du Zn par extraction par solvant et électrodéposition**

Le TBP (pureté supérieure à 97%, Sigma-Aldrich, Oakville, Ontario, Canada) a été utilisé comme agent de modification. Cet agent de modification rend les complexes métalliques plus solubles dans la phase organique, ce qui empêche donc la formation d'une troisième phase (Habashi, 1999).

Les conditions opératoires d'extraction du Zn ont été déterminées en faisant varier le pH d'extraction et en considérant le volume stœchiométrique du solvant organique nécessaire à l'extraction totale du Zn (Tableau 1.8). Afin de récupérer le Zn sous forme de sulfate de Zn, le solvant organique a été mélangé avec une solution d'acide sulfurique. Un procédé d'électrodéposition a ensuite été réalisé à partir de la solution de lavage contenant $ZnSO_4$ afin de récupérer le Zn sous forme métallique. Le dispositif experimental d'électrodéposition (Figure 1.6) est composé de cathodes en acier inoxydable et d'anodes en titane recouvert d'oxyde d'iridium (Ti/IrO_2). Elles étaient connectées à une alimentation OC XFR4 Xantrex-70 (Aca TMETRIX Inc., Mississauga, ON, Canada). L'électrodéposition du Zn a eu lieu à un pH de 2 à 3, pendant 180 min et à une densité de courant de 360 A/m^2.

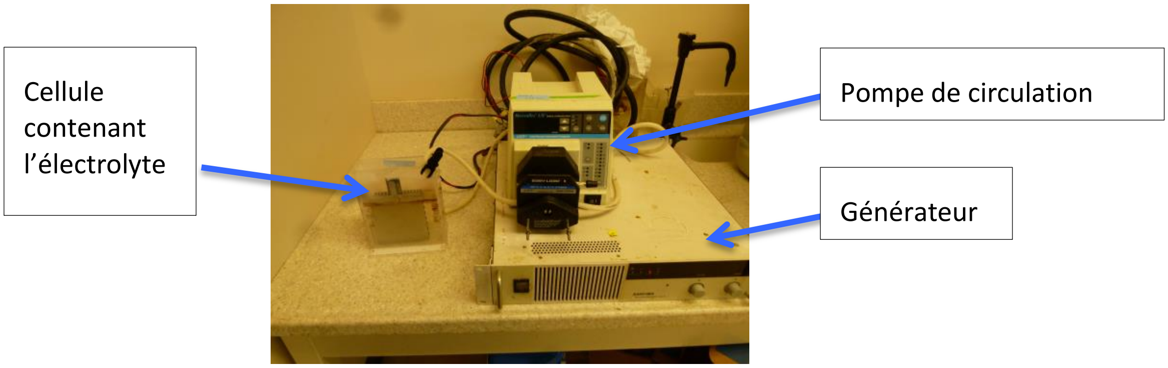


Figure 1.6 **Photographie du montage de la récupération du Zn par électrodéposition**

1.4.6.4.2 Choix de voie de récupération simultanée du Cd et du Mn présents dans la solution synthétique par deux solvants organiques (D2EHPA et Cyanex 272)

Il existe plusieurs possibilités pour récupérer le Mn et le Cd après une première étape d'extraction du Zn par Cyanex 272. Le schéma général du procédé d'extraction est présenté à la Figure 1.7.

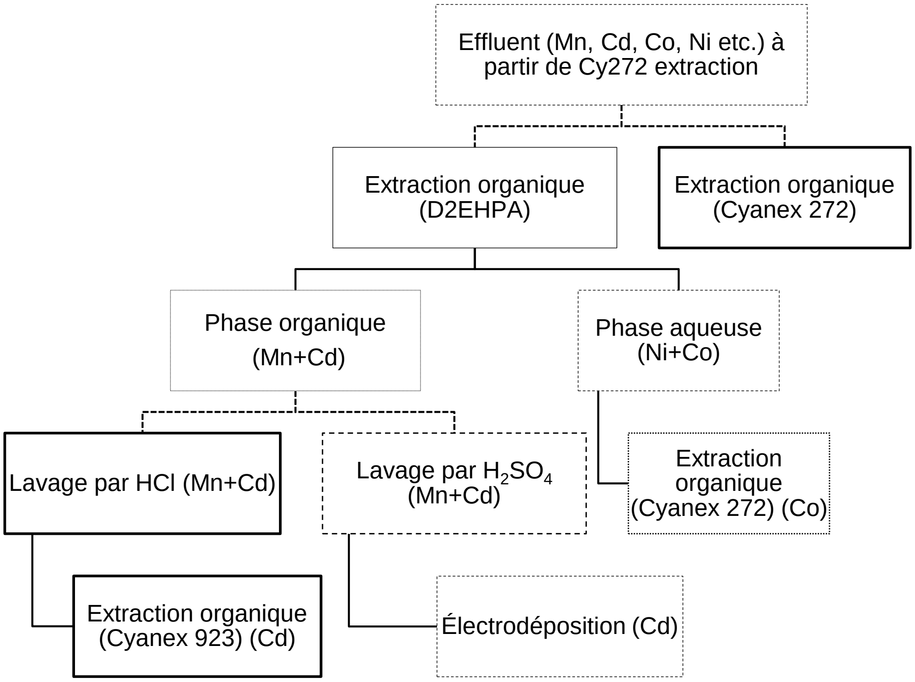


Figure 1.7 **Récupération simultanée du cadmium et du manganèse en utilisant des procédés d'extraction par solvant et d'électrodeposition**

Deux types de solvants organiques ont été testés et comparés, ce sont le Cyanex 272 et le D2EHPA. La solution synthétique a été utilisée dans les essais préliminaires. Les différentes valeurs de pH ont été testées afin de déterminer le pH approprié pour l'extraction.

Les essais avec la solution organique D2EHPA (Cytec Canada Inc., Niagara Falls, ON, Canada) ont été réalisés afin de comparer les résultats avec les essais d'extraction du Cd et du Mn par le Cyanex 272. Les conditions opératoires de cette étape sont résumées au Tableau 1.8. Des pH appropriés de 2,2 – 2,9 – 3,0 ont été appliqués dans les essais d'extraction avec le D2EHPA, ce qui est comparable à l'étude réalisée par Fatmehsari *et al.* (2009). Enfin, le D2EHPA a été choisi en raison de sa meilleure capacité d'extraction du Cd et du Mn à pH acide par rapport au Cyanex 272.

Une étape de lavage a été effectuée afin d'éliminer les impuretés comme le Co et le Ni. Dans cette étape, les ions de Co et de Ni présents dans la phase organique ont été remplacés par les ions de Mn et de Cd initialement présents dans la solution de lavage en raison de la plus grande affinité du D2EHPA pour le Co et le Ni sous un pH contrôlé.

La récupération des métaux (Cd et Mn) présents dans la phase organique a ensuite été effectuée en utilisant les acides sulfurique et chlorhydrique (Figure 1.8). Le HCl a été testé en premier étant donné que le Cyanex 923 est généralement complexé avec le métal dans la solution de chlorure. Les métaux forment plusieurs complexes avec les chlorures, ce qui augmente le taux de récupération des métaux dans la phase aqueuse lors de l'étape de stripping. Les formes complexées entre les métaux et les ions chlorure sont présentées aux Équations 1.35 à 1.38 (Leopold, 2010).

Équation 1-35 $\mathbf{Cd^{2+}{}_{(aq)} + Cl^{-}{}_{(aq)} \Leftrightarrow CdCl^{+}{}_{(aq)}}$

Équation 1-36 $\mathbf{CdCl^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \Leftrightarrow CdCl_{2\,(aq)}}$

Équation 1-37 $\mathbf{CdCl_{2\,(aq)} + Cl^{-}{}_{(aq)} \Leftrightarrow CdCl_3^{-}{}_{(aq)}}$

Équation 1-38 $\mathbf{CdCl_3^{-}{}_{(aq)} + Cl^{-}{}_{(aq)} \Leftrightarrow CdCl_4^{2-}{}_{(aq)}}$

L’acide sulfurique (H_2SO_4) a été utilisé avant l’étape d’électrodéposition.

1.4.6.4.3 Comparison des deux procédés de récupération sélective du Cd (solvant organique Cyanex 923 et électrodéposition) à partir de la solution synthétique contenant le Cd et le Mn

Deux procédés de récupération sélective du Cd ont été effectués. La solution synthétique contenant principalement du Cd (II) (~4,3 g/L) et du Mn (II) (~27 g/L) a été utilisée. L’étape de récupération dans cette partie est présentée à la Figure 1.8.

Afin de récupérer le Cd sélectivement à partir de la phase organique (D2EHPA chargée en Cd et Mn obtenue dans l’étape précédente), les phases organiques (D2EHPA) ont été lavés en utilisant une solution de HCl. La solution organique a été préparée en utilisant deux concentrations différentes de solvant organique (5% et 10% Cyanex 923 dilué dans du kérosène). Le pH de – 0,3 a été choisi pour l’extraction selon l’étude de Gupta *et al.* (2001).

Le deuxième essai de récupération sélective du Cd a été effectué en utilisant l'électrodéposition. Le D2EHPA chargé en Cd et Mn a été lavé avec une solution de H_2SO_4 avant le transfert dans l'étape d'électrodéposition.

L'électrodéposition a été faite à un pH de 2, sous agitation, pendant 360 min et avec une densité de courant allant de 180 à 360 A/m^2. La même cellule que celle utilisée lors de l'électrodéposition du Zn a été employée dans ces essais.

1.4.6.4.4 Précipitation de Mn à partir de la solution pure de $MnSO_4$ à partir de la solution synthétique

Après avoir obtenu la solution pure de $MnSO_4$ (sulfate de manganèse), le Mn a été précipité à pH 9 en utilisant du Na_2CO_3 (Fisher Scientific, réactif ACS). Le précipité de $MnCO_3$ (carbonate de manganèse) a été lavé trois fois avec un ratio solide/liquide de 10% ($MnCO_3$ solide/eau déminéralisée).

1.4.6.4.5 Élimination du Co par Cyanex 272 et récupération du Ni par précipitation

La solution aqueuse provenant de l'étape d'extraction du Cd et du Mn par D2EHPA a été utilisée dans cette étape (voir Figure 1.8). La solution contient principalement du Ni, et un peu d'impuretés telles que le Co, le Cd et le Mn. Ces impuretés ont été transférées dans la phase organique Cyanex 272 à pH 5,2. Les impuretés présentes dans la phase organique ont été lavées avec de l'acide sulfurique. Ensuite, la solution de $NiSO_4$ a été traitée par précipitation en utilisant du Na_2CO_3 sous agitation à 25°C. Le précipité généré a été lavé deux fois avec de l'eau déminéralisée afin d'éliminer les ions sulfate et sodium.

Tableau 1.8 **Résumé des conditions opératoires dans le procédé d'extraction par solvant**

Étapes	Conditions opératoires								
	Solvant organique (%)	pH	TBP (%)	ratio O/A (extraction)	Nb d'étapes d'extraction	Temps de réaction (min)	T (^oC)	Solution de lavage	ratio O/A (lavage)
Zn-Extraction par Cyanex 272	20	1,5-4,0	2-5	1/1 et 2/1	2	10	50	0,4 M H_2SO_4	2/1
Cd+Mn-Extraction par Cyanex 272	30	3,0-4,0	2	2/1	1	10	50	-	-
Cd+Mn-Extraction par D2EHPA	30	2,0-2,7	5	2/1	2	10	50	0,4 et 1,2 M H_2SO_4 1,2 M HCl	2/1 et 4/1
Séparation du Cd et Mn par Cyanex 923	5, 10	-0,3	-	2/1	1	10	50	-	-
Élimination de Co, Mn et Cd par Cyanex 272	10	5,0-5,5	2	0,5/1	1	10	50	0,4 M H_2SO_4	2/1

1.4.7 Récupération des métaux à partir d’un mélange de déchets de piles à partir de la solution réelle

Une solution de lixiviation réelle obtenue à partir d’un mélange de piles a été utilisée pour récupérer le Zn, le Cd, le Mn et le Ni en utilisant les conditions optimales obtenues à partir des essais réalisés sur la solution synthétique. Les étapes successives pour la récupération des métaux sont présentées à la Figure 1.8.

1.4.8 Mesures analytiques

1.4.8.1 Détermination de la répartition granulométrique du mélange de poudres métalliques

Le mélange de poudres métalliques de piles a été tamisé sur des tamis ayant une ouverture de 3,38 mm. Le profil granulométrique du mélange de poudres métalliques a été déterminé à l’aide d’un granulomètre Laser (Horiba La-950V2, Laser scattering particles size distribution analysis).

1.4.8.2 Détermination des solides totaux

Les solides totaux (ST) ont été mesurés en triplicats en se basant sur la méthode 2540 B de l’APHA (APHA, 1999). Les boues métalliques liquides ont été pesées dans une coupelle en aluminium. Les échantillons ont ensuite été mis à sécher pendant une nuit dans un four à 105°C. Après une nuit, la boue séchée a été pesée.

1.4.8.3 Détermination du pH

Le pH des solutions de lixiviation et de précipitation a été mesuré à l'aide d'un pH-mètre (Fisher Acumet modèle 915) muni d'une électrode double jonction de Cole Parmer avec une cellule de référence Ag/AgCl. Un étalonnage du pH-mètre a été réalisé à l'aide de solutions tampon certifiées (pH 2,00 – 4,00 et 7,00) lors de chaque série de mesures.

1.4.8.4 Détermination des teneurs en métaux présents dans les piles et le mélange de piles

Une digestion complète de chaque type de déchet de pile a été réalisée en triplicats selon la méthode APHA 3050 B (APHA, 1999) (digestion en présence d'HNO_3 (50%), d'HNO_3 concentré et de H_2O_2 (30%)). Après digestion, les échantillons ont été filtrés à l'aide d'un filtre Fisherbrand de type G6 en fibre de verre (taille des pores = 1,5 µm).

Une seconde méthode de digestion a été testée afin de caractériser les teneurs en métaux présents dans chaque type de déchets de piles et dans le mélange de piles. Il s'agit d'une méthode de digestion totale en présence d'acide perchlorique et fluorhydrique (Van Loon, 1985).

La spectroscopie d'émission atomique couplée à un plasma induit est une technique couramment utilisée pour déterminer les teneurs en éléments métalliques présents en solution. Dans le cadre de ce projet de recherche, les teneurs en métaux (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Ti, Zn) ont été déterminées par ICP-AES radial à l'aide d'un appareil Varian (modèle Vista AX CCO Simultaneous ICP-AES, Palo Alto, CA, États-Unis). Les solutions de calibration ont été préparées à l'aide de solutions certifiées (SCP Science, Montréal, QC, Canada) et des solutions « contrôle » (SCP Science Multi éléments, Montréal, QC, Canada) ont été insérées dans la séquence d'analyse tous les 20 échantillons afin de mettre en évidence toute dérive de l'appareil. Tous les échantillons aqueux obtenus à différentes étapes du procédé (lixiviation, précipitation, extraction par solvant et électrodéposition) ont été filtrés (G6- Glass fiber, Fisher Scientific), puis dilués en utilisant une solution de HNO_3 à 5 %.

1.5 Principaux résultats

1.5.1 Choix de l'agent de lixiviation et optimisation des conditions opératoires

Parmi les divers agents de lixiviation testés dans cette étude, il a été prouvé que l'acide sulfurique est très efficace pour solubiliser tous les métaux. De plus, c'est la solution la moins coûteuse. Selon les résultats obtenus, le ratio S/L et la concentration en acide semblent être les paramètres influençant le plus la solubilisation des métaux à partir de la poudre de déchets de piles. Le meilleur taux de lixiviation a été obtenu dans les conditions opératoires suivantes: densité de pulpe = 180 g/L (p/v), [H_2SO_4] = 1 M, nombre d'étapes de lixiviation = 3 et temps de lixiviation = 30 min. Les rendements de solubilisation obtenus étaient de 65% pour le Mn, de 99,9% pour le Cd, de 100% pour le Zn, de 74% pour le Co et de 68% pour le Ni.

1.5.2 Deuxième optimisation des conditions opératoires pour la lixiviation avec un agent réducteur

Les résultats de la première optimisation ont montré un taux de lixiviation plus faible pour le Mn. Cela est dû au fait que le Mn(IV) est moins soluble que le Mn(II). Pour y remédier, un deuxième plan d'expériences a dû être effectué en présence de métabisulfite de sodium, utilisé comme agent réducteur. Les résultats ont mis en évidence l'effet positif de cet agent réducteur sur les rendements de solubilisation des métaux, surtout pour le Mn. Le ratio S/L a été mis en évidence comme étant le facteur influençant le plus le taux de lixiviation des métaux présents dans les piles usagées car la lixiviation est normalement contrôlée par la diffusion à travers la barrière entre la surface du métal et la solution acide (Cao *et al.*, 2006).

Les conditions optimales obtenues à partir du plan d'expériences Box Behnken pour la lixiviation sont: une étape de lixiviation, un ratio S/L = 10,9% (p/v), $[H_2SO_4] = 1,34$ M, une quantité de métabisulfite de sodium = 0,45 g/g de poudre de piles usagées et un temps de rétention = 45 min. Dans de telles conditions, les rendements de lixiviation atteignent 94% pour le Mn, 81% pour le Cd, 99% pour le Zn, 96% pour le Co et 68% pour le Ni.

1.5.3 Récupération des métaux à partir de la solution synthétique

Pour chaque étape de récupération, une solution synthètique a été préparée. La composition chimique de chaque solution est présentée au Tableau 1.9.

Tableau 1.9 **Concentrations en métaux (g/L) dans la solution synthétique pour les essais d'extraction par solvant et électrodéposition**

Étape	Zn	Fe	Mn	Cd	Ni	Co
Zn-Extraction Cyanex 272	19,9	0,53	27,5	3,17	3,51	0,26
Cd+Mn-Extraction D2EHPA	0,32	n.a	26,3	3,75	3,29	0,28
Récupération sélective du Cd par Cyanex 923	n.a	n.a	24,3	2,60	0,49	0,04
Électrodéposition sélective du Cd	n.a	n.a	27,0	4,30	n.a	0,00

n.a = non appliqué

1.5.3.1 Récupération du Zn

L'extraction par solvant avec le Cyanex 272 permettrait de récupérer sélectivement le Zn à partir de la solution contenant des quantités élevées de Zn, de Mn, de Cd, de Ni, de Co et de Fe (Tableau 1.9). La sélectivité d'extraction des métaux par les réactifs Cyanex 272 et D2EHPA est fortement contrôlée par le pH, car chaque métal possède une affinité distincte pour ces solvants organiques à différentes valeurs du pH (Wolfgang *et al.*, 2004). Plusieurs facteurs incluant la densité électronique des atomes d'oxygène des réactifs, l'acidité, la force ionique et la géométrie des liaisons formées dans la sphère de coordination interne, etc., influencent la sélectivité du métal dans le processus d'extraction (Gloe *et al.*, 2013). Selon l'information obtenue par Cytec Canada, l'extraction des métaux en présence de Cyanex 272 suit la séquence: $Fe^{3+}/Fe^{2+} > V^{4+} > Zn^{2+} > Al^{3+} > Cu^{2+} > Mn^{2+} > Co^{2+} > Mg^{2+} > Ca^{2+} > Ni^{2+}$ (Cytec, 2008c). Grace à cette différence d'affinité, il est possible d'extraire sélectivement le Zn à partir d'une solution contenant du Zn, du Mn, du Co et du Ni.

Les résultats ont montré qu'en utilisant le réactif Cyanex 272 comme agent extractant à pH 2,5, environ 97,6% du Zn présent dans la solution de lixiviation se retrouve dans la phase organique. Après lavage de la phase organique avec 0,4 M H_2SO_4, 81,8% du Zn a été récupéré sélectivement sous forme de $ZnSO_4$. Les teneurs résiduelles en Fe présentes dans la phase organique ont été éliminées par un deuxième lavage avec 1 M H_2SO_4 afin de recycler la solution organique dans le processus. L'acide de lavage peut aussi être recyclé dans le processus afin de diminuer le coût du procédé. L'étape d'extraction par solvant a été suivie par une électrodéposition afin de récupérer le Zn sous forme métallique. Un taux de récupération de 82,4% a été obtenu au bout de 3 heures. Cette partie de résultats est détaillée au Chapitre 5.

1.5.3.2 Récupération du Cd et Mn après élimination du Zn

1.5.3.2.1 Extraction du Cd et Mn dans la phase organique D2EHPA

Après une étape de récupération du Zn réalisée dans la section précédente, la solution aqueuse obtenue contenait principalement du Cd (3,75 g/L), du Co (0,28 g/L), du Mn (26,31 g/L), du Ni (3,29 g/L) et du Zn (0,32 g/L). Le Mn et le Cd ont été extraits simultanément par D2EHPA. Le pH de la solution aqueuse après l'extraction de Zn est très bas et le réactif D2EHPA a été choisi pour récupérer simultanément le Cd et le Mn à cause de son efficacité à pH 2,5 (Fatmehsari *et al.*, 2009). Il n'est donc pas nécessaire d'augmenter de beaucoup le pH après la première étape d'extraction. Comme il a été déjà mentionné, la sélectivité du solvant envers un métal est généralement contrôlée par le pH. La sélectivité des métaux en fonction du pH_{50} dans la solution de sulfate par D2EHPA suit la séquence suivante: Fe(II) > Zn(II) > Mn(II) > Cd(II) > Cu(II) > Mg(II) > Co(II) > Ni(II) (Cheng, 2000). Il est donc possible de transférer simultanément le Mn et le Cd vers la phase organique avant le Co et le Ni en contrôlant le pH. Le solvant organique D2EHPA a permis d'extraire 95-98% du Cd et 98,7-99,6% du Mn. Plus de détails sur les résultats d'extraction sont donnés au Chapitre 6.

1.5.3.2.2 Élimination du Co et du Ni à partir de Cd-Mn-Ni-Co-D2EHPA solvant organique (étape de scrubbing)

Les impuretés présentes dans la phase organique ont été éliminées par une étape de lavage. La solution de lavage concentrée en Mn et en Cd a été mélangée avec la solution organique contenant les impuretés (Co et Ni) sous agitation magnétique. Le Cd présent dans la solution de lavage va se substituer au Ni et au Co (impuretés) initialement présent dans la phase organique. Le taux d'élimination du Co est faible dans les essais réalisés avec la solution synthétique parce que la quantité initiale était plus élevée.

1.5.3.2.3 Lavage du solvant organique D2EHPA par l'acide sulfurique

Ensuite, la solution organique contenant majoritairement du Cd et du Mn a été lavée avec de l'acide sulfurique (H_2SO_4) afin d'obtenir une solution contenant du $CdSO_4$ (sulfate de cadmium) et du $MnSO_4$ (sulfate de manganèse). Les efficacités d'enlèvement du Cd et du Mn étaient de 94 - 100% et de 84 - 100%, respectivement. Cette solution sera utilisée dans l'étape d'électrodéposition.

1.5.3.2.4 Comparaison des essais de récupération sélective du Cd par le Cyanex 923 et électrodéposition

Afin de déterminer la méthode la plus efficace pour la récupération du Cd, l'extraction par solvant a été comparée avec la méthode d'électrodéposition.

La solution organique contenant majoritairement du Cd et du Mn (obtenue à la section 1.5.3.2.2) a également été lavée par de l'acide chlorhydrique afin d'obtenir une solution contenant des complexes métal-chlorures. Cette solution a été utilisée dans l'étape d'extraction sélective du Cd par Cyanex 923. Comme il a déjà été mentionné dans la partie bibliographique, le Cyanex 923 est un agent de solvatation, il faut donc que le métal soit sous forme de complexe avec une charge neutre (Équation 1.36) afin de pouvoir être extrait par ce type de solvant organique. Presque 99% du Cd a été récupéré sélectivement.

Par comparaison, la quasi-totalité du Cd a été récupérée par électrodéposition. Les deux méthodes ont été efficaces. Cependant, l' électrodéposition a été choisie à cause des conditions opératoires moins drastiques comparées à celles du Cyanex 923. Par conséquent, la solution contenant $CdSO_4$ et $MnSO_4$ obtenue après une étape de lavage avec H_2SO_4 a été utilisée pour les essais d'électrodéposition. Dans la réaction électrochimique, le Cd est réduit et déposé sur la cathode tandis que le Mn est oxydé. Le Mn ne s'est donc pas déposé sur la cathode. À cause de cette raison, seul le Cd s'est déposé à la surface de la cathode sous forme métallique.

Une diminution de la concentration en Cd de 4,2 g/L à 0,01 g/L a été observée après 90 min d'électrodéposition. Une étape de lavage avec de l'eau déminéralisée a été utilisée afin d'enlever le Mn dissous dans la poudre métallique du Cd. Après lavage, une quantité de 4,2 g de Cd métallique pur à 99%, a été obtenue.

1.5.3.2.5 Précipitation du Mn à partir de la solution $MnSO_4$

L'effluent issu de l'étape d'électrodéposition (section 1.5.3.2.4) contient principalement du Mn. Une masse de 25 g de $MnCO_3$ a été récupérée à partir de 200 mL de cette solution après trois lavages successifs avec une pureté de 94%.

1.5.3.3 Récupération du Ni

L'effluent aqueux obtenu à l'étape précédente après l'élimination du Cd et du Mn (section 1.5.3.2.1) contient principalement du Ni (2,5 g/L) et de faibles concentrations de Mn (0,3 g/L), de Cd (0,2 g/L) et de Co (0,2 g/L). Près de 96,5% du Co, 96% du Cd et 98,5% du Mn ont été éliminés par le Cyanex 272 à un pH contrôlé compris entre 5,0 et 5,5 tandis que seulement 4,5% du Ni a été perdu.

Concernant le mécanisme d'extraction du Co et du Ni par le Cyanex 272, l'électron libre sur l'atome d'oxygène dans le solvant forme une structure tétraédrique avec le Co tandis qu'avec le Ni, il forme une structure octaédrique (Habashi, 1999). À cause de cette différence, il est facile de séparer les deux métaux sous des conditions contrôlées. Les impuretés (Co, Mn et Cd) ont été éliminées à partir du solvant avec une étape de lavage en présence de H_2SO_4. La solution obtenue après lavage acide contient pricipalement du Ni. Le pH de la solution a été monté jusqu'à 10 afin de préciter le Ni sous forme de carbonates. Le précipité obtenu a été lavé à l'eau distillée. Après deux étapes de lavage, un précipité de $NiCO_3$ ayant une pureté de 95% a été obtenu. Les résultats sont détaillés au Chapitre 6.

1.5.4 Récupération des métaux à partir de la solution réelle

La composition chimique de la solution réelle obtenue dans les conditions optimales de lixiviation est donnée au Tableau 1.10.

Tableau 1.10 Composition moyenne en métaux dans le lixiviat produit dans les conditions optimales: 1,34 M H_2SO_4, 0,45 g $Na_2S_2O_5$/g de poudre de piles, S/L ratio = 10,9% (p/v), temps de réaction = 45 min et T = 25°C

Métaux	Concentration (g/L)
Zn	20,8
Cd	3,58
Mn	28,6
Ni	4,41
Co	0,29
Fe	0,69

La Figure 1.8 présente le procédé global utilisé pour récupérer les métaux (Zn, Mn, Cd et Ni) à partir des déchets de piles mélangées, ainsi que le bilan de masse global de chaque étape. La section suivante sera consacrée à la discussion des résultats obtenus dans la solution réelle comparativement aux résultats obtenus avec la solution synthétique (présentés à la section 1.5.3).

1.5.4.1 Récupération du Zn

Concernant l'essai avec la solution réelle, près de 99% du Zn a été récupéré en présence de 30% Cyanex 272 tandis que 98,5% du Zn a été extrait à partir de la solution synthétique en utilisant 20% Cyanex 272. Une plus grande concentration de Cyanex 272 a été utilisée avec la solution réelle à cause de la grande concentration en Zn obtenue dans la solution réelle comparativement à la solution synthétique. Les efficacités d'extraction pour les deux solutions étaient quasi-identiques.

Lors du lavage de la phase organique pour récupérer le Zn, aucune différence notable n'a été observée entre les deux solutions (synthétique ou réelle). En effet, l'efficacité de récupération était de 92% pour la solution réelle comparée à 91% pour la solution synthétique.

Dans l'étape d'électrodéposition du Zn, le rendement moyen obtenu pour la solution réelle était de 70%, tandis qu'avec la solution synthétique, il était de 82,4%. Le faible rendement d'électrodéposition pour la solution réelle pourrait être dû à la plus faible concentration en Zn pour les essais réalisés avec la solution réelle (Gamburg *et al.*, 2011). Cette faible concentration en métal diminue le rendement faradique à la cathode (Gamburg *et al.*, 2011).

1.5.4.2 Récupération du Cd et du Mn

La solution de D2EHPA a été utilisée afin de récupérer simultanément le Cd et le Mn. Les efficacités d'extraction du Cd et du Mn obtenus ont été plus faibles pour la solution réelle. Les faibles rendements sont dus au pH d'équilibre plus faible pendant l'étape d'extraction. Malgré la même quantité de NaOH utilisée pendant l'extraction, le pH d'équilibre obtenu dans l'essai avec la solution réelle (pH ~ 2,2) est inférieur à celui obtenu avec la solution synthétique (pH ~ 2,7). Les quantités de métaux extraits augmentent avec l'augmentation du pH. Les rendements moyens pour l'extraction du Cd et du Mn étaient de 97% et 99% pour la solution synthétique et de 93% et 91% avec la solution réelle, respectivement.

Après l'étape de lavage, 97% du Cd et 92% du Mn ont été récupérés dans l'essai réalisé avec la solution synthétique, tandis que seulement 85% du Cd et 91% du Mn ont été récupérés dans l'essai réalisé avec la solution réelle. La même concentration en acide a été utilisée pour l'étape de lavage pour les deux solutions. Cependant, les volumes d'acide (100 mL pour les essais avec la solution synthétique et 800 mL pour les essais avec la solution réelle) et les vitesses d'agitation (400 rpm pour la solution synthétique et 500 rpm pour la solution réelle) étaient différents, ce qui peut expliquer les différences observées.

Concernant l'électrodéposition sélective du Cd à partir de la solution contenant du $MnSO_4$ et du $CdSO_4$, près de 99,7% du Cd a été déposé à partir de la solution synthétique après 90 min, tandis que 240 min ont été nécessaires pour avoir la même efficacité lors de l'essai avec la solution réelle. Ces différents résultats peuvent être expliqués par la plus faible concentration en Cd présent dans la solution réelle par rapport à la solution synthétique. Seulement 2,4 g de Cd (1 L de solution) (99,7% pureté) ont été récupérés après une étape de lavage tandis que 4,3 g du Cd (1 L de solution) (98% pureté) a été obtenu à partir de la solution synthétique. Le dépôt d'une plus grande masse de Cd est dû à la plus grande concentration en Cd présent dans l'effluent de l'étape du lavage issu de l'essai réalisé avec la solution synthétique.

Presque 100% du Mn a été précipité à partir de la solution synthétique et de la solution réelle. Une masse de 60 g de $MnCO_3$ avec une pureté de 94% a été obtenue à partir de la solution synthétique (1 L), tandis qu'une masse de 50 g de $MnCO_3$ avec une pureté de 97% a été obtenue à partir de la solution réelle (1 L). Ces différents résultats sont dûs aux différentes concentrations en Mn obtenues après l'étape de lavage avec le réactif D2EHPA.

1.5.4.3 Récupération du Ni

Les efficacités d'enlèvement pour le Cd, le Mn, le Co étaient semblables pour les deux essais (essai avec la solution synthétique et essai avec la solution réelle). Des proportions de 97% Co, 96% Cd et 99% Mn ont été transférées vers la phase organique à partir de la solution synthétique en comparaison à 100%, 99% et 100% à partir de la solution réelle, respectivement. Les faibles concentrations des impuretés ont été éliminées efficacement malgré le grand volume de lixiviat utilisé. Une étape de lavage a été ajoutée afin de régénérer le solvant organique. Les taux d'élimination des impuretés obtenus lors des essais réalisés avec la solution synthétique sont faibles comparativement aux essais réalisés avec la solution réelle. Un rendement de lavage supérieur à 90% a été obtenu pour les essais réalisés avec la solution réelle.

Finalement, 4,8 g du Ni ont été précipités sous forme de carbonate à partir de 1 L de solution $NiSO_4$ avec une pureté de 96,7% tandis que 4,0 g du Ni ont été récupérés à partir de la solution synthétique (95% pureté) (1 L de solution).

Le Tableau 1.11 compare les rendements de récupération des métaux obtenus lors des essais réalisés avec la solution synthétique et la solution réelle. Les conditions opératoires utilisées pour les deux essais (solution synthétique et solution réelle) ne sont pas différentes pour les étapes d'extraction par solvant et de précipitation. Pour les essais d'électrodéposition, les conditions opératoires sont les mêmes pour les deux essais sauf que le temps d'électrodéposition est plus long pour les essais réalisés avec la solution réelle.

Tableau 1.11 Comparaison des résultats entre les essais réalisés avec la solution synthétique et ceux réalisés avec la solution réelle

Étape	**Solution synthétique**	**Solution réelle**
Zn- Extraction Cyanex 272		
Récupération Zn (après extraction)(%)	99	99
Récupération Zn (après lavage) (%)	82	95
Cd+Mn- Extraction D2EHPA		
Récupération Cd et Mn (après extraction) (%)	97 (Cd) et 99,2 (Mn)	93 (Cd) et 91 (Mn)
Récupération Cd et Mn (après lavage) (%)	97 (Cd) et 92 (Mn)	85 (Cd) et 91 (Mn)
Récupération Zn-Électrodéposition (%)	82	70
Récupération Cd-Électrodéposition (%)	100	100
Récupération Mn-Précipitation (%)	100	100
Récupération Ni-Précipitation (%)	100	100
Élimination des impuretés par Cyanex 272		
Extraction du Co, Cd et Mn (%)	97 (Co), 96 (Cd) et 99 (Mn)	99 (Co), 99 (Cd) et 100 (Mn)
Récupération du Co, Cd et Mn - Lavage (%)	67 (Co), 67 (Cd) et 49 (Mn)	92 (Co), 99 (Cd) et 97 (Mn)

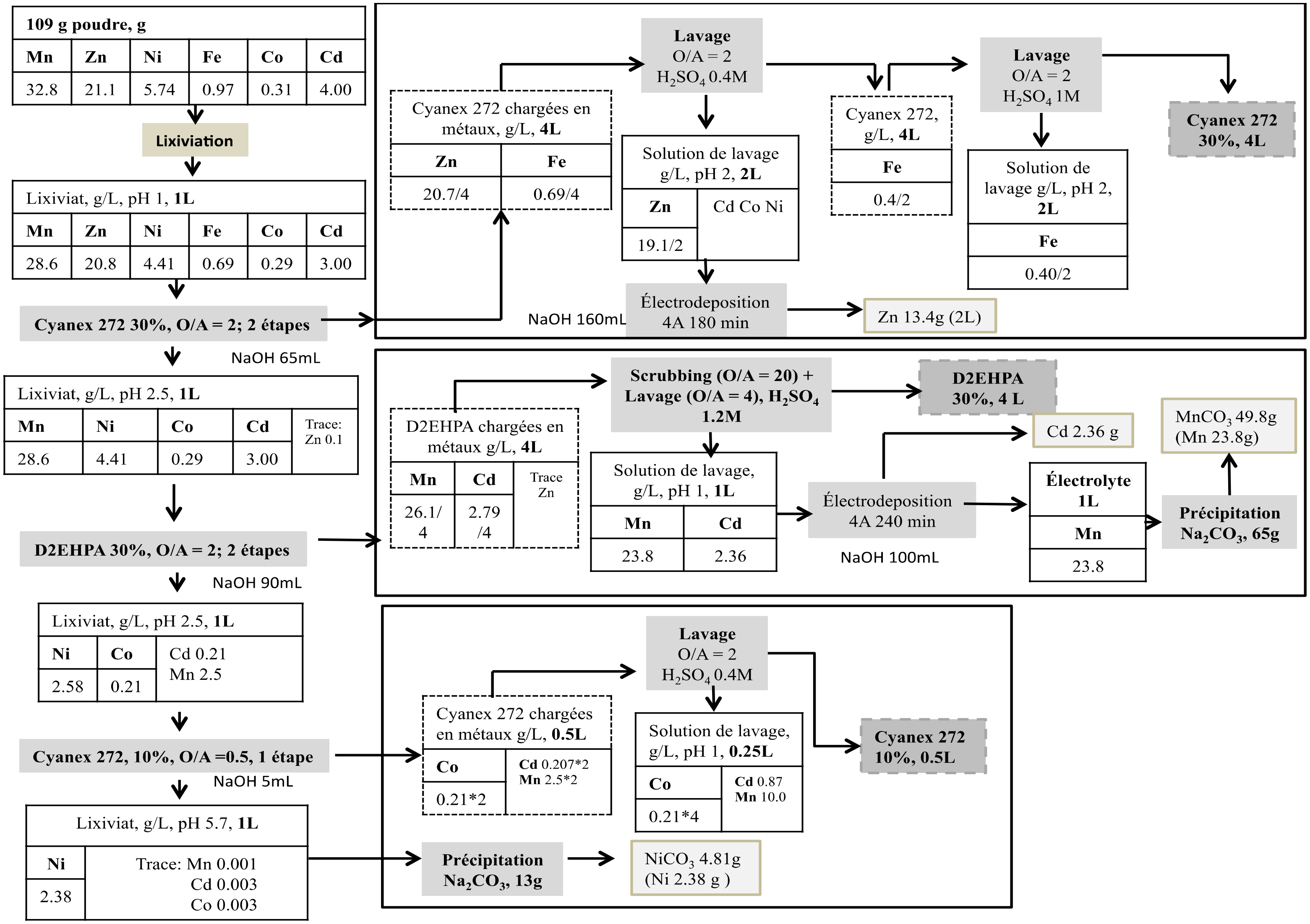


Figure 1.8 **Schéma du procédé global utilisé pour recycler des métaux à partir de déchet de piles mélangé**

1.6 Conclusion

Les travaux réalisés dans le cadre de cette étude visaient à développer un procédé simple et efficace pour la récupération sélective des métaux à partir des déchets de piles mélangées. Le traitement direct des déchets de piles mélangées permet d'éviter une étape de tri et, par conséquent, d'économiser sur le coût élevé de la main d'œuvre. Cela permet également de réduire le nombre d'opérations unitaires. Les mélanges ont été préparés en respectant les proportions de chaque type de piles retrouvés dans les sites de recyclage au Québec. Les piles alcalines sont les plus présentes dans le mélange suivi par les piles Zn-C, les piles Ni-Cd, les piles Ni-MH, les piles Li-ion et les piles au Li. Une fois mélangées, les piles sont broyées afin d'obtenir une fine poudre. Les métaux présents dans cette poudre ont été solubilisés avant d'être récupérés.

L'optimisation des conditions opératoires a été effectuée en utilisant un modèle Box Behnken. Nos résultats ont montré que la lixiviation des métaux présents dans cette poudre de piles mélangées en présence d'acide sulfurique 1,34 M avec une fraction de solide de 10,9% (p/v) durant 120 min et en présence de métabisulfite de sodium, a permis d'extraire 94% du Mn, 81% du Cd, 99% du Zn, 96% du Co et 68% du Ni. Plusieurs procédés ont été utilisés pour récupérer sélectivement chaque métal à partir de la solution de lixiviation. Une extraction par Cyanex 272 suivie d'une électrodéposition a permis de récupérer 64% du Zn à partir de la poudre de pile. En combinant une extraction par D2EHPA et une électrodéposition, 59% du Cd a été récupéré sous forme métallique et 73% du Mn a été récupéré sous forme de carbonates à partir de la poudre de piles. Enfin, la solution appauvrie en Zn-Cd-Mn a été purifiée par

Cyanex 272 à pH 5. Une solution pure de $NiSO_4$ a donc été obtenue. Près de 41% de $NiCO_3$ a été récupéré par le procédé de précipitation avec Na_2CO_3.

Les faibles taux de récupération des métaux sont dus aux pertes accumulées lors des étapes d'extraction. Il serait donc important de réduire ces pertes afin d'améliorer les rendements.

La comparaison entre les résultats obtenus avec la solution synthétique et ceux obtenus avec la solution réelle n'a montré aucune différence importante pour les étapes d'extraction par solvant. Cependant, les rendements d'électrodéposition étaient moins élevés pour les essais réalisés avec la solution réelle à cause des faibles concentrations en Zn et en Cd initialement présentes dans les solutions. En effet, une faible concentration en métal conduit à un faible rendement faradique. Toutefois, ce dernier pourrait être amélioré en utilisant un additif ou en concentrant les métaux par le procédé d'extraction par solvant.

Les métaux ont été récupérés avec une grande pureté grâce à l'utilisation de la méthode d'extraction par solvant. Contrairement aux autres procédés, le solvant peut être réutilisé dans le procédé, ce qui représente un avantage économique. Selon nos résultats, ce procédé permet de décontaminer les effluents contenant plusieurs métaux toxiques pour l'environnement et de répondre à la règlementation québécoise, sauf pour le Cd (~3 ppm) (Environnement Canada, 1999).

Par la présente étude, nous avons démontré qu'il est possible de récupérer les métaux à haute valeur présents dans les déchets de piles sans aucune étape préalable de tri. L'élimination de cette étape permettrait de diminuer les coûts élevés, au Canada, de la main d'œuvre et de réduire le nombre d'opérations unitaires. L'existence d'un procédé simple et efficace pour le traitement des déchets de piles usagées offrirait une alternative viable et économique à l’enfouissement et/ou à l’incinération. Toutefois, le passage à l’échelle pilote serait nécessaire pour valider le procédé à plus grande échelle.

1.7 Références

Almeida MF, Xara SM, Delgado J & Costa CA (2006) Characterization of spent AA household alkaline batteries. *Waste Management* 26(5):466-476.

APHA (1999) *Standards methods for examination of water and wastewaters.* American Public Health Association, USA.

Babakhani A, Rashchi F, Zakeri A & Vahidi E (2014) Selective separation of nickel and cadmium from sulfate solutions of spent nickel-cadmium batteries using mixtures of D2EHPA and Cyanex 302. *Journal of Power Sources* 247:127-133.

Barnard KR (2010) Identification and characterisation of a Cyanex 272 degradation product formed in the Murrin Murrin solvent extraction circuit. *Hydrometallurgy* 103(1-4):190-195.

BEBAT (2016) *Pour une meilleure utilisation des piles et petits accus*. BEBAT, Tienen, Belgique, http://www.villapila.be/pdf/BeBat-PourUneMeilleureUtilisation-FR.pdf (visité le 5 juin 2016).

Bégin D & Gérin M (2002) *Les grandes familles de solvants organiques: Utilisations et aspects physio-chimiques*. *(santé, sécurité, substitution)*. Université de Montréal, Montréal, QC, Canada,http://www.dsest.umontreal.ca/recherche_rayonnement/documents/RR_SolvInd5_Chapitre2.pdf (visité le 5 juin 2016).

Bingol D, Canbazoglu M & Aydogan S (2005) Dissolution kinetics of malachite in ammonia/ammonium carbonate leaching. *Hydrometallurgy* 76(1-2):55-62.

Biswas RK, Karmakar AK, Kumar SL & Hossain MN (2015) Recovery of manganese and zinc from waste Zn-C cell powder: Characterization and leaching. *Waste Management* 46:529-535.

Blais JF, Djedidi Z, Ben Cheikh R, Tyagi RD & Mercier G (2008) Metals precipitation from effluents: Review. *Waste Management* 12:135-149.

Bourque C (2010) *Les résidus domestiques dangereux*. Recyc-Québec, Québec, QC, Canada, http://www.recyc-quebec.gouv.qc.ca/Upload/Publications/Fiche-rdd.pdf (visité le 5 juin 2016).

Brito PSD, Patricio S, Rodrigues LF & Sequeira CAC (2012) Electrodeposition of Zn-Mn alloys from recycling Zn-MnO_2 batteries solutions. *Surface Coating Technology* 206(13):3036-3047.

Buzatu T, Popescu G, Birloaga I & Saceanu S (2013a) Study concerning the recovery of zinc and manganese from spent batteries by hydrometallurgical processes. *Waste Management* 33(3):699-705.

Call2Recycle (2012) *Call2Recycle*. http://www.call2recycle.ca/british-columbia (visité le 5 juin 2016).

Cao Y, Harjanto S, Shibayama A, Naitoh I, Nanami T, Kasahara K, Okumura Y & Fujita T (2006) Kinetic study on the leaching of Pt, Pd and Rh from automotive catalyst residue by using chloride solutions. *Materials Transactions* 47(8):2015-2024.

Charette SL (2014) *Récupération et traitement des piles grand public au Québec pour mettre en oeuvre la responsabilité élargie des producteurs*. Essai présenté au Centre universitaire de formation en environnement et développement durable en vue de l'obtention du grade de maître en environnement, Université de Sherbrooke, Sherbrooke, QC, Canada, 104 p.

Chauhan G, Pant KK & Nigam KDP (2015) Conceptual mechanism and kinetic studies of chelating agent assisted metal extraction process from spent catalyst. *Journal of Industrial and Engineering Chemistry* 27:373-383.

Chen GH (2004) Electrochemical technologies in wastewater treatment. *Separation and Purification Technology* 38(1):11-41.

Cheng CY (2000) Purification of synthetic laterite leach solution by solvent extraction using D2EHPA. *Hydrometallurgy* 56(3):369-386.

Cholico-Gonzalez D, Chagnes A, Cote G & Avila-Rodriguez M (2015) Separation of Co(II) and Ni(II) from aqueous solutions by bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) using trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) as solvent. *Journal of Molecular Liquids* 209:203-208.

Cook CC & Wagner MJ (2013) Ceramic/polymer solid electrolyte based lithium water primary battery. *Electrochemical Acta* 89:778-783.

Cuthbertson (2014) *Tesla to Create World's Largest Lithium-ion Battery Factory*. http://popsop.com/2014/08/worlds-largest-battery-factory-gigafactory-to-be-created-by-tesla-and-panasonic-in-the-u-s/ (visité le 5 juin 2016).

Cytec (2008) *Cyanex 272 Extractant*. Cytec, Niagara Falls, ON, Canada, https://www.cytec.com/sites/default/files/datasheets/CYANEX 272 Brochure.pdf (visité le 5 juin 2016), 16 p.

de Souza CCBM, de Oliveira DC & Tenorio JAS (2001) Characterization of used alkaline batteries powder and analysis of zinc recovery by acid leaching. *Journal of Power Sources* 103(1):120-126.

Denkhaus E & Salnikow K (2002) Nickel essentiality, toxicity, and carcinogenicity. *Critical Review in Oncology/Hematology* 42(1):35-56.

Diniz CV, Ciminelli VST & Doyle FM (2005) The use of the chelating resin Dowex M-4195 in the adsorption of selected heavy metal ions from manganese solutions. *Hydrometallurgy* 78(3-4):147-155.

École Polytechnique de Montréal (2006) *Fiche d'information, les piles domestiques 2006*. École Polytechnique de Montréal, Montréal, QC, Canada, http://www.polymtl.ca/durable/docs/documents/Fiche_info_piles_domestiques.pdf (visité le 5 juin 2016).

Environnement Canada (1999) *Recommandations canadiennes pour la qualité des sols: Environnement et santé humaine*. Gouvernement du Canada, Ottawa, ON, Canada.

EPBA (2010) *2010 sustainability report: looking back, looking ahead.* EBPA, Bruxelles, Belgique, http://www.epbaeurope.net/documents/EPBASustainabilityreport2010_final.pdf (visité le 5 juin 2016), 72 p.

Farouk T (2003) *Perfectionnement apporté au traitement des piles électriques usagées par voie hydrométallurgique.* Brevet français No. 2,827,710.

Fatmehsari DH, Darvishi D, Etemadi S, Hollagh ARE, Alamdari EK & Salardini AA (2009) Interaction between TBP and D2EHPA during Zn, Cd, Mn, Cu, Co and Ni solvent extraction: A thermodynamic and empirical approach. *Hydrometallurgy* 98(1-2):143-147.

Fernandes A, Afonso JC & Dutra AJB (2012) Hydrometallurgical route to recover nickel, cobalt and cadmium from spent Ni-Cd batteries. *Journal of Power Sources* 220:286-291.

Fowler BA (2009) Monitoring of human populations for early markers of cadmium toxicity: A review. *Toxicology and Applied Pharmacology* 238(3):294-300.

Freeman MH (1997) *Standard handbook of hazardous waste treatment and disposal.* McGraw Hill Inc., New York, NY, USA, 1097 p.

Friedli CKW (2005) *Chimie générale pour ingénieur*. Press polytechniques et universitaires romandes, Lausanne, Suisse, 739 p.

Frohlich S & Sewing D (1995) The BATENUS process for recycling mixed battery waste. *Journal of Power Sources* 57(1-2):27-30.

Furlani G, Moscardini E, Pagnanelli F, Ferella F, Veglio F & Toro L (2009) Recovery of manganese from zinc alkaline batteries by reductive acid leaching using carbohydrates as reductant. *Hydrometallurgy* 99(1-2):115-118.

Gamburg YD & Giovanni Z (2011) *Theory and Practice of Metal Electrodeposition.*Springer-Verlage New York., New York, NY, USA, 378 p.

Gloe K, Gloe K, Wenzel M, Lindoy LF & Li F (2013) *Supramolecular chemistry in solvent extraction: Toward highly selective extractants and a better understanding of phase-transfer phenomena.* Dans: Ion Exchange and Solvent Extraction, Volume 21, Supramolecular Aspects of Solvent Extraction, Moyer BA (Éditeur), Taylor & Francis Group, CRC Press, Boca Raton, FL, USA, pp. 1-48.

GPI International (2009) *Primary lithium batteries*. GPI international, New Territories, Hong Kong, http://www.gpbatteries.it/allegati/cataloghi/primary_lithium.pdf (visité le 5 juin 2016).

Granata G, Pagnanelli F, Moscardini E, Takacova Z, Havlik T & Toro L (2012) Simultaneous recycling of nickel metal hydride, lithium ion and primary lithium batteries: Accomplishment of European guidelines by optimizing mechanical pre-treatment and solvent extraction operations. *Journal of Power Sources* 212:205-211.

Guillaume P, Leclerc N, Lapicque F & Boulanger C (2008) Electroleaching and electrodeposition of zinc in a single-cell process for the treatment of solid waste. *Journal of Hazardous Materials* 152(1):85-92.

Gupta B, Deep A & Malik P (2001) Extraction and recovery of cadmium using Cyanex 923. *Hydrometallurgy* 61(1):65-71.

Habashi F (1999) *Textbook of hydrometallurgy.* Metallurgie Extractive Quebec, Québec, QC, Canada, 689 p.

Hazotte C, Meux E, Leclerc N & Lapicque F (2015) Electroassisted leaching of black mass solids from Ni-Cd batteries for metal recovery: Investigation of transport and transfer phenomena coupled to reactions. *Chemical Engineering and Processing* 96:83-93.

Housecroft CE (2010) *Chimique inorganique.* De Boeck, Bruxelles, Belgique, 3, 1042 p.

Huang K, Li J & Xu Z (2009) A novel process for recovering valuable metals from waste nickel-cadmium batteries. *Environmental Science & Technology* 43(23):8974-8978.

Hutton-Ashkenny M, Ibana D & Barnard KR (2015) Reagent selection for recovery of nickel and cobalt from nitric acid nickel laterite leach solutions by solvent extraction. *Minerals Engineering* 77:42-51.

Innocenzi V & Veglio F (2012) Recovery of rare earths and base metals from spent nickel-metal hydride batteries by sequential sulphuric acid leaching and selective precipitations. *Journal of Power Sources* 211:184-191.

International Zinc Association (2010) *Le zinc et le développement durable.* International Zinc Association, http://www.zinc.org/general/zinc_sustainable_material_french.pdf (visité le 5 juin 2016).

Japan Battery Association (2016) *Secondary battery sales statistics by volume*. Japan Battery Association, Tokyo, Japon, http://www.baj.or.jp/e/ (visité le 16 juillet 2016).

Klaassen P & Lagourgue D (2012) *Measuring recyclers'performance, The challenges & processes of battery recycling.* Call2recycler, Canada, http://www.cw2rc.ca/Portals/0/2015%20Presentations/DL%20PK%20FINAL%20v2.pdf (visité le 5 juin 2016). (visité le 5 juin 2016).

Leopold AA, Coll MT, Fortuny A, Rathore NS, Sastre AM (2010) Mathematical modeling of cadmium (II) solvent extraction from neutral and acidic chloride media using Cyanex923 extractants as a metal carrier. *Journal of Hazardous Materials* 182:903-911.

Li J, Shi P, Wang Z, Chen Y & Chang CC (2009) A combined recovery process of metals in spent lithium-ion batteries. *Chemosphere* 77(8):1132-1136.

Li KK, Peng CH & Jiang KQ (2011) The recycling of Mn-Zn ferrite wastes through a hydrometallurgical route. *Journal of Hazardous Materials* 194:79-84.

Li L, Ge J, Chen R, Wu F, Chen S & Zhang X (2010) Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries. *Waste Manag* 30(12):2615-2621.

Li L, Lu J, Ren Y, Zhang XX, Chen RJ, Wu F & Amine K (2012) Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries. *Journal of Power Sources* 218:21-27.

Li Y & Xi G (2005) The dissolution mechanism of cathodic active materials of spent Zn-Mn batteries in HCl. *J Hazard Mater* 127(1-3):244-248.

Mantuano DP, Dorella G, Elias RCA & Mansur MB (2006) Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid-liquid extraction with Cyanex 272. *Journal of Power Sources* 159(2):1510-1518.

Meshram P, Pandey BD & Mankhand TR (2016) Process optimization and kinetics for leaching of rare earth metals from the spent Ni-metal hydride batteries. *Waste Management* 51:196-203.

MDDELCC (2012) *Guide d'application du règlement sur la récupération et la valorisation de produits par les entreprises*. , Le ministère du Développement durable, de l’Environnement et de la Lutte contre les changements climatiques, Canada, http://www.mddelcc.gouv.qc.ca/matieres/reglement/recup-valor-entrepr/guide-application.pdf (visité le 5 Juin 2016).

Monier V, Deprouw A, Berthoux B & Lhomme KL (2014) *Rapport annuel du registre piles et accumulateurs*. Agence de l'Environnement et de la Maîtrise de l'Énergie, Paris, France, http://www.developpement-durable.gouv.fr/IMG/pdf/piles-accumulateurs-2013-rapport-annuel-registre.pdf (visité le 5 juin 2016).

Moradkhani D, Rasouli M, Behnian D, Arjmandfar H & Ashtari P (2012) Selective zinc alkaline leaching optimization and cadmium sponge recovery by electrowinning from cold filter cake (CFC) residue. *Hydrometallurgy* 115:84-92.

Mwema MD, Mpoyo M & Kafumbila K (2002) Use of sulfur dioxide as reducing agent in cobalt leaching at Shituru hydrometallurgical plant. *The Journal of the South African Institute of Mining and Metallurgy* Jan/Feb, 4 p.

Namias J (2013) *The future of electronic waste recycling in the United States*. Colombia University, New York, NY, USA, 66 p.

Nan JM, Han DM, Yang MJ, Cui M & Hou XL (2006) Recovery of metal values from a mixture of spent lithium-ion batteries and nickel-metal hydride batteries. *Hydrometallurgy* 84(1-2):75-80.

Nayl AA, Elkashab RA, Badawy SM & El-Khateeb MA (2014) Acid leaching of mixed spent Li-ion batteries. *Arabian Journal of Chemistry* 10.1016/j.arabic.2014.04.001:8.

Ndlovu S (2008) Biohydrometallurgy for sustainable development in the African minerals industry. *Hydrometallurgy* 91(1-4):20-27.

Nogueira CA & Margarido F (2004) Leaching behaviour of electrode materials of spent nickel–cadmium batteries in sulphuric acid media. *Hydrometallurgy* 72(1-2):111-118.

Nriagu J (2007) *Zinc toxicity in humans*. School of Public Health, University of Michigan, Ann Arbour, MI, USA, 7 p.

Oishi T, Yaguchia M, Koyama K, Tanaka M & Lee JC (2008) Effect of phosphate on lead removal during a copper recycling process from wastes using ammoniacal chloride solution. *Hydrometallurgy* 90(2-4):161-167.

Olivetti E, Gregory J & Kirchain R (2011) *Life cycle impacts of alkaline batteries with a focus on end-of-life*. Massachusetts Institute of Technology, Boston, MA, USA, 110 p.

Owusu G (1998) Selective extractions of Zn and Cd from Zn-Cd-Co-Ni sulphate solution using di-2-ethylhexyl phosphoric acid extractant. *Hydrometallurgy* 47(2-3):205-215.

Pakarinen J & Paatero E (2011) Recovery of manganese from iron containing sulfate solutions by precipitation. *Minerals Engineering* 24(13):1421-1429.

Pant D, Joshi D, Upreti MK & Kotnala RK (2012) Chemical and biological extraction of metals present in E waste: A hybrid technology. *Waste Management* 32(5):979-990.

Peppard DF, Driscoll WJ, Sironen RJ & McCarty S (1957) Nonmonotonic ordering of lanthanides in tributyl phosphate-nitric acid extraction systems. *Journal of Inorganic and Nuclear Chemistry* 4(5-6):326-333.

Provazi K, Campos BA, Espinosa DCR & Tenorio JAS (2011) Metal separation from mixed types of batteries using selective precipitation and liquid-liquid extraction techniques. *Waste Management* 31(1):59-64.

Racz R & Ilea P (2013) Electrolytic recovery of Mn_3O_4 and Zn from sulphuric acid leach liquors of spent zinc-carbon-MnO2 battery powder. *Hydrometallurgy* 139:116-123.

Recybat (2010) *Traitement des déchets de piles ou d'accumulateurs d'automobiles*. Recybat, , Houyet, Belgique, http://www.recybat.be/index.php?page=traitement-des-dechets&hl=fr_FR (visité le 5 juin 2016).

RIS International (2007) Canadian consumer battery baseline study. RIS International Limited, Toronto, ON, Canada, http://www.docstoc.com/docs/79783916/Canadian-Consumer-Battery-Baseline-Study-Final-Report (visité le 5 juin 2016).

Roberge J (2010) *Les piles domestiques.* Recyc-Quebec, Quebec, QC, Canada, http://www.recyc-quebec.gouv.qc.ca/Upload/Publications/Fiche-piles.pdf, consulté le 23 déc 2015.

Salgado A (2003) Recovery of zinc and manganese from spent alkaline batteries by liquid–liquid extraction with Cyanex 272. *Journal of Power Sources* 115(2):367-373.

Sayilgan E, Kukrer T, Civelekoglu G, Ferella F, Akcil A, Veglio F & Kitis M (2009a) A review of technologies for the recovery of metals from spent alkaline and zinc-carbon batteries. *Hydrometallurgy* 97(3-4):158-166.

Sayilgan E, Kukrer T, Ferella F, Akcil A, Veglio F & Kitis M (2009b) Reductive leaching of manganese and zinc from spent alkaline and zinc-carbon batteries in acidic media. *Hydrometallurgy* 97(1-2):73-79.

Senanayake G, Shin SM, Senaputra A, Winn A, Pugaev D, Avraamides J, Sohn JS & Kim DJ (2010) Comparative leaching of spent zinc-manganese-carbon batteries using sulfur dioxide in ammoniacal and sulfuric acid solutions. *Hydrometallurgy* 105(1-2):36-41.

Shin SM, Senanayake G, Sohn JS, Kang JG, Yang DH & Kim TH (2009) Separation of zinc from spent zinc-carbon batteries by selective leaching with sodium hydroxide. *Hydrometallurgy* 96(4):349-353.

Sloop SE & Bend OR (2007) *System and method for removing an electrolyte from an energy storage and/or conversion device using a supercritical fluid.* Brevet US 2007/0292746 A1 (20 décembre 2007).

Sun L & Qiu KQ (2012) Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries. *Waste Management* 32(8):1575-1582.

Tokuda H, Kuchar D, Mihara N, Kubota M, Matsuda H & Fukuta T (2008) Study on reaction kinetics and selective precipitation of Cu, Zn, Ni and Sn with H(2)S in single-metal and multi-metal systems. *Chemosphere* 73(9):1448-1452.

Uniross (2007) *Etude UNIROSS sur l'impact environnemental des piles*. Uniross, Lognes, France, http://techno.freou.free.fr/animatech/docs_divers/UNIROSS_impact_piles_environnement.pdf (visité le 5 juin 2016).

Vahidi E, Rashchi F & Moradkhani D (2009) Recovery of zinc from an industrial zinc leach residue by solvent extraction using D2EHPA. *Minerals Engineering* 22(2):204-206.

Van Loon JC (1985) *Selected methods of trace metal analysis: biological and 464 environmental samples.* John Wiley & Sons Inc., New York, NY, USA, 357 p.

Vatistas N, Bartolozzi M & Arras S (2001) The dismantling of the spent alkaline zinc manganese dioxide batteries and the recovery of the zinc from the anodic material. *Journal of Power Sources* 101(2):182-187.

Velgosova O, Kadukova J, Marcincakova R, Palfy P & Trpcevska J (2013) Influence of H_2SO_4 and ferric iron on Cd bioleaching from spent Ni-Cd batteries. *Waste Management* 33(2):456-461.

Veloso LRS, Rodrigues LEOC, Ferreira DA, Magalhaes FS & Mansur MB (2005) Development of a hydrometallurgical route for the recovery of zinc and manganese from spent alkaline batteries. *Journal of Power Sources* 152(1):295-302.

WHO (2001) *Chapter 6.8 Manganese*. World Health Organization, Genève, Suisse, http://www.euro.who.int/__data/assets/pdf_file/0003/123078/AQG2ndEd_6_8Manganese.pdf (visité le 5 juin 2016).

Wolfgang H, Kiefer R, Sto C & Bartosch C (2004) *Metal separation by pH-driven parametric pumping*. Dans: Ion exchange and solvent extraction, Volume 16, Arup KSVM (Éditeur), Taylor & Francis Group, LLC, New York, NY, USA, 3 p.

Xie F, Zhang TA, Dreisinger D & Doyle F (2014) A critical review on solvent extraction of rare earths from aqueous solutions. *Minerals Engineering* 56:10-28.

Yang CC (2003) Recovery of heavy metals from spent Ni-Cd batteries by a potentiostatic electrodeposition technique. *Journal of Power Sources* 115(2):352-359.

Zangari YDGG (2011) *Theory and practice of metal electrodeposition.* Springer, Londres, Angleterre, 375 p.

Zhu SG, He WZ, Li GM, Zhou X, Zhang XJ & Huang JW (2012) Recovery of Co and Li from spent lithium-ion batteries by combination method of acid leaching and chemical precipitation. *Transactions of the Nonferrous Metal Society* 22(9):2274-2281.

RÉCUPÉRATION PAR VOIE HYDROMÉTALLURGIQUE DES MÉTAUX À PARTIR DES DÉCHETS DE PILES MÉLANGÉES

PARTIE II: ARTICLES SCIENTIFIQUES

2 CHAPITRE 2

METAL RECYCLING TECHNOLOGIES FOR BATTERY WASTE

Revue : Recent Patents on Engineering 2014, 8, 13-23

Auteurs : Kulchaya Tanong[a], Jean-François Blais[b*], Guy Mercier[c]

[a] Ph.D. student, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-4677 ext. 4473, Fax: (418) 654-2600, email: kulchaya.tanong@ete.inrs.ca

[b] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-2575, Fax: (418) 654-2600, email: jean-francois.blais@ete.inrs.ca

[c] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-2633, Fax: (418) 654-2600, email: guy.mercier@ete.inrs.ca

*Corresponding author:
Tel: (418) 654-2575, Fax: (418) 654-2600
email: **jean-francois.blais@ete.inrs.ca**

Note

L’étudiante est le premier auteur de cet article. La recherche bibliographique ainsi que la rédaction de l’article ont été effectués par l’étudiante sous la supervision des autres co-auteurs.

Modifications exigées par le comité de lecture de la revue

L’article a été accepté.

2.1 Résumé

Les déchets de batteries et de piles usagées utilisées dans la vie quodidienne se caractérisent par une très grande diversité tant dans leur composition que dans leur utilisation. Les batteries les plus fréquement utilisées sont les suivantes: alcaline (Zn-MnO_2), saline (Zn-carbone), lithium (Li-$SOCl_2$, Li-MnO_2), nickel-cadmium (Ni-Cd), nickel-hydrure métallique (NiMH), plomb, lithium-ion (Li-CoO_2, Li-MnO_2) et lithium-polymère. La pénurie annoncée des métaux entrant dans la composition des batteries (Zn, Mn, Ni, Cd, Li) a poussé les industriels et les chercheurs à développer de nouvelles techniques pour parvenir à récupérer ces métaux sous formes pures et valorisables, tout en décontaminant les déchets de piles et de batteries. Divers traitements ont été développés pour parvenir à récupérer ces métaux. Trois principales approches technologiques sont utilisées: la pyrométallurgie, l'hydrométallurgie et des traitements physiques. Ce document présente un état de l’art des techniques proposées dans 14 brevets pour la récupération des métaux à partir de déchets de piles et de batteries.

Mots clés: déchets de batterie, métal, pyrométallurgie, hydrométallurgie, traitement physique, recyclage

2.2 Abstract

This review is related to the process development for batteries and related waste. The review's primary focus is the metal recovery and remediation of the following types of battery waste: alkaline ($Zn-MnO_2$), saline (Zn-carbon), lithium ($Li-SOCl_2$, $Li-MnO_2$), nickel-cadmium (Ni-Cd), nickel-metal hydride (NiMH), lead-acid, lithium-ion ($Li-CoO_2$, $Li-MnO_2$) and lithium-polymer. Various treatments have been developed to diminish the impact of hazardous metals on the environment and to preserve the valuable metal (e.g., Cd, Co, Cu, Fe, Li, Mn, Ni, Pb and Zn) resources. Three main technological approaches, namely, pyrometallurgy, hydrometallurgy and physical treatments, have been proposed. This paper covers the developments in the field of technology for metal recovery from battery waste based on an analysis of 14 patents.

Keywords: Battery waste, Metal, Pyrometallurgy, Hydrometallurgy, Physical treatment, Recycling

2.3 Introduction

The growth of the electric and electronic markets has led to a large quantity of batteries discharging from their end-of-life devices. The metals contained in the used cells, such as cadmium (Cd), cobalt (Co), lithium (Li), manganese (Mn), nickel (Ni) and zinc (Zn), are considered hazardous waste when discharged into the environment. Due to their high persistence and toxicity, several environmental laws and regulations related to these metals have been established to prevent health problems for humans and animals as well as other negative effects on the ecosystem [1-3]. Furthermore, the predicted scarcity of these metal resources in the near future and their importance in battery production in large quantities have led to the improvement of resource recovery technologies.

In the last several years, some physical [4-5], chemical [6-9], biological [10-11] and thermal [12-13] processes have been proposed for the recovery of metallic compounds found in the different types of battery waste: alkaline ($Zn-MnO_2$), saline (Zn-carbon), lithium ($Li-SOCl_2$, $Li-MnO_2$), nickel-cadmium (Ni-Cd), nickel-metal hydride (NiMH) and lithium-ion ($Li-CoO_2$, $Li-MnO_2$).

In the same way, various companies around the world operate processes for recycling certain types of cells and batteries, including Accurec, Atech, Batenus, Batrec, EcoBatRec, Eramet, Inmetco, Recytec, RRBC, RMC, Sab Nife, Snam-Savam, Sumitomo, TNO, Toxco, Umicore, Valdi, Varta and Waelz. Review papers prepared by Sullivan and Gaines [13], Espinosa *et al.* [14] and Bernandes *et al.* [15] describe the technologies exploited for the recycling of metals from used batteries.

In this review, the methods that are mostly frequently applied are hydrometallurgy, pyro-metallurgy and physical treatment or a combination thereof. The operating conditions of these processes have generally been optimized to reduce costs and achieve high metal recovery rates. The details of each patent will be provided in the following sections.

2.4 Lithium ion batteries

Lithium is used for the preparation of primary (non-rechargeable) and secondary (rechargeable) batteries. Primary lithium batteries are generally composed of a Li metal anode and a metal (e.g., Mn) oxide cathode. The following chemical reactions are produced in this type of cell:

Equation 2-1 $\mathbf{Li \rightarrow Li^+ + e^-}$ **(anode)**

Equation 2-2 $\mathbf{Li^+ + e^- + MnO_2 \rightarrow LiMnO_2}$ **(cathode)**

Secondary (rechargeable) lithium batteries usually include a LiC_x anode and a CoO_2 cathode. The following reactions take place in this type of battery:

Equation 2-3 $\mathbf{LiC_x \rightarrow C_x + Li^+ + e^-}$ **(anode)**

Equation 2-4 $\mathbf{Li^+ + e^- + CoO_2 \rightarrow LiCoO_2}$ **(cathode)**

LiC_x corresponds to Li-intercalated graphitic carbon, which has a reactivity comparable to that of Li metal but allows a reversible reaction.

Primary and secondary lithium batteries require the use of non-aqueous electrolytes, which are usually composed of a lithium salt dissolved in an alkyl carbonate. One of the most commonly used electrolytes in lithium batteries is the salt lithium hexafluorophosphate ($LiPF_6$) dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC).

The invention developed by Sloop [16] is a method for processing end-of-life lithium batteries via a supercritical fluid. The remaining Li metal in the electrode can react with carbon dioxide (CO_2), moisture or oxygen (O_2); therefore, it must be discharged before operation. In this method, the cells are cooled before processing to prevent an exothermic reaction. This procedure begins with placing the used cells in a container and then adding a fluid. The cells are dropped inside a high-pressure extraction vessel that is placed inside a water bath. CO_2 is injected at room temperature. Next, this gas is transformed into a supercritical liquid by increasing the temperature and pressure until the critical point is exceeded. This liquid subsequently behaves as a dense gas and exhibits different properties, such as solubility and surface tension. The electrolyte and some of the contaminants in the opened cell then dissolve in the supercritical carbon dioxide and are moved to a precipitation vessel for subsequent treatment. Others gases, such as argon (Ar), helium (He) and nitrogen (N_2), might be used as the supercritical fluid. However, the advantage of a CO_2 supercritical phase is its low surface tension, which allows it to be in contact with sub-micron pores and thereby eliminates the need for a grinding method to transform the battery powder into small particles. Their experiments have yielded 76% EC/DEC (1:1) removal efficiencies and 92% EC/DEC/$LiPF_6$ removal efficiencies

(11% by weight of $LiPF_6$) at 50°C/4,100 psi. This patent also claims that the lithium salt can be $LiAsF_6$, $LiBF_4$, $LiClO_4$, $LiPF_6$, lithium pentafluorothiodifluoromethane sulfonate, lithium bis-perfluoroethanesulfonimide (LiBETI), lithium trifluoromethanesulfonate (LiTF), lithium bis-trifluorosulfonimide (LiTFSI), and lithium trifluoromethanesulfonylmethide (LiTFSM). In the same way, the following solvents can also be used: EC, DEC, dimethoxyethane (DME), dimethyl carbonate (DMC), dipropyl carbonate (DPC), dioxolane, ethyl methyl carbonate and propylene carbonate.

A continuous process for use in the invention described above has been proposed by Sloop and Parker [17]. Further details of an electrolyte refilling process as well as sealing and testing capacity methods are provided (Figure 2.1). In this embodiment, a resealable battery is fabricated to facilitate the electrolyte removal and the filling process. A threaded valve closure is assembled with the cell and can be removed easily before exposure to the supercritical fluid. To prevent short-circuiting, this valve allows only the fluid, not the electric current, to pass through the cell. After the lithium cell is treated by the method described above [16], the cell is refurbished by adding a new electrolyte and sealing using a fast-setting epoxy. The results show that the cell capacities are increased from 737 and 963 mAh to approximately 1,000 MAh. Compared with the original capacity, 1,200 MAh, this method is proven to be efficient. The advantages of Sloop's method are as follows: 1) the reaction of Li with CO_2 does not produce hydrogen gas, 2) oligocarbonates and oligoethers are dissolved in the CO_2 supercritical fluid and therefore do not impact the anhydrous character of the system and 3) the (supercritical) fluid can be reused in the system. The disadvantage is the need to completely discharge the lithium battery before operation.

In another patent, McLaughlin and Adams [18] describe a process for Li recovery from used lithium batteries. The batteries are first frozen using liquid N_2 and then shredded to expose the Li compounds. Water is added to react with the Li according to the following reaction:

Equation 2-5 $Li + H_2O \rightarrow LiOH + \frac{1}{2} H_2$

The reaction produces H_2 gas, which is burned during processing. The pH is controlled by the addition of LiOH. Different Li compounds are produced during the reaction and precipitate out of solution. These salts are mechanically dewatered. Then, the salts are dissolved in mild sulfuric acid and the purification of the Li^+ ions is carried out using an electrolytic cell membrane to form LiOH. Finally, the hydroxide is either dewatered or transformed to Li_2CO_3 by reacting with CO_2 gas.

2.5 Nickel-Cadmium batteries

Melin and Svensson [19] propose a method to recover metals from scrap Ni-Cd cells (Figure 2.2). Normally, the environmental and safety costs to dissemble this type of battery are quite high. Nevertheless, it is necessary to recover these metals before discharging to the environment due to their high toxicity. This type of battery can be vented (open) or sealed. The sealed batteries are normally used in households, while the vented type is widely applied in industry. Ni-Cd batteries use Cd as the cathode and nickel oxide hydroxide (NiO(OH)) as the anode. The discharging reactions are as follows:

Equation 2-6 $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$ **(anode)**

Equation 2-7 $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$ **(cathode)**

In the present invention, the scrap sealed cells are fed into a drum, where they are demolished by a crushing mill. Next, the powder is fed into a hot blast furnace and mixed with the hot air. This air both removes the moisture and heats the materials. A conveyer device sends the hot materials via a basket to the pyrolysis and distillation furnace, where a controlled oxidizing atmosphere (N_2 containing 5% by volume of oxygen (O_2)) is introduced. The pyrolysis process generally lasts approximately 24 h. In this process, the gas is burnt at 900°C. The combustion gas by-product then discharges at the outlet pipe and enters the cleaning gas system. Once the pyrolysis is completed, the temperatures in the distillation and pyrolysis furnace are set at 750°C, 820°C and 885°C to remove the Cd. These changes in temperature cause the oxidizing gases to transform to reducing gases, reducing cadmium oxide (CdO) to metallic Cd. The liquid Cd is then transported to a holding vessel connected to a heat container. Next, it is transferred to a cooled casting tool, after which it flows into a depression and travels down again to the cylindrical mold cavities. Finally, the cast Cd rods are collected. The Cd residue in the scrap is less than 0.01%. The residue inside the furnace is a mixture of Ni and iron (Fe) scrap and is further recovered.

Aiken *et al.* [20] present an invention related to the battery recycling system. The specific objective is to optimize the methodology for safety and recovery of valuable metals from the spent cells. The system consists of a continuous thermal oxidizing system incorporated into a rotary furnace. Waste batteries enter the furnace via the valve feed pipe. The furnace (a rotary kiln) is heated by a muffle consisting of several burners. Natural gas is used as a heat source. The furnace has three heating zones, which are heated to 538-677°C. Each zone has six burners, which generate the heat to burn the used battery. Significant heat is also generated by the combustion of the polymers and plastics contained in the batteries. An atomizing spray lance with several nozzles supplies the water used to absorb the heat generated inside the furnace. The temperature of the combustion product is detected and limited to approximately 760°C. Air supplied by an air atomizer and water are constantly passed through the lance to protect the lance and nozzle. Once the combustion process is completed (retention time = 1 h), a shell cooler is used to decrease the temperature of the roasted batteries before they are subjected to further treatment. The condensate from the cooling chamber is discharged to a floor trench and then to the wastewater treatment. The final product is drained from the shell via the isolation valve to the container. The kiln continues to burn to prevent fugitive emissions. Finally, the hot gas should be treated properly. The treated batteries, which consist of Ni, Cd and Fe, are transported for further processing for metal recovery. This method can be applied to other battery types, such as Ni-MH, Li-CoO_2 or Li-MnO_2, Zn-carbon and button cells.

A pyrometallurgical method for recovering Cd and Ni from waste batteries is proposed by Delisle *et al.* [21]. This process can be applied to waste containing Cd, such as cell scrap, unused positive and negative electrodes and residual industrial waste. First, batteries are crushed into small pieces and sent to the furnace. The pyrolysis is conducted at different temperatures. Ar or N_2 gases are used as the reducing agents inside the kiln. Temperatures in the range of 250 to 300°C are used to evaporate the water. The temperature is then increased to 500-800°C to destroy H_2 and non-metallic substances, such as plastics. Next, the temperature is increased to 900-1000°C to volatilize the Cd metal, which is then condensed in a condensing chamber (temperature = 135-200°C). The liquid Cd is then formed into a cube shape in the preparation mold. This liquid contains very high-purity Cd (approximately 99.9999%) and could therefore be used in battery fabrication. The Ni-Fe concentrate recovered from the furnace contains approximately 35% Ni and could be sold to refineries or manufactures or subjected to further processing to recover pure Ni. The advantages of this system include the following: 1) it does not require additional secondary operations and is thus simple to manage; 2) high-purity Cd can be obtained from the process, decreasing the environmental impact; and 3) the residual from the process is a valuable material in the market.

2.6 Lithium-ion, Li-polymer, Nickel-cadmium and Nickel-Metal Hydride batteries

Cheret and Santen [22] have developed a metal recycling process that can be applied to several types of batteries, such as lithium-ion, Co-bearing and NiMH batteries (Figure 2.3). Ni is a valuable metal found in NiMH batteries, and its discharging is similar to that of Ni-Cd batteries. Its reactions are as follows:

Equation 2-8 $\mathbf{Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-}$ **(anode)**

Equation 2-9 $M + H_2O + e^- \rightarrow MH + OH^-$ **(cathode)**

The drawback of the conventional process to treat these types of batteries using pyrometallurgy with two furnaces is these high investment and operational costs. Thus, the objective of this development is to provide a relatively low-cost process. The useful charge normally comprises 30% of battery scrap mixes, with 20% of Fe, 20% of Co or 20% of Ni. The process begins with feeding the used batteries into a vertical shaft furnace with small quantities of coke, slag and metal-oxide-containing materials. The shaft is divided into three zones:

- The preheating zone: the temperature is slowly increased to a maximum of 300°C (to prevent explosion) to evaporate the electrolyte;
- The secondary zone: the temperature is increased to 700°C, at which the plastic is melted from the battery pack;
- The smelting and reducing zone: the preheat air is injected from the bottom of the shaft furnace. The metallic material is transformed into two different portions: 1) a slag containing aluminum (Al), silica (Si), calcium (Ca) and Fe and 2) the metal alloy, which is mainly composed of Co, copper (Cu) and Ni.

In fact, the three examples in this patent show a metal alloy fraction containing between 29-58% for Co, 15-36% for Cu, and 1.3-5.6% for Ni.

The migration of Fe into the slag phase is economically feasible because more Ni and Co can be transformed into the metal alloy. However, this selective phase change is controlled by a proper redox potential (pO_2). This value cannot be measured directly and must be determined by phase analysis. It can be adjusted by changing the amount of reducing agents used.

2.7 Alkaline and Zn-Carbon batteries

Household sealed-cell alkaline and Zn-carbon batteries can be recycled for use in the steel industry. This type of battery is widely used and occupies a large share of the market. Alkaline batteries have a similar structure to Zn-carbon batteries, differing in the electrolyte used inside the cell. Their cathode and anode discharging reactions are as follows:

Alkaline cell:

Equation 2-10 $\mathbf{Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-}$ **(anode)**

Equation 2-11 $\mathbf{MnO_2 + H_2O + e^- \rightarrow MnO(OH) + HO^-}$ **(cathode)**

Zn-carbon cell:

Equation 2-12 $\mathbf{Zn \rightarrow Zn^{2+} + 2e^-}$ **(anode)**

Equation 2-13 $\mathbf{2MnO_2 + 2e^- + 2NH_4Cl \rightarrow Mn_2O_3 + 2NH_3 + H_2O}$ **(cathode)**

Normally, a chemical process is used to recycle this type of battery. However, this method suffers from many drawbacks, limiting its use, such as the high price of the chemicals used, the low value of the recycled material and the waste stream produced, the treatment of which is expensive. To overcome these drawbacks, Elliott [23] offers an alternative method consisting of the following steps (Figure 2.4): 1) pulverization (grinding, crushing, demolishing, etc.), 2) an acid bath, 3) rinsing, 4) drying, 5) the mixture of 25% of the pulverized batteries with granulated carbon and 6) the compression of this mixture into briquettes. Finally, the briquettes are used into steel making furnaces.

In total, 95% portable batteries are alkaline cells. Their main components are carbon (C), Zn, potassium (K) and Mn. The use of a chemical process for this type of battery is not profitable due to the low prices of these metals on the market (˜2 $/kg). The patent proposed by Stevens [24] describes a physical method for the separation of a valuable powder fraction containing zinc oxide (ZnO), manganese dioxide (MnO_2) and potassium hydroxide (KOH). These compounds are mostly found in alkaline, Zn-carbon and Zn-chloride batteries. In this method, the batteries are first shredded to form a feedstock mixture (Figure 2.5). This shredded feedstock is then heated (between ambient temperature and the boiling point of mercury (Hg)) in an oven and rolled to produce a dried material, which is screen separated into a powder fraction and a coarse fraction containing the shredded steel casing, brass, graphite, cellulose paper and plastics. The system also includes a conveyor to insert the material into the oven and a rotatable tunnel placed in the drying unit. During the drying, the Hg present in the battery waste is evaporated and recovered in a scrubber. A magnetic separator can also be used for the separation of the coarse fraction into a magnetic component and a non-magnetic component. This patent also proposed modified versions of the previously described system for processing NiMH battery waste or lithium battery waste.

Shin *et al.* [25] present an invention for obtaining manganese sulfate ($MnSO_4$) and zinc sulfate ($ZnSO_4$) from alkaline batteries using a spray-drying method (Figure 2.6). This method is proven to be cost effective. The details of the procedure are as follows. A Zn- and Mn-rich powder is obtained from crushing magnetic separation and size separation. As a consequence, the contents of such impurities as Fe, Cu, Al, Ni and Cd are reduced. The powder is then divided into two parts for use in the two leaching steps. The first leaching uses a mixture of sulfuric acid (H_2SO_4) and a reducing agent mixed with the first portion of the battery powder. The reducing agent is chosen from the group including coal, pyrite (FeS_2), ferrous sulfate ($FeSO_4$), sulfur dioxide (SO_2), hydrogen sulfide (H_2S), and hydrogen peroxide (H_2O_2).

The solid fraction and the leaching solution obtained from the previous step will be used again in the second leaching step. If the concentration of H_2SO_4 is less than 0.5 M, the leaching efficiency of Zn is low. However, if the concentration is increased to 1.0 M or above, the process is not profitable due to the price of H_2SO_4. Thus, it is advantageous to use H_2SO_4 concentrations in the range of 0.5 to 1.0 M. The economical selection of the concentration is applied to the reducing agents as well. A reaction time of 30 to 120 min and a temperature program from room temperature to 80°C are applied in both leaching steps. It is found that the leaching rates of Zn and Mn increase with time and temperature. However, when the experiment continues beyond 120 min, the leaching efficiency ceases to increase. The optimum conditions for the two leaching experiments are similar. After the second leaching, the heavy metal and organic material are removed and Cd and Ni remain at a pH of 4.0 to 6.5. Thus, the Zn powder is added as a substitute. Activated carbon is then added to ensure the absence of any residual organic substances. In an example, the concentrations of Zn and Mn in a treated solution were 33.0 and

28.1 g/L, respectively. The leached solution then is spray-dried. Finally, $MnSO_4$ and $ZnSO_4$ are obtained.

2.8 Lead batteries

Lead (Pb) batteries are one of oldest types of batteries. These batteries are most commonly used in vehicles due to their high power-to-weight ratio and low price. This type of battery is expensive relative to the other types. Its cathode and anode discharging reactions are as follows:

Equation 2-14 $\mathbf{Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-}$ **(anode)**

Equation 2-15 $\mathbf{PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O}$ **(cathode)**

Bitler and Baranski [26] focus on the treatment of Pb-contaminated soil and battery casting using a plasma arc furnace (Figure 2.7). The process begins with the separation of soil and battery casting using a mechanical process (specific gravity apparatus, vibratory and non-vibratory screens). Next, the soil component is transferred to a soil hopper, and the battery casting is transferred to a casing hopper to be cut into 1.0-1.25-cm pieces by a crusher. Control valves are used to ensure the appropriate soil-casting ratio before sending the mixture to the hopper of the plasma arc. This system considers the battery casting to be an organic material. The greater the amount of casting in the charge before being sent to the arc furnace, the greater the amount of carbon monoxide (CO) produced. This gas could be then used as a primary fuel for a conventional smelting furnace. The plasma flame produced from the previous step is then placed in contact with the charge in the crucible. If the soil content in the charge is acidic, limestone may be added before sending it to the furnace. Pyrolysis then occurs. Agitation is applied to ensure the complete reaction of the charge with the flame. The combustible gas and the vaporized Pb are then transferred via the pipeline to the smelting furnace system (SFS) to recover the Pb. The vitrified slag is transported to the crusher via the pipeline and broken into pieces of the selected size. If the vitrified slag test is nontoxic, it may be sent to a landfill. The SFS system is composed of a smelting furnace and downstream environmental control equipment, which may include a cooler section, dust collector section and a final gas scrubbing section. The particulates recovered from the cooler and dust collector are recycled back into the smelting furnace to recover all of the Pb contaminant.

In 1998, Bitler and Baranski [27] confirmed their research using the previous embodiment [26]. The results from the previous study show that the Pb removal efficiencies in three different tests are 87%, 68% and 62%.

2.9 Mixed batteries

Pudas *et al.* [28] offer a mechanical treatment for recycling waste batteries. This method could be applied to various types of batteries, including Pb, Li-CoO_2 or Li-MnO_2, Li-$SOCl_2$, Li-MnO_2, Ni-Cd, NiMH, alkaline and button cells. The process begins by sorting the batteries according to battery type and composition. Next, three different waste compositions are separated: 1) electric waste, 2) burnable waste and 3) non-recyclable waste. The batteries are then transferred to the crusher. For Li-type batteries, the cells are broken into pieces of approximately 1-2 cm in length. The temperature is maintained at 40-50°C, and the H_2 and O_2 gases produced are removed by a cyclonic air filter. The mixture of light plastic and cardboard from the Li crushing can be used as a heat source for NiMH battery smelting. The batteries are crushed again by the secondary blade, yielding a powder comprised of particulates of 0-6 mm in diameter. This powder is then transported to a magnetic separator to remove the Fe. The Co and Cu remaining in the powder can be recovered by a refining method. This invention can be applied to NiMH and alkaline cells, as mentioned above. The final products of NiMH batteries after crushing are mainly Co, Ni, Fe, Al, Cd and rare earth elements, which are recovered later by refining as well. For alkaline batteries, the powder obtained from this method is composed of 20 to 33% Fe, which can be removed by a magnetic separator. Its residues, called black mass, mainly contain Zn (25%) and Mn (30%). These two latter metals are recovered by refining and other treatments.

Lee [29] developed a method to sort and separate the various types of valuable materials from scrap batteries containing significant amounts of Pb (Figure 2.8). The conventional method used for this type of battery has the disadvantage of manual operation, during which this material's hazardous composition can be harmful to human health. Furthermore, it is impossible to operate the system continuously. To solve both of these problems, the present invention was developed. The system begins with the addition of waste batteries to a cutter by a conveyer. The batteries are then cut, and the electrolyte is removed. The products, including paste and polypropylene, are automatically sorted and separated by a vibration screen. The crushed cell fraction smaller than 100 Mesh, called the paste, is separated by the predetermined size. The particles larger than 100 Mesh are transferred to a hydro-separator. This component is used to extract polypropylene. The low-density materials, such as polypropylene, float on the water surface, whereas the high-density materials, such as the separators and grids, are submerged in the water. An agitator is used to desulfurize the paste, and a Fe separator is used to separate the Fe from the scrap batteries using a strong magnetic force. The system is controlled automatically by a computer. Finally, the paste is recovered, the water is treated at a wastewater treatment unit, and the sodium carbonate is desulfurized.

2.10 Conclusions

Battery consumption is increasing due to technological advancement. Batteries contain significant quantities of hazardous materials, such as heavy metals. Due to their toxicity, these metals are strongly detrimental to the environment and human health. As a result, a number of studies have been performed to develop new technological options for the reuse of different types of battery waste. This paper summarizes 14 new patents proposing new technologies for treating and recycling end-of-life batteries and related waste. The most widely used methods include hydrometallurgy, pyrometallurgy and simple physical methods. One of the most important issues in the development of recycling processes for battery waste is the need to separate different types of batteries before treatment. The development of new technologies able to recover metallic resources from battery waste without separation would facilitate their recycling and would most likely increase the proportion of battery waste to be reused. One promising approach would be the solubilization of all metals from mixed battery wastes by chemical leaching, and their subsequent recovery using selective precipitation [30], ion-exchange [31], adsorption [32] and electrochemical techniques [33].

2.11 References

[1] Allen HE. Bioavailability of metals in terrestrial ecosystems: importance of partitioning for bioavailability to invertebrates, microbes, and plants. Society of Environmental Toxicology and Chemistry (SETAC), Pensacola, Florida, 176 p., 2002.

[2] Kabata-Pendias A, Pendias H. Trace elements in soils and plants. 3rd Ed., CRC Press LLC, Boca Raton, Florida, 413 p., 2001.

[3] Lippmann M. Environmental toxicants. Human exposures and their health effects. John Wiley & Sons Inc., New York, NY, 987 p., 2000.

[4] Huang K, Li J, Xu Z. Characterization and recycling of cadmium from waste nickel-cadmium batteries. Waste Manag 2010; 30: 2292-2298.

[5] Huang K, Li J, Xu Z. Enhancement of the recycling of waste Ni-Cd and Ni-MH batteries by mechanical treatment. Waste Manag 2011; 31: 1292-1299.

[6] Buzatu T, Popescu G, Birloaga I, Saceanu S. Study concerning the recovery of zinc and manganese from spent batteries by hydrometallurgical processes. Waste Manag 2011; 33: 699-705.

[7] Li L, Ge J, Chen R, Wu F, Chen S, Zhang X. Environmental friendly leaching reagent for cobalt and lithium recovery from spent lithium-ion batteries. Waste Manag 2010; 30: 2615-2621.

[8] Provazi K, Campos BA, Espinosa DCR, Tenorio JAS. Metal separation from mixed types of batteries using selective precipitation and liquid-liquid extraction techniques. Waste Manag 2011; 31(1): 59-64.

[9] Sun L, Qui K (2012) Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries. Waste Manag 2012; 32: 1575-1582.

[10] Lee JC, Pandey BD. Bio-processing of solid wastes and secondary resources for metal extraction – a review. Waste Manag 2012; 32: 3-18.

[11] Velgosova O, Kadukova J, Marcincakova R, Palfy P, Trpcevska J. Influence of H_2SO_4 and ferric iron on Cd bioleaching from spent Ni-Cd batteries. Waste Manag 2013; 33: 456-461.

[12] Belardi G, Lavecchia R, Medici F, Piga L. Thermal treatment for recovery of manganese and zinc from zinc-carbon and alkaline spent batteries. Waste Manag 2012; 32: 1945-1951.

[13] Sullivan JL, Gaines L. Status of life cycle inventories for batteries. Energy Conv Manag 2012; 58: 134-148.

[14] Espinosa DCR, Bernardes AM, Tenorio JAS. An overview on the current processes for the recycling of batteries. J Power Sources 2004; 135: 311-319.

[15] Bernardes AM, Espinosa DCR, Tenorio JAS. Recycling of batteries: a review of current processes and technologies. J Power Sources 2004; 130: 291-298.

[16] Sloop SE: US7198865 (2007).

[17] Sloop SE, Parker R: US8067107B2 (2011).

[18] McLaughlin W, Adams TS: **US5888463** (1999).

[19] Melin AL, Svensson VH: **US4401463** (1983).

[20] Aiken VH, Bleakney RR, Hanewald RH, Vahed A, Warner AEM: **US6228143B1** (2001).

[21] Delisle RJ, Martin HE, Wilkerson A: **US5437705** (1995).

[22] Cheret, D., Santen, S.: **US7169206B2** (2007).

[23] Elliott KW: **US5456992** (1995).

[24] Stevens CW: **US8210456B2** (2012).

[25] Shin SM, Kang JG, Sohn JS, Kim HG, Kim MH: **US8440153B2** (2013).

[26] Bitler JA, Baranski JP: **US5284503** (1994).

[27] Bitler JA, Baranski JP: **US5788735** (1998).

[28] Pudas J, Erkkila A, Viljamaa J: **WO2011/113860A1** (2011).

[29] Lee YH: **WO2008/111709A1** (2008).

[30] Djedidi Z, Bouda M, Ben Cheikh R, Blais JF, Mercier G, Tyagi RD. Development of a new chemical equilibrium and techno-economic model for the treatment of metal-polluted effluents by precipitation techniques. Can J Civ Eng 2011; 38(5): 593-604.

[31] Vilensky MY, Berkowitz B, Warshawsky A. *In situ* remediation of groundwater contaminated by heavy- and transition-metal ions by selective ion-exchange methods. Environ Sci Technol 2002; 36(8): 1851-1855.

[32] Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J Hazard Mater 2003; 97(1-3): 219-243.

[33] Janin A, Blais JF, Drogui P, Zaviska F, Mercier G. Selective recovery of metals in leachate from chromated copper arsenate wastes using electrochemical technology and chemical precipitation. Hydrometallurgy 2009; 96(4): 318-326.

2.12 List of figures

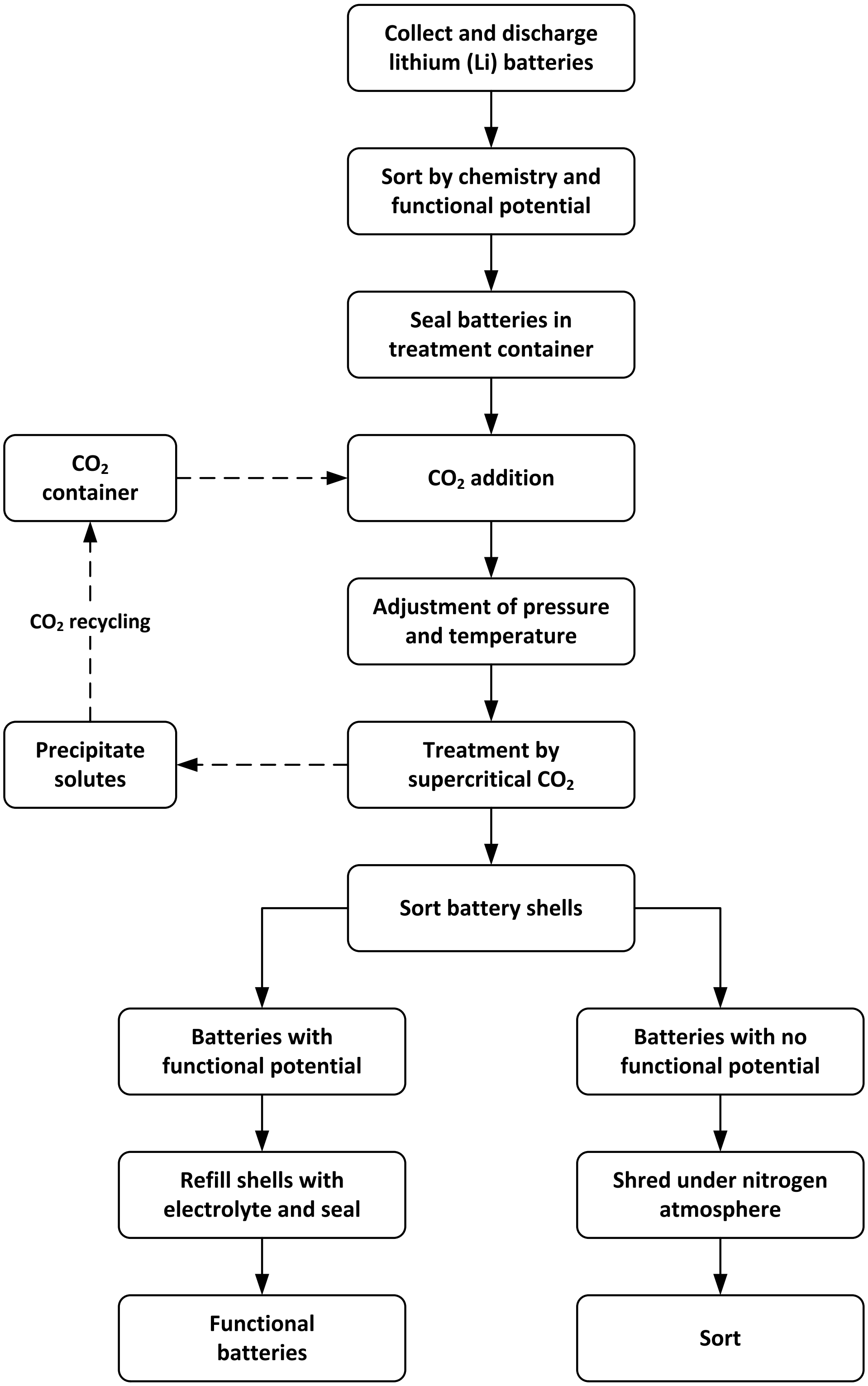


Figure 2.1 Flowsheet of Sloop's process for the reuse of lithium batteries by treatment with a supercritical fluid

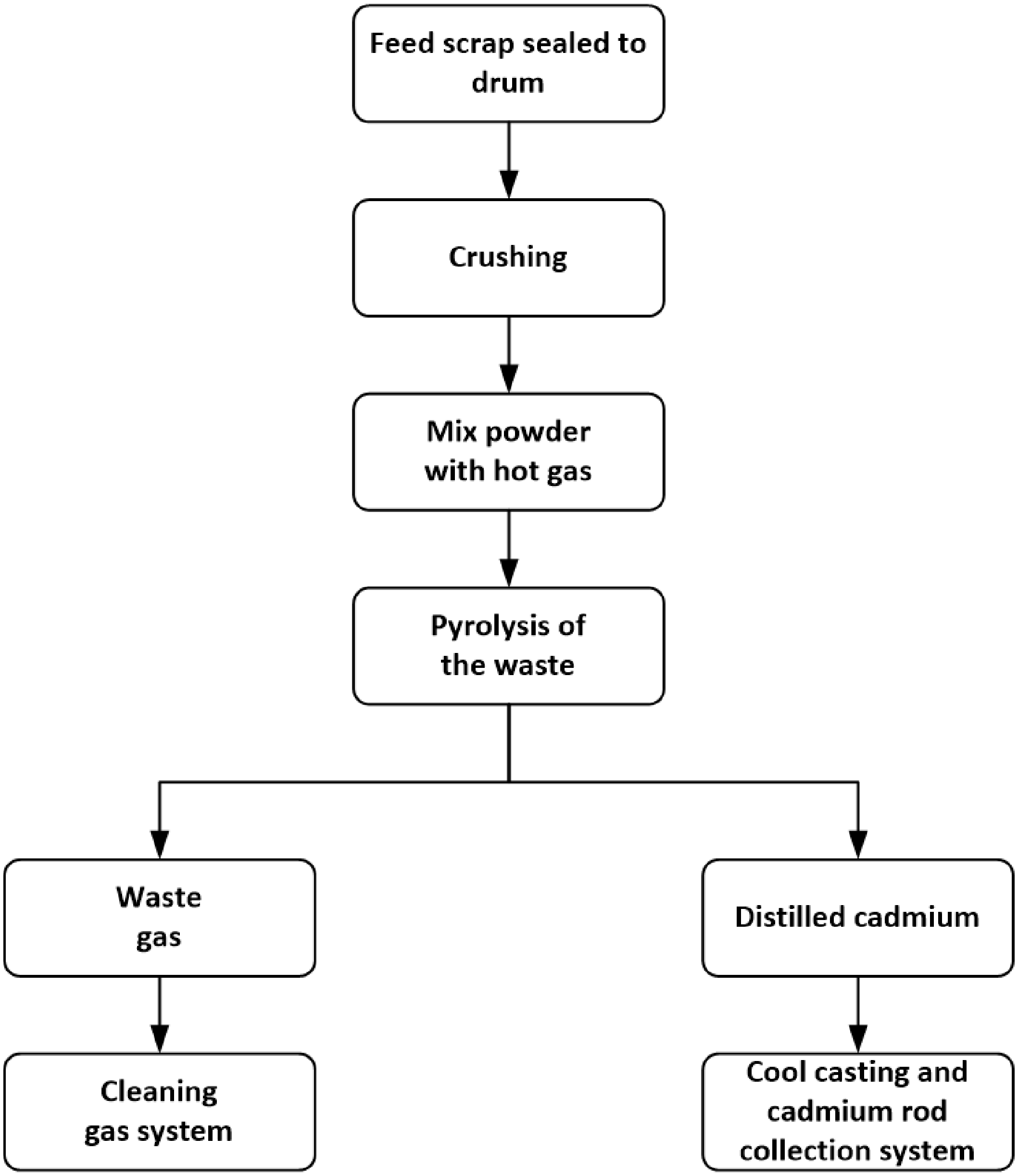


Figure 2.2 **Flowsheet of Melin and Svensson's process for the recycling of components from scrap sealed batteries**

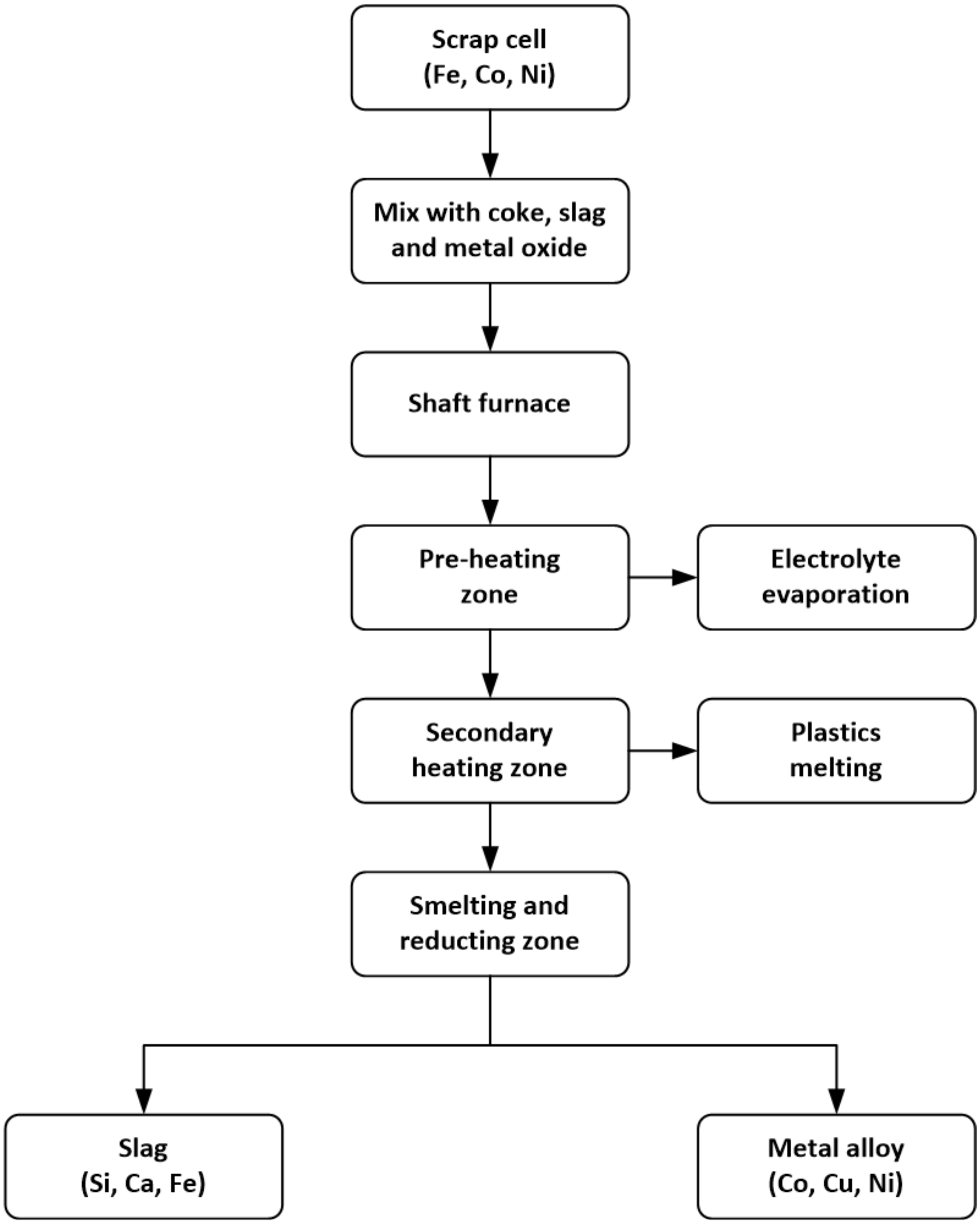


Figure 2.3 Flowsheet of Cheret and Santen's process for the recycling of components from scrap sealed batteries

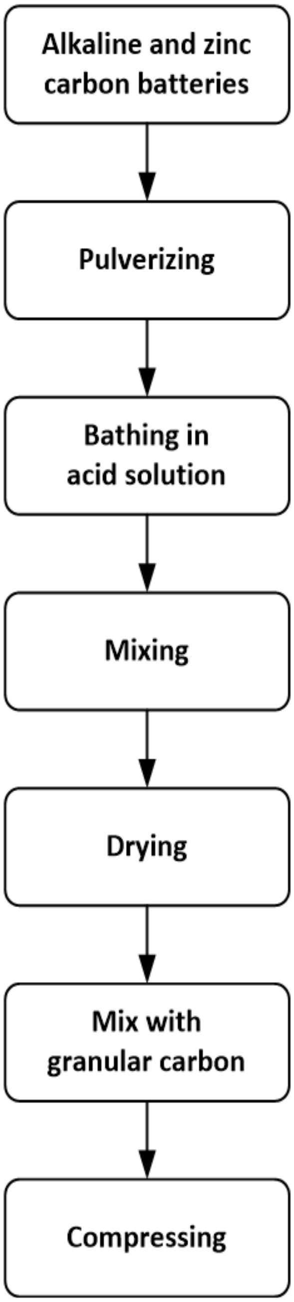


Figure 2.4 Flowsheet of Elliott's process for the recycling of components from alkaline and zinc-carbon batteries

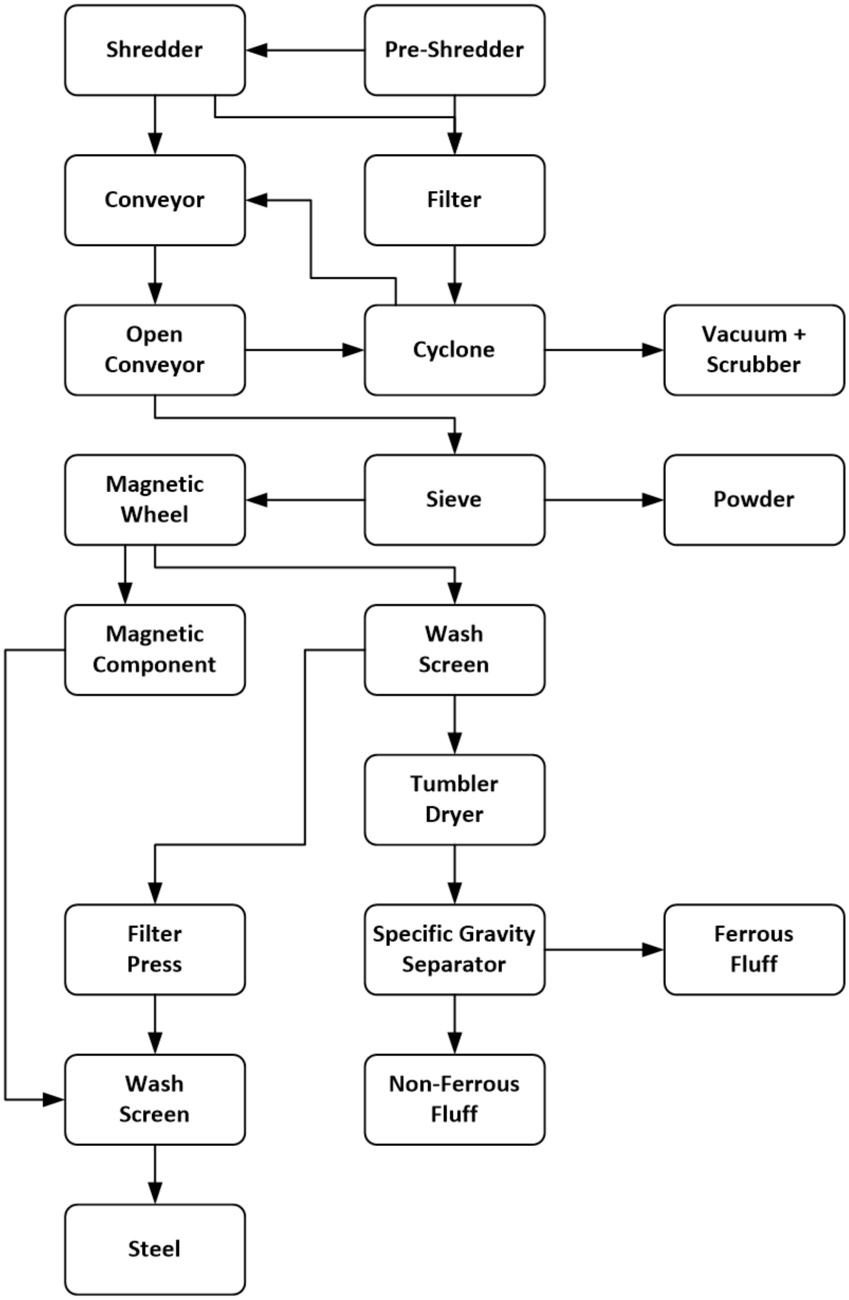


Figure 2.5 Flowsheet of Stevens's process for the recycling of components from several types of batteries

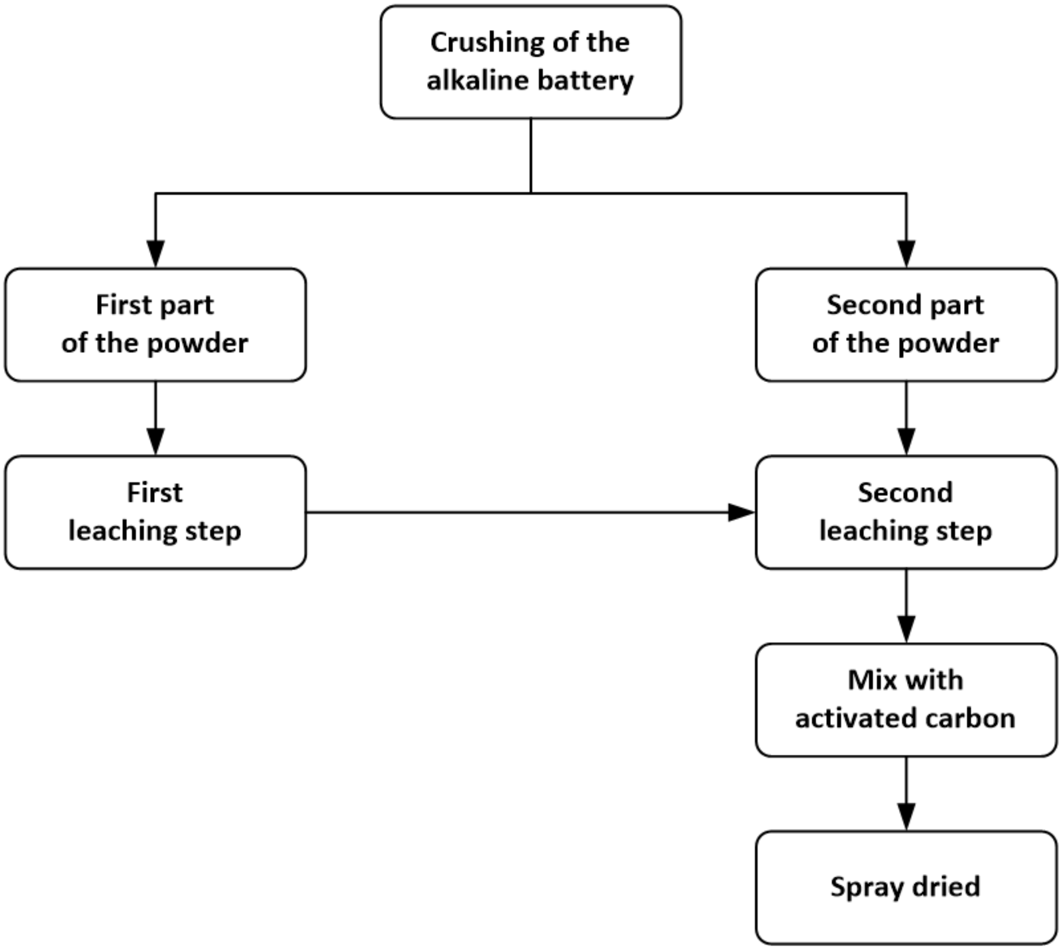


Figure 2.6 **Flowsheet of Shin's process for the recycling of components from alkaline batteries**

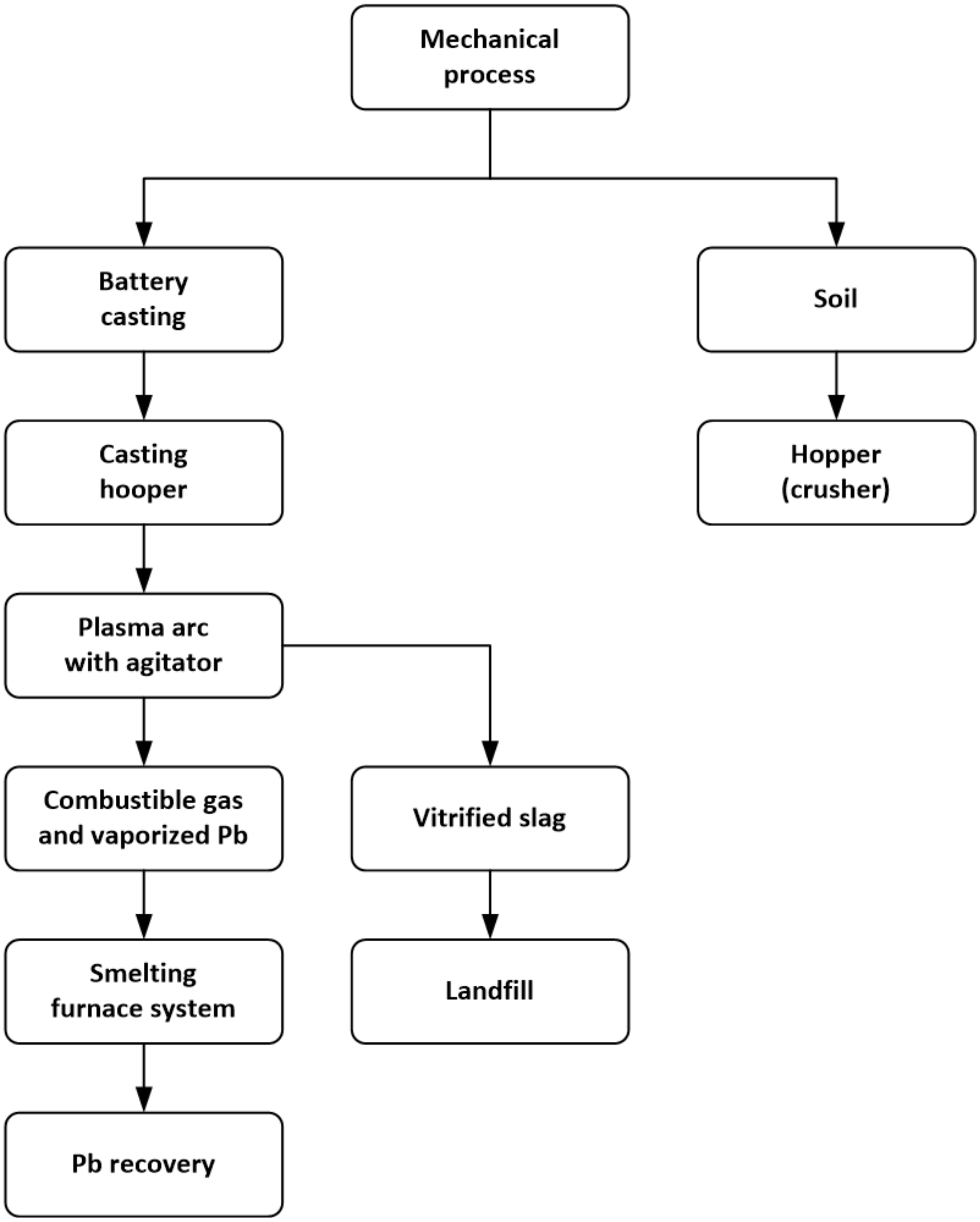


Figure 2.7 **Flowsheet of Bitler and Baranski's process for the recycling of components from battery casting contamination in soil**

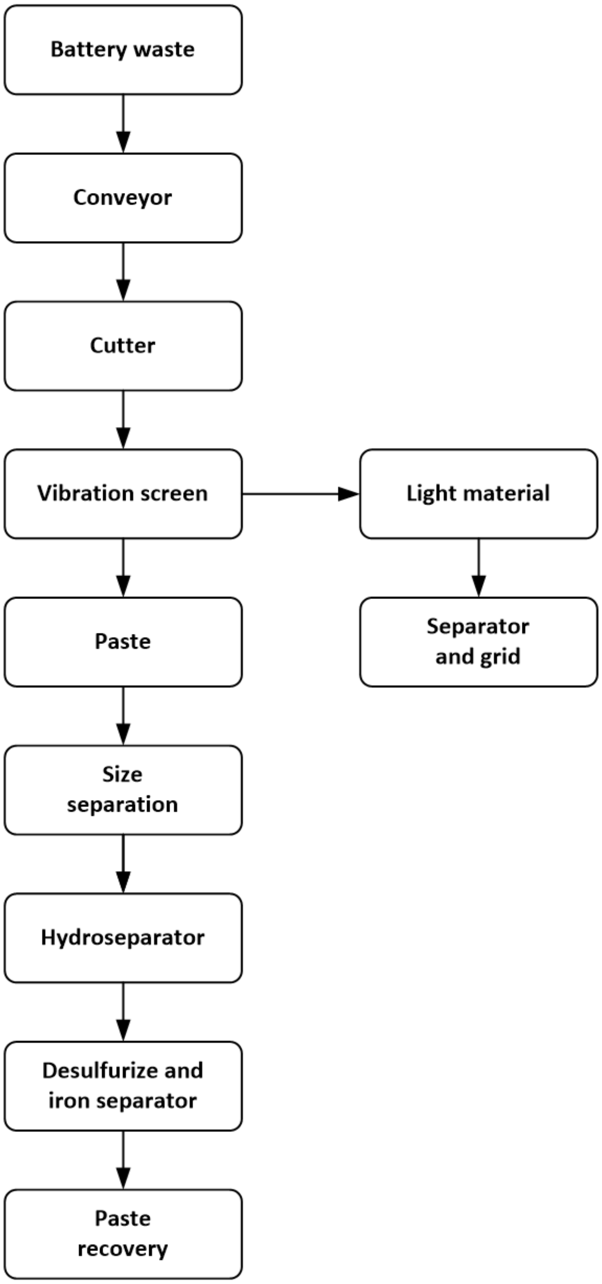


Figure 2.8 **Flowsheet of Lee's process for the recycling of components from scrap batteries**

3 CHAPITRE 3

RECOVERY OF METALS FROM A MIXTURE OF VARIOUS SPENT BATTERIES BY A HYDROMETALLURGICAL PROCESS

Revue : Journal of Environmental Management, 2016, 181, 95-107

Auteurs : Kulchaya Tanong[a], Lucie Coudert[b], Guy Mercier[c], Jean-Francois Blais[d*]

[a] Ph.D. student, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-4677, Fax: (418) 654-2600, email: kulchaya.tanong@ete.inrs.ca

[b] Research Associate, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-3793, Fax: (418) 654-2600, email: lucie.coudert@ete.inrs.ca

[c] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-2633, Fax: (418) 654-2600, email: guy.mercier@ete.inrs.ca

[d] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-2575, Fax: (418) 654-2600, email: jean-francois.blais@ete.inrs.ca

*Corresponding author:
Tel: (418) 654-2575, Fax: (418) 654-2600
email: jean-francois.blais@ete.inrs.ca

Note

L’étudiante est le premier auteur de cet article. Toutes les manipulations, le traitement des données ainsi que la rédaction ont été effectués par l’étudiante sous la supervision des autres co-auteurs.

Modifications exigées par le comité de lecture de la revue

L’article a été accepté et les commentaires les plus significatifs demandaient plus de détails sur la méthodologie de surface de réponses utilisée pour l’optimisation des paramètres.

3.1 Résumé

Les piles et batteries usagées contiennent des matières dangereuses, y compris de nombreux métaux (cadmium, plomb, nickel, zinc,etc.) qui sont présents à des concentrations élevées. Ces métaux présentent un risque non négligable pour l’environnement et la santé humaine lorsqu’ils sont présents à fortes concentrations. L’objectif de cet article est de développer un procédé hydrométallurgique viable pour parvenir à récupérer les métaux tout en décontaminant les déchets de piles et de batteries, de la manière la plus efficace et la plus économique possible. Les procédés actuels de recyclage se concentrent principalement sur le traitement séparé de chaque type de déchets de piles et de batteries. Dans cette étude de laboratoire, un procédé hydrométallurgique a été développé pour solubiliser simultanément les métaux d’intérêt à partir d’un mélange de déchets de piles et de batteries. Parmi les divers agents de lixiviation utilisés, l'acide sulfurique est le réactif le moins cher et le plus efficace. Un plan d’expériences de type Box Behnken a été utilisé pour identifier l'influence de plusieurs paramètres (concentration en acide, rapport S/L, temps de rétention et nombre d'étapes de lixiviation) sur la solubilisation des métaux à partir des déchets de piles et batteries. Le rapport S/L et la concentration en acide sont les paramètres principaux influençant la solubilisation du Zn, du Mn, du Ni, du Cd et du Co. Les conditions optimales de lixiviation sont les suivantes: (ratio S/L = 180 g/L (p/v), [H_2SO_4] = 1 M, trois étapes de lixiviation et temps de lixiviation = 30 min). Dans ces conditions, les rendements d'élimination obtenus sont de 65% pour le Mn, de 99,9% pour le Cd, de 100% pour le Zn, de 74% pour le Co et de 68% pour le Ni.

D'autres études seront effectuées pour améliorer la solubilisation du Mn et récupérer sélectivement les différents métaux.

Mots-clés: Piles usagées, Lixiviation, Box Behnken, Acide sulfurique, Procédé hydrométallurgique, Métaux.

3.2 Abstract

Spent batteries contain hazardous materials, including numerous metals (cadmium, lead, nickel, zinc, etc.) that are present at high concentrations. Therefore, proper treatment of these wastes is necessary to prevent their harmful effects on human health and the environment. Current recycling processes are mainly applied to treat each type of spent battery separately. In this laboratory study, a hydrometallurgical process has been developed to simultaneously and efficiently solubilize metals from spent batteries. Among the various chemical leaching agents tested, sulfuric acid was found to be the most efficient and cheapest reagent. A Box-Behnken design was used to identify the influence of several parameters (acid concentration, solid/liquid ratio, retention time and number of leaching steps) on the removal of metals from spent batteries. According to the results, the solid/liquid ratio and acid concentration seemed to be the main parameters influencing the solubilization of zinc, manganese, nickel, cadmium and cobalt from spent batteries. According to the results, the highest metal leaching removals were obtained under the optimal leaching conditions (pulp density = 180 g/L (w/v), [H_2SO_4] = 1 M, number of leaching step = 3 and leaching time = 30 min). Under such optimum conditions, the removal yields obtained were estimated to be 65% for Mn, 99.9% for Cd, 100% for Zn, 74% for Co and 68% for Ni. Further studies will be performed to improve the solubilization of Mn and to selectively recover the metals.

Keywords: Spent batteries, Leaching, Box-Behnken design, Sulfuric acid, Hydrometallurgical process, Metals

3.3 Introduction

Over the last decades, the development of electronic technologies using a battery as a source of energy has led to an increase in the amount of spent batteries reaching landfill sites or incinerators (Inglezakis and Moustakas, 2015). Alkaline batteries are the most commonly used across the world compared to the other types of batteries (RIS international Ltd, 2007). According to an estimation of the amounts of batteries sold in 2015 in Canada, the alkaline batteries (74%) are the most commonly commercialized followed by zinc carbon batteries (15%), lithium dioxide manganese batteries (5%), zinc air button cell batteries (4%) and silver oxide button cell batteries (2%) (Lachapelle-Charette, 2014). For the secondary one, nickel cadmium batteries are the most consumed (32%), followed by nickel-metal hydride batteries (42%), lithium ion batteries (22%), lithium polymer batteries (2%) and small sealed lead acid battery (2%) (Lachapelle-Charette, 2014). A decrease in Ni-Cd batteries consumption was observed in many countries, especially in Europe, because of their high toxicities (Rudnik and Nikiel, 2007). Alternative batteries, including Ni-MH and Li-ion, have replaced this type of battery for many applications because they contain less toxic metals (Zhang et al., 1998). Alkaline batteries are mainly used in radios, recorders, toys, remote controls, watches, calculators, cameras and in other applications where small quantities of power are required (Sayilgan et al., 2009). For secondary batteries, including Ni-MH, Ni-Cd, and Li-ion, they are considered an important source of energy for many applications across the world. Ni-MH and Li-ion batteries are widely used in several portable electronic applications such as personal computers, video recorders and phones (Zhang et al., 1998). Spent alkaline batteries are not considered hazardous materials according to the IATA Dangerous Goods Regulations, ICAO Technical Instructions and the U.S. hazardous materials regulations (49 CFR) (Bonhomme et al., 2013; Energizer, 2009) whereas spent secondary batteries containing toxic metals such as Cd potentially pose a high risk to human health and living organisms. In Canada, the huge majority of spent batteries are disposed in landfill sites because of the lack of available technologies to collect and recycle spent batteries. Therefore, the Call2Recycle project was adopted by the government of Canada 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 has promoted the recycling or the reuse of huge amounts of spent batteries (more than 500 000 kg of rechargeable batteries), restricting their landfilling (Call2Recycle, 2012). Several pyro- and hydrometallurgical processes have been developed to allow the recycling of one or various types of spent batteries. For example, Accurec, a German company, has developed a pyrometallurgical process, which is currently applied at the industrial scale to treat Ni-MH, Ni-Cd, alkaline and lithium batteries (Accurec, 2010). SNAM Company, created in 1981, developed a hydrometallurgical process to recover the metals from saline batteries and sorted batteries according to their chemical and physical properties (SNAM, 2015). Hydrometallurgical processes have several advantages (low energy consumption, ease of operation, low emission of toxic gas, lower costs, etc.) compared to the pyrometallurgical ones (Yazici and Deveci, 2013). Therefore, the use of hydrometallurgical processes to recover the metals from spent batteries has been intensively studied at the laboratory scale and proved to be very promising (Espinosa et al., 2004; Kursunoglu and Kaya, 2014; Smith et al., 2014; Morcali, 2015). Buzatu et al. (2013) developed a hydrometallurgical process to recover the Zn and Mn from spent alkaline cells. The battery powder was dissolved in the presence of H_2SO_4 (2 M) at 60 °C for 60 min. With these conditions, 96.0% of Zn and only 43.0% of Mn could be recovered. Nan et al. (2006) found the optimum conditions for recovering the metals from Li-ion and Ni-MH batteries by using H_2SO_4 (3 M) in the presence of H_2O_2 (3.0%, v/v) with a temperature fixed at 70 °C. The results showed that 99.5% of Co and Ni could be recovered with these optimum conditions after 5 h Zeytuncu (2016) solubilized more than 98% of Zn and Mn from alkaline batteries after 120 min at 100 °C in the presence of H_2SO_4 (2 M) and elemental sulfur. To the best of our knowledge, none of the promising hydrometallurgical processes developed at the laboratory or industrial scales are able to selectively and efficiently recover metals from a mixture of spent batteries comprising alkaline, Zn-C, Ni-MH, Ni-Cd, Li-ion and Li-M batteries, without sorting spent batteries according to their physical and chemical properties. From the previous reason, the objective of the present study was to design an efficient and economically attractive hydrometallurgical process to recycle spent batteries without any sorting step according to the type of spent batteries. A Box Behnken Design was used in this study to evaluate the influence of several operating conditions (retention time, concentration of leaching agent and solid/liquid ratio) and their potential interaction and to model the leaching of metals from spent batteries. The Box-Behnken methodology was also used to determine the optimal operating conditions for the leaching of metals from spent batteries, considering the processing costs (chemical reagents costs) and the revenues related to the recovery of metals.

3.4 Materials and methods

3.4.1 Sample preparation and characterization

Spent battery samples, including alkaline, Zn-C, Ni-Cd, Ni-MH, Li-ion, and lithium primary batteries, were collected at the collection point located at the National Institute of Scientific Research (Quebec, Qc, Canada). Each type of battery was manually separated and dismantled to determine their metals composition. Because of the potential release of hydrogen gas from the spent batteries and the violent reaction of this gas with oxygen, the dismantlement procedure should be performed with care. The lithium primary batteries and Ni-MH spent batteries were frozen in liquid nitrogen and were then immediately dismantled because of their high reactivities.

After the dismantlement of each battery, the procedure used for the preparation of the fine powder slightly differs for each type of spent battery. For alkaline, Ni-MH and Ni-Cd batteries, the fine particles were removed from positive and negative electrodes using manual crushing and grinding (with a mortar) steps. Li-ion batteries were manually crushed and the cathode material was uncurled and cut into small pieces and the material was then manually grinded with a mortal. For all the type of spent batteries, the undesirable coarse particles (iron scraps, paper, collector pin, plastic and electrode plaque) present in the samples (Figure 3.1a.) were then removed by screening through 1 mm and a 2 mm sieves. The remaining material was then dried at 25°C for 24 h and manually grinded again using the mortar. After this preparation, all the types of spent batteries were then mixed. To achieve the main objective of the present study, 5 kg of a mixture of the spent batteries was prepared according to their proportion in the

Canadian market share. The amounts of each type of spent batteries used to prepare the mixture were selected using the consumption of batteries in the Canadian market (RIS international Ltd., 2007, Lachapelle-Charette, 2014). Finally, the mixture obtained was repeatedly grinded for 5 min using a grinder (Fritsh pulverisette, Serial no. 06 2000/01908, Germany) to obtain the fine powder (Figure 3.1b.). The samples were then homogenized and collected to determine the contents of the metals (Al, As, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, S, Zn, etc.). The mixture of spent batteries contained 66.5% Zn-MnO2, 15.4% Zn-C, 15.4% Ni-Cd, 1.7% Ni-MH, 0.3% Li-ion and 0.7% Li-primary batteries.

3.4.2 Selection of the leaching agent

Several experiments were carried out to evaluate the influence of the nature and the concentration of the leaching agents, the temperature and the retention time on the solubilisation of metals from the mixture of spent batteries. In these experiments, different types of leaching agents including inorganic and organic acids, alkaline and chelating agents were tested (Sun et al., 2012; Senanayake et al., 2010; Shin et al., 2009; Oishi et al., 2008; Vatistas et al., 2001; Nan et al., 2006). The leaching experiments were performed using sulfuric acid ([H_2SO_4] = 0.5 and 2.0 M), hydrochloric acid ([HCl] = 0.5 and 2.0 M), oxalic acid ([$H_2C_2O_4$] = 0.5 M), acetic acid ([CH_3COOH] = 0.5 and 2.0 M), sodium hydroxide ([NaOH] = 0.5 and 2.0 M), ammonium chloride ([NH_4Cl] = 1.0 and 4.0 M) and ethylenediaminetetraacetic acid ([EDTA] = 0.125 and 0.250 M). The leaching solutions were prepared by diluting analytical grade reagents in distilled water. For all the experiments, the solid/liquid ratio was fixed to 10% (w/v). The leaching experiments were carried out onto 20 g of the mixture of spent batteries mixed with the leaching solution (200 mL) in a 500 mL baffled shaker flask. The experiments were conducted at two different temperatures (room temperature and 80 ± 10°C). The agitation rate was fixed at approximately 200 rpm. The total leaching time was fixed at six hours and different samples were taken at 30, 60, 120, 240 and 360 min. Finally, all samples were filtered with G6 filters (porosity = 1.5 µm) and preserved onto 5% HNO_3.

3.4.3 Box Behnken methodology

A Box-Behnken design approach was chosen in order to evaluate the influence of several parameters (concentration of leaching agent, solid/liquid ratio, retention time and number of leaching steps) on the solubilization of metals and to determine the optimum operating conditions for metals leaching from the mixture of spent batteries. Usually, this methodology is used to estimate the linear, the first order interactions and the quadratic effects on a response. The design is formed by the combination of 2k factorial design with an incomplete block design. The number of experiments in a Box Behnken design can be calculated using the Equation 3.1 (Mocellin et al., 2015).

Equation 3-1 $$N = n (2 k (k-1) + C_0)$$

where N is the number of experiments, k is the number of numerical factor (k = 3), C_0 is the number of replicates (central points – C_0 = 5) and n is a number of leaching step (n = 3).

In this study, three numerical factors (retention time, concentration of sulfuric acid and solid/liquid ratio) were chosen as the factors and three levels of the categorical factor (number of leaching step) were defined. Therefore, the Expert Design 8.0 software generated the experimental region composed of 51 assays. These experiments were conducted to evaluate the influence of different factors including the solid/liquid ratio (2, 10 and 18%, (w/v)), the concentration of H_2SO_4 (1, 2 and 3 M) and the leaching retention time (0.5, 1 and 1.5 h). The coded levels of each factor were defined. For example, for the solid/liquid ratio, the value of S/L = 20 g/L was coded as -1, whereas the 100 g/L and 180 g/L values were coded as 0 and +1, respectively. All the Box Behnken design experiments were conducted onto 200 mL leaching solution at room temperature in 500-mL baffled shaker flasks (Cole Parmer, Montreal, Canada). The leaching solutions were prepared using analytical grade sulfuric acid diluted in distilled water. A mixing speed of 200 rpm was applied during all the experiments using an orbital shaker. After each leaching steps, a solid/liquid separation was performed by filtration with G6 filters (porosity = 1.5 µm). Then, a 1 mL of each liquid sample was collected and preserved in 5% HNO_3 in order to determine the amounts of metals solubilized.

3.4.4 Analytical methods

At the beginning of this study, each type of spent batteries was digested separately using the 3050B method in order to determine its metals composition (USEPA, 2013). In this method, 1 g of sample was mixed with 10 mL of 50% HNO_3 and the mix was heated at 95°C for 10 min. Then, 5 mL of concentrated HNO_3 were added and refluxed during 30 min, this step was repeated until the digestion of the sample was completed (no brown fume). The sample was then heated at 95°C until all the liquid was evaporated. Then, 3 mL of H_2O_2 (30%) and 1 mL of H_2O were added (USEPA, 2013). The sample was filtered on G6 filters (porosity = 1.5 µm) and the concentrations of the elements presents were determined by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy, ICP-AES, Varian 725-ES). The digestion method using perchloric acid ($HClO_4$) as an oxidizing agent was then chosen to determine the amounts of metals present in the mixture of spent batteries (Van Loon, 1985). Due to its strong oxidizing property, all metals were completely dissolved. A 0.25 g of spent batteries sample was digested in 10 mL of HNO_3 during one hour at 100 – 140°C. Then, 4 mL of perchloric acid were added to the mixture and let to react at 140°C for 2 hours. The sample was then let to cool down and 10 mL of hydrofluoric acid (HF) were added and let to react at ambient temperature for 12 –14 hours to allow a complete digestion of the sample. The sample was then heated in order to evaporate the liquid and the dried sample was collected in concentrated HNO_3 before to complete the volume of the solution at 50 mL with distilled water. The sample was filtered with G6 filters. An ICP-AES apparatus was used to determine the concentrations of dissolved metals. Spiked samples and certified solutions (SCP Science, Lasalle, Canada) were also analyzed to confirm the precision of the experimental results.

3.4.5 Estimation of process costs and metal revenues

The costs related to the consumption of chemical reagents (CRC) and expressed in US$ per ton of battery powder were calculated using the Equation 3.2. The revenues, expressed in US$ per ton of battery powder, related to the sales of the metals recovered were estimated using the Equation 3.3. The unit price of Mn, Zn, Ni, Co, Li and Cd considered in the present study were 2.1, 1.8, 13.8, 28.0, 32.0 and 2.1 $/kg, respectively (Investmine, 2013; US Geological Survey, 2013).

Equation 3-2 **CRC = (number of leaching step x [acid] (M) x mass molar (g/mol) x unit price of acid (US$/t) /(solid/liquid ratio (g/L))**

Equation 3-3 **Metal revenue = Amount of metal recovered (kg/t of battery powder) x metal unit price (US$/kg)**

3.5 Results and discussion

3.5.1 Spent battery sample characterization

The metal concentrations (mg/kg) measured in the different types of spent batteries and in the mixture of the spent batteries are shown in Table 3.1. To compare the metallic composition of the different types of spent batteries, the percentage of each metal present was calculated using the Equation 3.4.

Equation 3-4
$$\text{Percentage of metal } M^{z+} (\%) = \frac{\text{Concentration of metal } M^{z+} \left(\frac{mg}{kg}\right) \times 100}{\text{Sum of the concentration of all the metals present } \left(\frac{mg}{kg}\right)}$$

As expected, the chemical analysis highlighted variable and high metal contents in the powder obtained from the different types of spent batteries. According to these results, the alkaline batteries and the Zn-C battery sample mainly contained Zn (34.0-36.0% of the total metal contents for the alkaline samples and 52.0% for the Zn-C sample) and Mn (55.0-56.0% for the alkaline samples and 48.0% for the Zn-C sample). For the Ni-MH and Ni-Cd batteries, the main metal found was nickel, with concentrations reaching 66.0% in the Ni-MH battery and 53.0% in the Ni-Cd battery. The concentration of Cd measured in the Ni-Cd batteries represented 33.0% of the total metal contents. Some metallic impurities, including Co (1.5%-6.0%) and Fe (0.1-13.0%), were also found in the Ni-MH and Ni-Cd samples. According to these results, the Li-ion batteries are mainly made of Co (54.5%) and Cu (33.2%), whereas Li represented only 6.6% of the total metal contents. The concentration of Li measured in the Li-primary sample represented 16.7% of the total metal contents, which agree with the observations made by Granata et al. (2012). The huge amounts of sulfur observed in the Li-primary sample (33.5%) were due to the use of $SOCl_2$ as a cathode in these batteries (Cook and Wagner, 2013). After the characterization of each type of spent battery powder, a mixture was prepared in accordance with the proportions of the spent batteries discarded each year in the Province of Quebec (RIS international Ltd., 2007). The granulometric analysis carried out on the mixture of the spent batteries revealed that the average size of particles was approximately 333 µm. The mixed powder obtained was mainly composed of Mn (43.5% of the total metal contents), Zn (31.8%), Ni (9.8%), Cd (4.2%) and Fe (3.3%). These different metals could be recovered selectively and reused as secondary raw materials. Considering the content of Mn, Zn, Ni, Co, Li and Cd in the spent batteries and the unit price of these metals on the market, estimated at 2.1, 1.8, 13.8, 28.0, 32.0 and 2.1 $/kg, respectively, spent batteries can be considered as a promising source of raw materials (Investmine, 2013; US Geological Survey, 2013).

3.5.2 Selection of the leaching agent

Over the last decades, several organic, inorganic acids and basic solutions have been used to allow the solubilization of metals from various solid matrixes, including contaminated soils and solid wastes. Usually, the solubilization of divalent or trivalent metallic species in acidic solutions is due to the formation of hydrogen bounds or soluble complexes or to another phenomenon called ion exchange. In the present study, eight reagents were tested to evaluate their abilities to selectively extract metals from the mixture of spent batteries at different temperatures (20 and 80°C) and at various concentrations, ranging from 0.5 to 2.0 M acetic acid, NaOH, H_2SO_4 and HCl, from 1.0 to 4.0 M for NH_4Cl and NaCl, from 0.125 and 0.25 M for EDTA and 0.5 M for oxalic acid. Table 3.2 summarizes the removal yields obtained for the different metals studied (Cd, Co, Li, Mn, Ni, and Zn) from the mixture of spent batteries, depending on the nature and concentration of the leaching agent and the temperature used.

3.5.2.1 Performances of sodium hydroxide on metals solubilization

Sodium hydroxide has been used in previous studies to selectively extract zinc or lead from spent batteries without removing iron from the residue (Jha et al., 2001). According to our results, the amounts of Cd and Zn solubilized when using NaOH showed that increasing the concentration of this leaching agent led to an improvement of the solubilization of Cd and Zn because of the formation of Cd and Zn hydroxocomplexes. These results were in agreement with the observation made by Jha et al. (2001). However, increasing the NaOH concentration was not economically interesting, even if this solution could be recycled after the electrodeposition of Zn (Jha et al., 2001). Only 12% of Zn was solubilized from the mixture of spent batteries after 4 h of leaching using 2 M of NaOH at 80°C, whereas Shin et al. (2009) observed that approximately 82% of Zn might be solubilized from Zn-C batteries when using 4 M of NaOH. The performances of the Zn solubilization differ between these studies, and this may be due to the lower concentrations of NaOH used in our experiments.

3.5.2.2 Performances of chloride solutions on metals solubilization

Chloride solutions such as NaCl or NH_4Cl are usually used to enhance the solubilization of metallic sulfides, allowing the formation of a soluble and stable chloro-complex with metals (Skrobian et al., 2005; Ekmekyaper et al., 2003; Steer et al., 2013). According to our results, sodium chloride was not efficient for the solubilization of metals, with removal yields lower than 10% for all of the experiments. Hence, it was not interesting to further consider this solution as a leaching agent. Ammonium chloride is commonly used to extract metal hydroxides such as Co and Ni (Anderson, 2009) from a solid matrix. According to our results, the use of a solution of NH_4Cl (2M) seemed to allow the solubilization of Zn, Cd and Ni, with removal yields of 44%, 56% and 40%, respectively, at 80°C, whereas the Mn remained in its solid form (<4% of Mn solubilized). These results were in agreement with the observation made by Senanayake et al. (2010) in the presence of NH_4OH (90% of Zn were removed, while <1% of Mn was solubilized).

Katsiapi et al. (2010) stated that a more stable complex could be formed between metals such as Ni, Co, Zn and ammonia than a Mn-ammonia complex. According to several studies, the solubilization of Zn, Cd and Ni in the presence of NH_4Cl was increased when increasing the temperature (Basir and Rabah, 1999; Babaei-Dehkordi et al., 2013). In our experiments carried out in the presence of NH_4Cl (4.0 M), only 27% Cd, 2.9% Co, 7.2% Li, 0.35% Mn, 14% Ni and17%

Zn were solubilized at ambient temperature, whereas more than 56% Cd, 12% Co, 20% Li, 4% Mn, 40% Ni and 43% Zn were removed at 80°C. Similar results were obtained in the study carried out by Deniz Turan et al. (2012).

3.5.2.3 Performances of EDTA on metals solubilization

EDTA is a chelating agent widely used at the laboratory scale in the rehabilitation of soils contaminated by heavy metals because of its good ability to form chelates with metals through its carboxylic groups (Jiang et al., 2011). According to the study carried out by Vatistas et al. (2001), approximately 53% of zinc could be solubilized in the presence of EDTA. The results obtained in this experiment showed that satisfactory removal yields were achieved in the presence of EDTA. Indeed, approximately 46% Cd, 38% Zn, 26% Co, 22% Li, 15% Ni and 2% Mn were extracted from the mixture of spent batteries.

3.5.2.4 Performances of oxalic acid on metals solubilization

According to our results, when a solution of oxalic acid (0.5 M) was used as the leaching agent, lithium was selectively extracted from the mixture of spent batteries, with removal yields reaching 33% at 80^{o}C. The dissolution of $LiCoO_2$ in the presence of oxalic acid can be explained by the Equation 3.5 (Sun et al., 2012).

Equation 3-5 $$4\ H_2C_2O_4 + 2\ LiCoO_2(s) \leftrightarrow Li_2C_2O_4 + 2\ CoC_2O_4(s) + 4\ H_2O + 2\ CO_{2(g)}$$

The low solubilization rate of Co observed in the present study (<1%) can be due to the strong bond between cobalt and oxygen in $LiCoO_2$, which is difficult to break down, and/or to the precipitation of CoC_2O_4 (Sun et al., 2012). Furthermore, Li is an element that belongs to the first alkaline metal group and tends to easily lose electrons compared to the transition metals (Zn, Mn, Cd, etc.). According to our experiments, Li seemed to be selectively solubilized when using oxalic acid (Erkel, 1995). Because of the high cost of oxalic acid (730 US$/t) and the low performances of Li solubilization, this chemical agent was not further considered in our study.

3.5.2.5 Performances of acid acetic on metals solubilization

Moreda-Pineiro et al. (2006) studied the solubilization of Cd and Ni from sediments using acetic acid (8 M) under pressure. According to these authors, 97% Cd and 103% Ni were solubilized from sediments. These results were better than the results obtained in the present study, with removal yields ranging from 47 to 68% for Cd and from 40 to 60% of Ni depending on the concentration of acetic acid and the temperature used. The lower performances observed in our study compared to the results obtained by Moreda-Pineiro et al. (2006) could be due to the lower concentration of acetic acid used in our experiment and to the different method applied in both experiments. Nevertheless, even if this leaching agent seemed to be promising in terms of the Cd and Ni recoveries, this reagent was not chosen because it does not allow a selective solubilization of the metals from the mixture of spent batteries. The increasing in the CH_3COOH concentration slightly increased the amounts of metal solubilized. These results were in agreement with the observation made by Janin et al. (2009) and Habbache et al. (2009).

3.5.2.6 Performances of inorganic acids on metals solubilisation

Inorganic acids such as sulfuric and hydrochloric acids are commonly used as leaching agents in hydrometallurgical processes to enhance the solubilization of metals (Sayilgan et al., 2009). The results obtained from this preliminary study indicated that the highest metals removal yields were achieved in the presence of hydrochloric acid (2.0 M) after 4 hours at 80°C. Indeed, more than 63% Cd, 59% Co, 35% Li, 35% Mn, 65% Ni and 61% Zn were removed from the mixture of the spent batteries in these conditions. These removal yields obtained in the presence of HCl were slightly better than those obtained in the presence of sulfuric acid, though H_2SO_4 showed good removal yields under the different conditions tested. Indeed, more than 66% Cd, 50% Co, 23% Li, 30% Mn, 65% Ni and 62% Zn were removed from the mixture of spent batteries in the presence of sulfuric acid (2.0 M) after 4 h. These results were in agreement with those obtained by Shin et al. (2009), who observed approximately 76% Zn and 45% Mn removals in the presence of sulfuric acid at 60°C (S/L = 100 g/L, 200 rpm, leaching time = 1 h). The solubilization of these metals in the presence of sulfuric acid is mainly due to the formation of soluble complexes ($CdSO_4$, $CoSO_4$, $MnSO_4$, $NiSO_4$ and $ZnSO_4$), as shown in Equations 3.6 to 3.8 (Innocenzi et al., 2012).

Equation 3-6 $Ni_{(s)} + H_2SO_4 + \frac{1}{2} O_2 \leftrightarrow NiSO_{4\,(aq)} + H_2O$

Equation 3-7 $ZnO + H_2SO_4 \leftrightarrow ZnSO_{4\,(aq)} + H_2O$

Equation 3-8 $Mn_2O_3 + H_2SO_4 \leftrightarrow MnO_2 + MnSO_{4\,(aq)} + H_2O$

Gharabaghi et al. (2013) observed the positive effect of the temperature on the solubilization of Ni in the presence of H_2SO_4 (8%, v/v). The low effect of the temperature on metal leaching rates with an inorganic acid observed in our experiments could be due to the high acid concentration applied, which was enough to solubilize all metals at ambient temperature. These improvements of metal solubilization, when increasing the concentration of inorganic acids, can be explained by the increase of protons able to react with the metals by ion exchange and to the increase of sulfate or chloride ions able to form soluble complexes with metals (Souza et al., 2007). In conclusion, the solubilization of metals from the mixture of the spent batteries seemed to be better in inorganic acids than in organic acids or alkaline solutions (Janin et al., 2009; Habbache et al., 2009). The highest removal yields were obtained when HCl and H_2SO_4 were used. Oxalic acid, NaCl and NH_4Cl were not efficient for the solubilization of metals, and acetic acid seemed to be the most powerful leaching agent when compared to the other organic solutions. Therefore, sulfuric acid was chosen for the following experiments due to its performances and lower cost compared to hydrochloric acid.

3.5.3 Box-Behnken design

According to the previous experiments, sulfuric acid was considered as the best compromise in terms of metal solubilization performances and operational costs. As this leaching agent did not allow more than 65% removal of the metals from the mixture of spent batteries, further experiments were carried out to optimize the leaching conditions to improve metal recoveries.

A Box-Behnken methodology was used to evaluate the influence of the parameters (acid concentration, solid/liquid ratio, retention time and number of leaching step) on the solubilisation of metals. Table 3.3 presents the Cd, Co, Mn, Ni and Zn removal yields obtained during the different experiments recommended by Expert Design 8.0 and the estimation of the metal revenues based on the amount of metal solubilized (Equation 3.2) and the costs related to the consumption of chemical products (Equation 3.3). According to these results, a large variation of metal removal yields was observed, ranging from 23 to 91% for Cd, from 15 to 79% for Co, from 20 to 79% for Mn, from 8.5 to 74% for Ni and from 12 to 100% for Zn. These results indicated that the experimental region was well-defined in the present study. Mathematical models were established using Expert Design 8.0 software to model the experimental responses (metal removal yields). Figure 3.2 presents the correlation between the response obtained experimentally (actual values) and the values predicted by the software according to the mathematical models established. All predicted and actual values were close to a linear regression, indicating good agreement between the experimental and predicted values for all of the metals studied. These results implied that the quadratic models established were suitable for predicting the response as a function of the experimental conditions in the experimental region.

Table 3.4 presents the correlation coefficients (R^2, adjusted R^2, and predicted R^2) and the values of the adequation precision defined from the analysis variance (ANOVA) by the Expert Design 8.0 software. According to these results, the correlation coefficients (R^2, adjusted R^2 and predicted R^2) were in the range of 0.83 to 0.92 for all of the metals, except for Mn, which had correlation coefficients between 0.63 and 0.76. R^2 values higher than 0.80 indicated good agreement between the experimental values and the predicted values determined using the quadratic models. The five replicates on the center points were conducted to estimate the experimental error and to provide an indication of the lack of fit (Coudert et al., 2013). For all of the mathematical models established, no significant lack of fit was observed, indicating that the models fitted well to the experimental data. Moreover, all of the adequate precision values were greater than 4, which is desirable for supporting the fitness of the mathematical models established (Kumar et al., 2008). In this experiment, the influence of various parameters, including the concentration of sulphuric acid (X_1), the solid/liquid ratio (X_2), the retention time (X_3) and the number of leaching step (X_4), and their interactions were investigated. These results, based on the analysis of variance (ANOVA), are shown in Table 3.5. The analysis of variance consisted on determining the sum of square, the degree of freedom, the mean square, the F-value and the p-value for each term of the mathematical models. The model or the selected variable is significant if the value of "Prob > F" is lower than 0.05. According to these results, all of the mathematical models defined to predict the removals of metals from the mixture of spent batteries were significant, confirming that the experimental values were in agreement with the predicted values. These results indicated that the influence of the different parameters studied was not significant for all of the metals. Three factors, including the acid concentration, the solid/liquid ratio and the number of leaching step, seemed to have a significant effect on the solubilization of Co, Ni and Zn from the mixture of the spent batteries. All of the studied factors seemed to have a significant influence on the solubilization of Cd, whereas the dissolution of Mn seemed to only be influenced by the solid/liquid ratio. The effects of the different factors studied on the solubilization of the metals are illustrated in

Figure 3.3. This figure shows that the solubilization of Cd and Zn was higher than those obtained for other metals (Co, Ni and Mn) in similar leaching conditions. The highest Co, Ni and Zn removal yields were observed when the solid/liquid ratio was fixed at its lower level and the concentration of acid was higher than 2.5 M (Figure 3.3). These observations were in agreement with the results obtained by Zhang et al. (2010), who stated that a high solid/liquid ratio (high viscosity of the pulp) could reduce the mass transfer of the reactant into the solid surface.

Nevertheless, the highest Cd removal yields were obtained at a high solid/liquid ratio (18% w/w) and a low acid concentration. This result could be due to the high solubility of Cd in dilute acid. The combination of the X_2 and X_3 factors had a significant effect on the solubilization of Co and Ni (Figure 3.4). For both of these metals, the highest removal yields were observed when the solid/liquid ratio was at its lowest level and the retention time was at its highest level. The mathematical equations, in terms of the coded factors, defined by the software Expert Design 8.0 to predict the Cd, Co, Mn, Ni and Zn removal yields are presented in Equations 3.9 to 3.13.

Equation 3-9

$$\% \mathrm{Cd} = 62.2 - 8.30\, X_1 - 6.40\, X_2 - 3.97\, X_3 - 10.5\, X_4 + 3.55\, X_5 - 12.7\, X_1X_2 + 3.49\, X_1X_3 - 2.59\, X_2X_3 - 4.04\, X_2X_4 + 1.15\, X_2X_5 + 6.95\, X_1^2 - 5.66\, X_2^2 + 2.23\, X_3^2$$

Equation 3-10

$$\% \mathrm{Co} = 31.1 - 5.34\, X_1 - 13.9\, X_2 - 2.27\, X_3 - 12.2\, X_4 + 2.57\, X_5 - 12.1\, X_1X_2 + 5.06\, X_2X_3 + 5.49\, X_1^2 + 11.5\, X_2^2 + 5.70\, X_3^2$$

Equation 3-11 $\% \text{Mn} = 55.8 - 1.38 X_1 - 9.88 X_2 - 1.59 X_3 - 12.5 X_4 + 4.56 X_5 - 2.30 X_1X_2 - 2.51 X_2X_3 - 6.32 X_2X_4 + 1.78 X_2X_5 + 1.22 X_3X_4 - 0.45 X_3X_5 + 2.40 X_1^2 - 7.36 X_2^2 + 2.78 X_3^2$

Equation 3-12 $\% \text{Ni} = 20.8 - 7.81 X_1 - 12.3 X_2 - 1.80 X_3 - 9.24 X_4 + 1.78 X_5 - 14.7 X_1X_2 - 4.31 X_2X_3 + 4.31 X_2X_4 - 0.71 X_2X_5 + 7.68 X_1^2 + 11.5 X_2^2 + 7.50 X_3^2$

Equation 3-13 $\% \text{Zn} = 33.5 - 15.8 X_1 - 21.1 X_2 - 2.60 X_3 - 12.5 X_4 + 2.11 X_5 - 13.9 X_1X_2 - 4.83 X_1X_4 - 2.32 X_1X_5 - 6.16 X_2X_3 + 16.2 X_1^2 + 18.4 X_2^2 + 7.49 X_3^2$

From all equations presented above and Table 3.5, it can be observed that the solid/liquid ratio was the most important parameter influencing the solubilization of all of the metals studied (highest coefficients in the mathematical models established in terms of coded factor and high F-values).

The influence of the solid/liquid ratio was negative, indicating that an increase of this ratio will result in a decrease of the metal solubilization, which seemed logical. According to these results, the use of three leaching steps could significantly enhance the performances of Cd, Co, Mn, Ni and Zn solubilization. The optimal leaching conditions were determined using the Expert Design 8.0 software considering the performances of metal solubilization, the costs of the chemical products and the potential revenues related to the sales of the metals solubilized. The criteria imposed for determining the optimal leaching conditions were as follows: 1) maximized Cd, Co, Mn, Ni and Zn removal yields and 2) maximized the metal revenues and 3) minimized the costs related to the consumption of chemicals (chemical reagent cost). Based on the imposed criteria, a series of five solutions, presented in Table 3.6, was proposed by the Expert Design 8.0 software. The suggested solutions predicted high removal yields for Zn (96.9-106%) and Cd (94.3-99.9%), whereas the removal yields predicted for Co, Mn and Ni were in the range of 66.9-74.4%, 58.2-66.2%, 64.6-67.7%, respectively. The low removal yields predicted for Mn were in agreement with the results obtained during the 51 experiments. According to the results obtained by Su et al. (2008), manganese could almost be dissolved in the solution with the following experimental conditions: 60 g/L molasses, 1.9 M H_2SO_4, 200 g/L S/L ratio and a leaching temperature equal to 90°C.

Three additional experiments were conducted under the optimal conditions ($[H_2SO_4]$ = 1.0 M, S/L = 180 g/L (w/v), retention time = 30 min, T = 25°C and number of leaching steps = 3) to validate the optimization results. The average removal yields obtained in these optimum conditions were estimated at 86% for Cd, 70% for Co, 30% for Mn, 70% for Ni and 100% for Zn. According to these results and the predicted removal yields, it appeared that the mathematical models established slightly over-estimated the solubilization of Cd, Co, Ni and Zn.

Variations observed between experimental and predicted values were low for all of the metals studied, except for Cd and Mn. The experimental removal yields obtained for Mn were much lower than the predicted values. This could be because of the low R^2 value (Table 3.4) obtained, which revealed the low precision of this quadratic model for this metal. Nevertheless, the low variations observed between the experimental and predicted values allowed us to validate the optimal leaching conditions identified by the software for most of the metals present in the mixture of spent batteries.

3.6 Conclusion

Several leaching agents, including inorganic acids, organic acids, chelating agents and alkaline agents, were tested in the present study to evaluate their performance to selectively and efficiently solubilize metals (Cd, Co Mn, Ni and Zn) from a mixture of spent batteries.

According to the results obtained, the metals contained in spent batteries could not be selectively solubilized from the mixture, regardless of the leaching agent used. Sulfuric acid was proved to be the most efficient and cheapest solution for the development of a promising leaching process.

A three level Box-Behnken design was applied to optimize the leaching conditions in terms of the metal removal performances. The results revealed that the solid/liquid ratio and concentration of sulfuric acid had a significant influence on the solubilization of metals from the mixture of spent batteries. The optimal leaching conditions were defined to maximize the solubilization of metals and to minimize the costs related to the consumption of chemical products. The best conditions were defined as three 30 min-leaching steps carried out in the presence of sulphuric acid (1 M), with a solid/liquid ratio fixed at 18% (w/w). Under these optimal conditions, more than 86% of Cd, 70% of Co, 30% of Mn, 70% of Ni and 100% of Zn were solubilized from the mixture of spent batteries. Further experiments should be performed in the presence of a reducing agent to improve the solubilization and recovery of Mn from spent batteries.

3.7 Acknowledgements

The work was supported by the National Sciences and Engineering Research Council of Canada.

Sincere thanks to Myriam Chartier for providing technical support for the experiments.

3.8 References

Accurec, 2010. Treatment & recycling technologies. Available at the following address: http://www.accurec.de/treatment-and-recycling/technologies/nicd-batteries. Consulted on 26-07-2015.

Almeida, M.F., Xara, S.M., Delgado, J., Costa, C.A., 2006. Characterization of spent AA household alkaline batteries. Waste Manage. 26, 466-476.

Anderson, P.A., Fisher, M., Fittock, J.E., Hulgren, V.M., Jones, E.M., Messenger, R.B., Moroney, A.S., 2009. Reductive ammoniacal leaching of nickel and cobalt bearing materials. Patent US 7601314.

Avraamides, J., Senanayake, G., Clegg, R., 2006. Sulfur dioxide leaching of spent zinc–carbon-battery scrap. J. Power Sources. 159, 1488-1493.

Babaei-Dehkordi, A., Moghaddam, J., Mostafaei, A., 2013. An optimization study on the leaching of zinc cathode melting furnace slag in ammonium chloride by Taguchi design and synthesis of ZnO nanorods via precipitation methods. Mater. Res. Bull. 48, 4235-4247.

Basir, S.M.A., Rabah, M.A., 1999. Hydrometallurgical recovery of metal values from brass melting slag. Hydromet. 53, 31-44.

Bing, P., Gao, H.M., Chai, L.Y., Shu, Y.D., 2008. Leaching and recycling of zinc from liquid waste sediments. T. Nonferr. Metal. Soc. 18, 1269-1274.

Bonhomme, R., Gasper, P., Hines, J., Miralda J.P., 2013. Economic Feasibility of a Novel Alkaline Battery Recycling Process A Major Qualifying Project Submitted to the Faculty of Worcester polytechnic institute. Available at the following address: https://www.wpi.edu/Pubs/E-project/Available/E-project-030913-100840/unrestricted/Economic_Feasibility_of_a_Novel_Alkaline_Battery_Recycling_Process.pdf. Consulted on 27-07-2015.

Buzatu, T., Popescu, G., Birloaga, I., Saceanu, S., 2013. Study concerning the recovery of zinc and manganese from spent batteries by hydrometallurgical processes. Waste Manage. 33, 699-705.

Call2Recycle, 2012. Quebec takes environmental preservation to next level with battery recycling. Available at the following address: http://www.call2recycle.ca/quebec-takes-environmental-preservation-to-next-level-with-battery-recycling/. Consulted on 26-07-2015.

Cook, C.C., Wagner, M.J., 2013. Ceramic/polymer solid electrolyte based lithium water primary battery. Electrochim. Acta. 89, 778-783.

Coudert, L., Blais, J.F., Mercier, G., Cooper, P., Morris, P., Gastonguay, L., Janin, A., Zaviska, F., 2013. Optimization of Copper Removal from ACQ-, CA-, and MCQ-Treated Wood Using an Experimental Design Methodology. J. Environ. Eng.-Asce 139, 576-587.

Deniz Turan, M., Sadegh Safarzadeh, M., 2012. Separation of zinc, cadmium and nickel from ZnO–CdO–NiO mixture through baking with ammonium chloride and leaching. Hydromet. 119-120, 1-7.

Ekmekyapar, A., Oya, R., Kunkul, A., 2003. Dissolution kinetics of an oxidized copper ore in ammonium chloride solution. Chem. Biochem. Eng. Q. 17, 261-266.

Erkel, J.V., 1995. Recovery of Cd and Ni from batteries. Patent US 5407463.

Gharabaghi, M., Irannajad, M., Azadmehr, A.R., 2013. Leaching kinetics of nickel extraction from hazardous waste by sulphuric acid and optimization dissolution conditions. Chem. Eng. Res. Des. 91, 325-331.

Granata, G., Pagnanelli, F., Moscardini, E., Takacova, Z., Havlik, T., Toro, L., 2012. Simultaneous recycling of nickel metal hydride, lithium ion and primary lithium batteries: Accomplishment of European Guidelines by optimizing mechanical pre-treatment and solvent extraction operations. J. Power Sources 212, 205-211.

Habbache, N., Alane, N., Djerad, S., Tifouti, L., 2009. Leaching of copper oxide with different acid solutions. Chem. Eng. J. 152, 503-508.

Innocenzi, V., Veglio, F., 2012. Recovery of rare earths and base metals from spent nickel-metal hydride batteries by sequential sulphuric acid leaching and selective precipitations. J. Power Sources 211, 184-191.

Investmine, 2013. Metal global price in 2013. Available at the following address: http://www.infomine.com/investment/. Consulted on 25-09-2015.

Janin, A., Blais, J.F., Mercier, G., Drogui, P., 2009. Optimization of a chemical leaching process for decontamination of CCA-treated wood. J. Hazard. Mater. 169, 136-145.

Jha, M.K., Kumar, V., Singh, R.J., 2001. Review of hydrometallurgical recovery of zinc from industrial waste. Resour. Conserv. Recy. 33, 1–22.

Jiang, W., Tao, T., Liao, Z., 2011. Removal of Heavy Metal from Contaminated Soil with Chelating Agent. Open Journal of Soil Science 1, 70-76.

Katsiapi, A., Tsakiridis, P.E., Oustadakis, P., Agatzini-Leonardou, S., 2010. Cobalt recovery from mixed Co-Mn hydroxide precipitates by ammonia-ammonium carbonate leaching. miner. Eng. 23, 643-651.

Kumar, A., Prasad, B., Mirsha, I.M., 2008. Optimisation of process parameters for acrylonitrile removal by a low cost adsorbent using a Box Behnken design. J. Hazard. Mater. 150, 174-183.

Li, J., Shi, P., Wang, Z., Chen, Y., Chang, C.C., 2009. A combined recovery process of metals in spent lithium-ion batteries. Chemosphere 77, 1132-1136.

Mantuano, D.P., Dorella, G., Elias, R .C.A., Mansur, M.B., 2006. Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid-liquid extraction with Cyanex 272. J. Power Sources 159, 1510-1518.

Melin, A.L., Svensson, V.H., 1983. Process for the recovery of metals from the scrap from nickel-cadmium electric storage batteries. Patent US 4401463.

Mocellin, J., Mercier, G., Morel, J.L., Blais, J.F., Simonnot, M.O., 2015. Factors influencing the Zn and Mn extraction from pyrometallurgical sludge from steel manufacturing industry. J. Environ. Manage. 158, 48-54.

Moreda-Pineiro, J., Alonso-Rodriguez, E., Lopez-Mahia, P., Muniategui-Lorenzo, S., Prada-Rodriguez, D., Moreda-Pineiro, A., Bermejo-Barrera, A., Bermejo-Barrera P., 2006. As, Cd, Cr, Ni and Pb pressurized marine sedime liquid extraction with acetic acid from nt and soil samples. Spectrochim. Acta. B. 61, 1304-1309.

Nan, J.M., Han, D.M., Yang, M.J., Cui, M., Hou, X.L., 2006. Recovery of metal values from a mixture of spent lithium-ion batteries and nickel-metal hydride batteries. Hydromet. 84, 75-80.

Oishi, T., Yaguchia, M., Koyama, K., Tanaka, M., Lee, J.C., 2008. Effect of phosphate on lead removal during a copper recycling process from wastes using ammoniacal chloride solution. Hydromet. 90, 161-167.

RIS international Ltd., 2007. Canadian Consumer Battery Baseline Study. Available at the following address: http://www.docstoc.com/docs/79783916/Canadian-Consumer-Battery-Baseline-Study-Final-Report. Consulted on 27-07-2015.

Rudnik, E., Nikiel, M., 2007. Hydrometallurgical recovery of cadmium and nickel from spent Ni-Cd batteries. Hydromet. 89, 61-71.

Sahoo, R.N., Naik, P.K., Das, S.C., 2001. Leaching of manganese from low-grade manganese ore using oxalic acid as reductant in sulphuric acid solution. Hydromet. 62, 157-163.

Sayilgan, E., Kukrer, T., Civelekoglu, G., Ferella, F., Akcil, A., Veglio, F., Kitis, M., 2009. A review of technologies for the recovery of metals from spent alkaline and zinc-carbon batteries. Hydromet. 97, 158-166.

Senanayake, G., Shin, S.M., Senaputra, A., Winn, A., Pugaev, D., Avraamides, J., Sohn, J.S., and Kim, D.J., 2010. Comparative leaching of spent zinc-manganese-carbon batteries using sulfur dioxide in ammoniacal and sulfuric acid solutions. Hydromet. 105, 36-41.

Shin, S.M., Senanayake, G., Sohn, J.S., Kang, J.G., Yang, D.H., Kim, T.H., 2009. Separation of zinc from spent zinc-carbon batteries by selective leaching with sodium hydroxide. Hydromet. 96, 349-353.

Skrobian, M., Havlik, T., Ukasik A., 2005. Effect of NaCl concentration and particle size on chalcopyrite leaching in cupric chloride solution. Hydromet. 77, 109-114.

SNAM, 2015. Treatment means. Available at the following address: http://www.snam.com/traitement/treatment-hydrometallurgy.php. Consulted on 26-07-2015.

Souza, A.D., Pina, P.S., Lima, E.V.O., da Silva, C.A., Leao, V.A., 2007. Kinetics of sulphuric acid leaching of a zinc silicate calcine. Hydromet. 89, 337-345.

Su, H., Wen, Y., Wang, F., Sun, Y., Tong, Z., 2008. Reductive leaching of manganese from low-grade manganese ore in H_2SO_4 using cane molasses as reductant. Hydromet. 93, 136-139.

Steer, J. M., Griffiths, A.J., 2013. Investigation of carboxylic acids and non-aqueous solvents for the selective leaching of zinc from blast furnace dust slurry. Hydromet. 140, 34-41.

Sun, L. and Qiu, K.Q., 2012. Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries. Waste Manage. 32, 1575-1582.

U.S. Department of the Interior, U.S. Geological Survey, 2012. Metal Prices in the United States Through 2010 Reston, Virginia, USA, 212 p., Available at the following address: http://pubs.usgs.gov/sir/2012/5188/sir2012-5188.pdf. Consulted on 10-10-2014.

USEPA, 2015. Acid Digestion of Sediments, Sludges and Soils, Method 3050B. United State Environmental Protection Agency. Available at the following address: http://minerals.usgs.gov/minerals/pubs/commodity/myb/. Consulted on 25-09-2013.

Van Loon, J.C., 1985. Selected methods of trace metal analysis: biological and environmental samples, John Wiley & Sons, Inc., USA, 357 p.

Vatistas, N., Bartolozzi, M., Arras, S., 2001. The dismantling of the spent alkaline zinc manganese dioxide batteries and the recovery of the zinc from the anodic material. J. Power Sources 101, 182-187.

Wuana, R.A., Okieimen, F.E., Imborvungu, J.A., 2010. Removal of heavy metals from a contaminated soil by using EDTA to remove the heavy metals from the contaminated soil. J. Environ. Sci. Technol. 7, 485-496.

Yazici, E.Y., Deveci, H., 2013. Extraction of metals from waste printed circuit boards (WPCBs) in H_2SO_4-$CuSO_4$-NaCl solution. Hydromet. 139, 30-38.

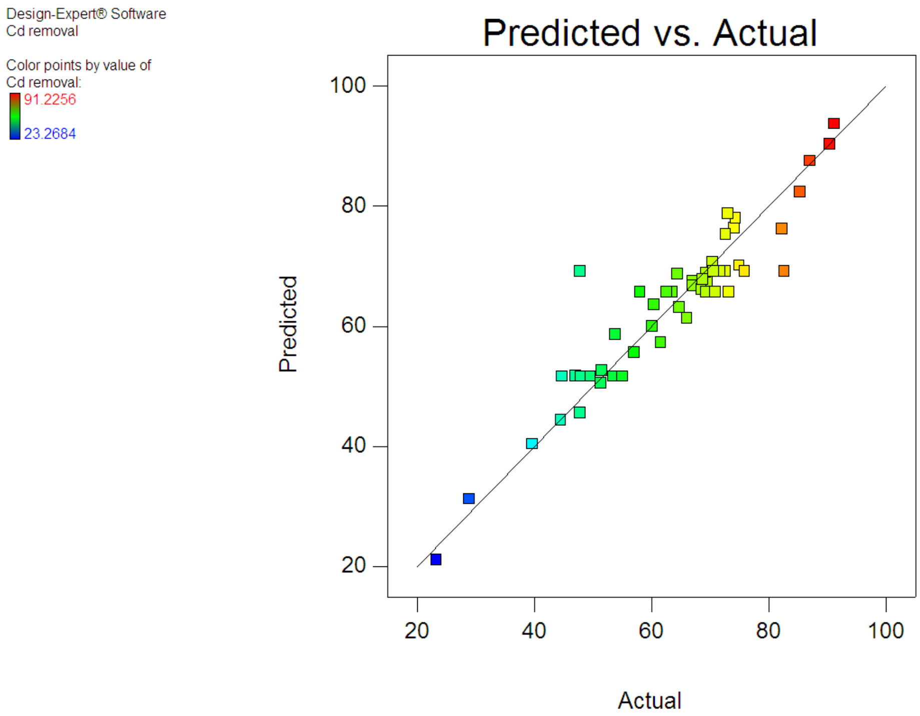
Zhang, P., Yokoyama, T., Itabashi, O., Suzuki, T.M., Inoue, K., 1998. Hydrometallurgical process for recovery of metal values from spent nickel-metal hydride secondary batteries. Hydromet.47, 259-271.

Zhang, Z.Y., Peng, J.H., Srinivasakannan, C., Zhang, Z.B.A., Zhang, L.B., Fernandez, Y., Menendez, J.A., 2010. Leaching zinc from spent catalyst: Process optimization using response surface methodology. J. Hazard. Mater. 176, 1113-1117.

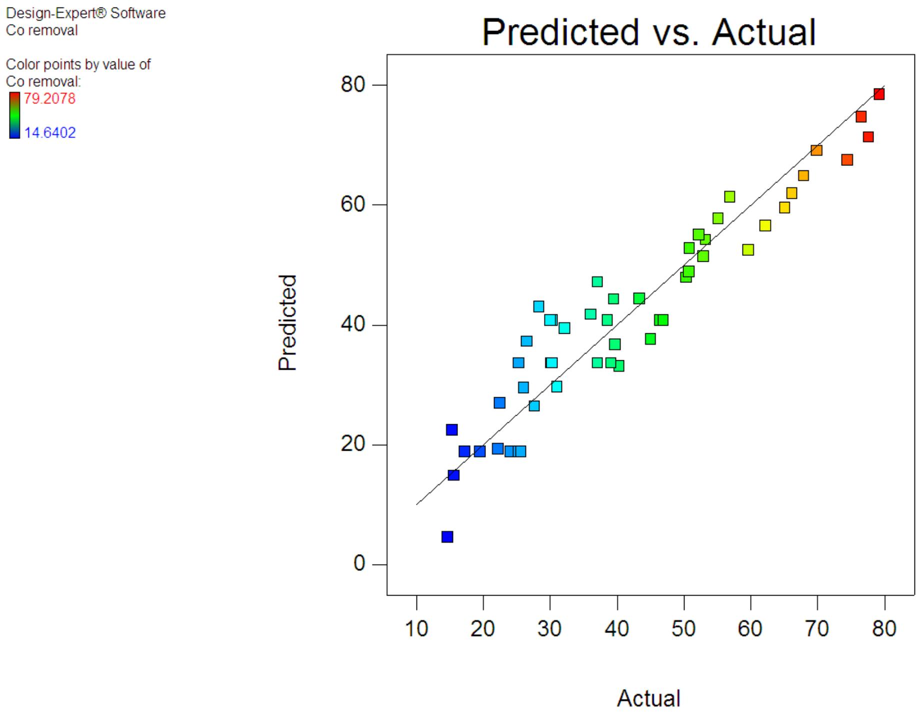
3.9 List of figures

3.10 List of tables

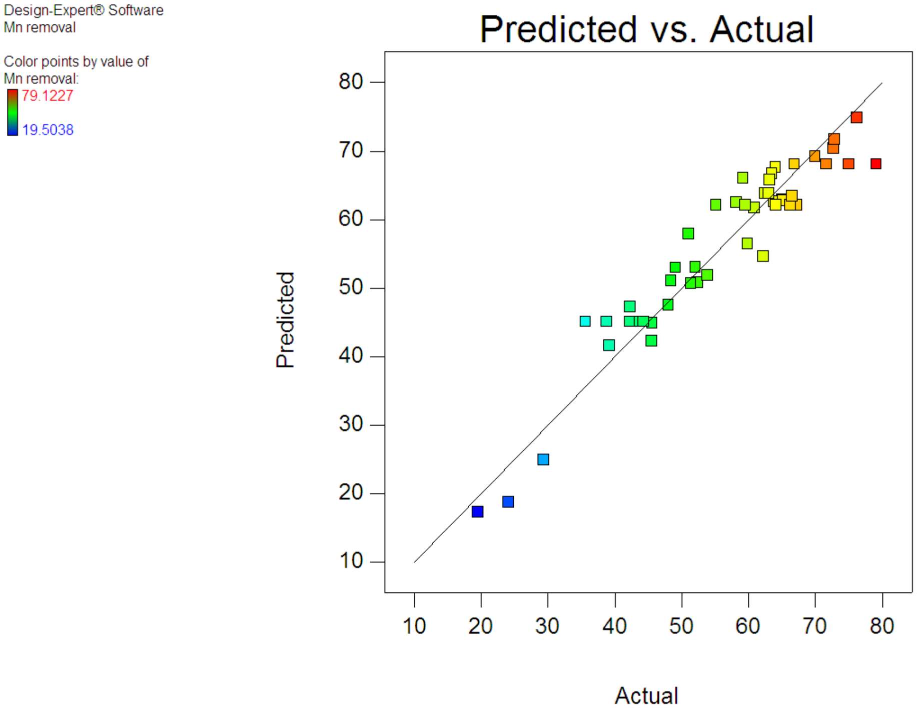
Figure 3.1 **Photography of the coarse particles that were removed from the powder after the grinding steps (a.), the fine battery powder before (b.) and after (c.) the leaching process performed with optimum conditions**


Design-Expert® Software
Cd removal
Color points by value of
Cd removal:
91.2256
23.2684
Predicted vs. Actual
Predicted
Actual
100
80
60
40
20
20
40
60
80
100

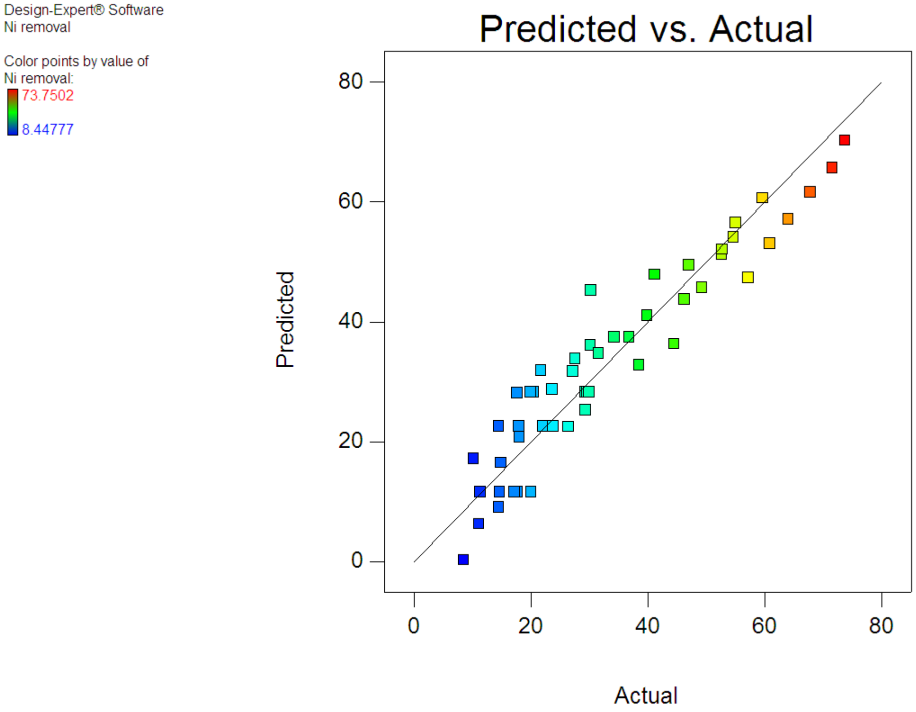
a.


Design-Expert® Software
Co removal
Color points by value of
Co removal:
79.2078
14.6402
Predicted vs. Actual
Predicted
Actual
80
60
40
20
0
10
20
30
40
50
60
70
80

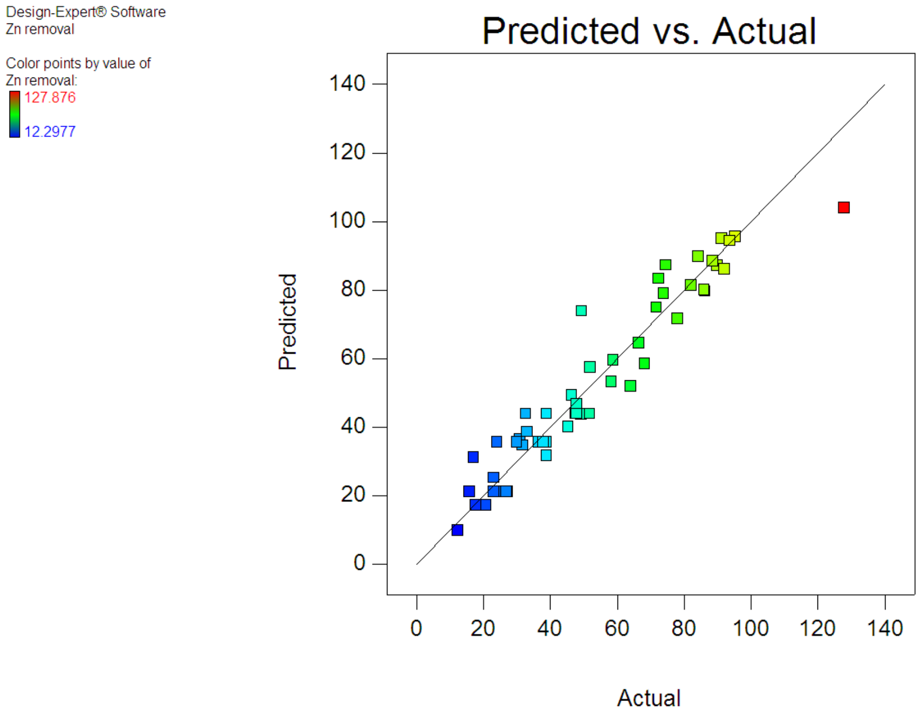
b.


Design-Expert® Software
Mn removal
Color points by value of
Mn removal:
79.1227
19.5038
Predicted vs. Actual
Predicted
Actual
10
20
30
40
50
60
70
80

c.

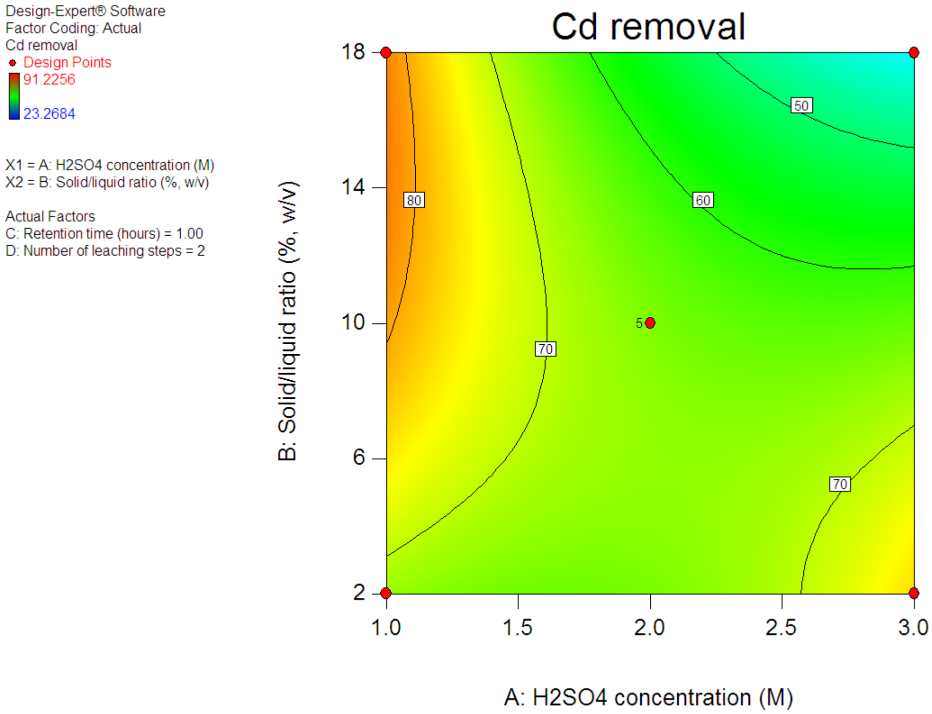

Design-Expert® Software
Ni removal
Color points by value of
Ni removal:
73.7502
8.44777
Predicted vs. Actual
Predicted
Actual
0
20
40
60
80

d.

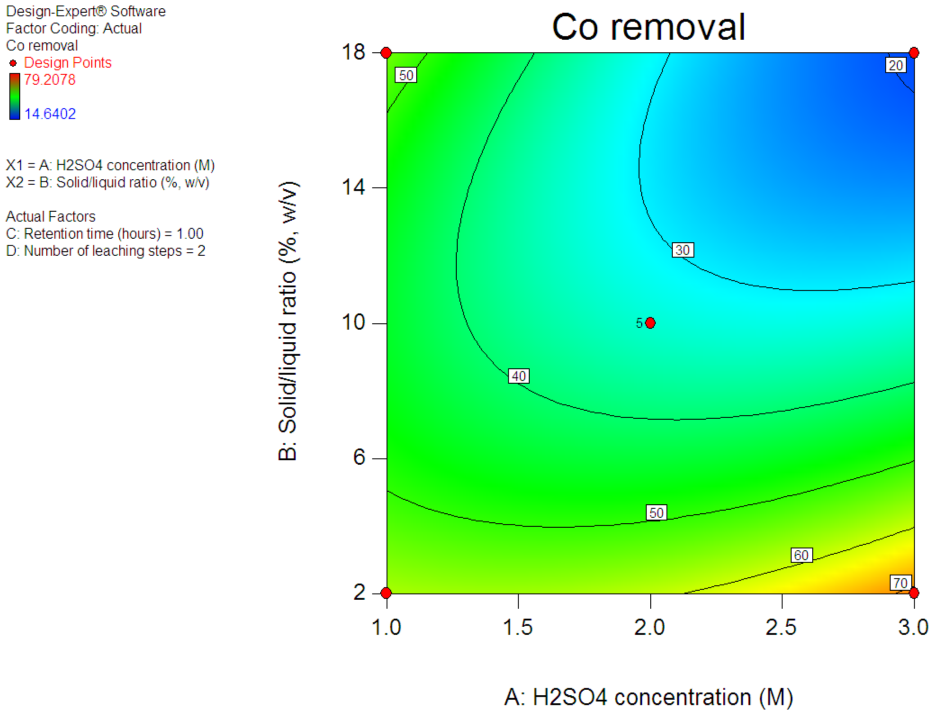


e.

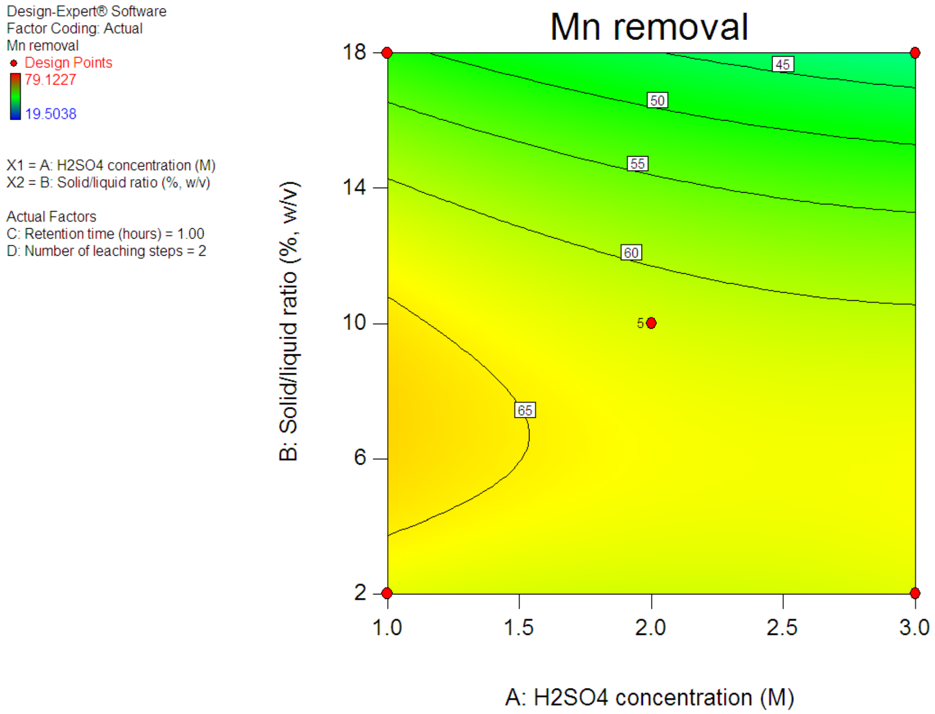
Figure 3.2 **Relationship between predicted values and actual values defined on the experimental region for Cd removal (a.), Co removal (b.), Mn removal (c.), Ni removal (d.) and Zn removal (e.)**


Design-Expert® Software
Factor Coding: Actual
Cd removal
Design Points
91.2256
23.2684
X1 = A: H2SO4 concentration (M)
X2 = B: Solid/liquid ratio (%, w/v)
Actual Factors
C: Retention time (hours) = 1.00
D: Number of leaching steps = 2
Cd removal
18
14
10
6
2
B: Solid/liquid ratio (%, w/v)
1.0
1.5
2.0
2.5
3.0
A: H2SO4 concentration (M)
80
70
60
50
70
5

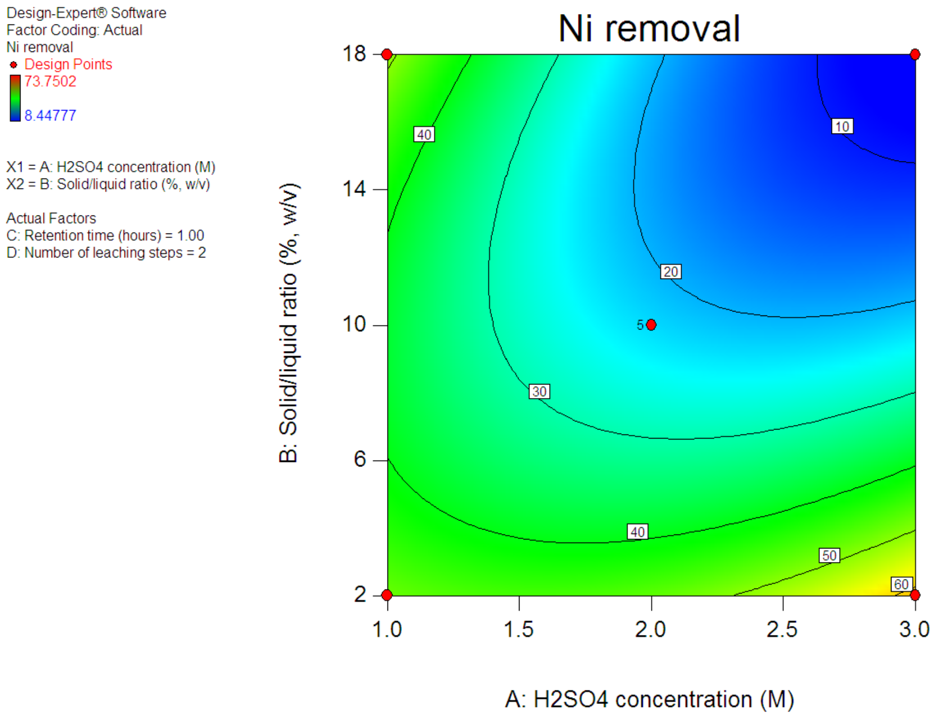
a.


Design-Expert® Software
Factor Coding: Actual
Co removal
Design Points
79.2078
14.6402
X1 = A: H2SO4 concentration (M)
X2 = B: Solid/liquid ratio (%, w/v)
Actual Factors
C: Retention time (hours) = 1.00
D: Number of leaching steps = 2
Co removal
18
14
10
6
2
B: Solid/liquid ratio (%, w/v)
1.0
1.5
2.0
2.5
3.0
A: H2SO4 concentration (M)
50
20
30
40
50
60
70
5

b.


Design-Expert® Software
Factor Coding: Actual
Mn removal
Design Points
79.1227
19.5038
X1 = A: H2SO4 concentration (M)
X2 = B: Solid/liquid ratio (%, w/v)
Actual Factors
C: Retention time (hours) = 1.00
D: Number of leaching steps = 2
Mn removal
B: Solid/liquid ratio (%, w/v)
A: H2SO4 concentration (M)
18
14
10
6
2
1.0
1.5
2.0
2.5
3.0
45
50
55
60
65
5

c.


Design-Expert® Software
Factor Coding: Actual
Ni removal
Design Points
73.7502
8.44777
X1 = A: H2SO4 concentration (M)
X2 = B: Solid/liquid ratio (%, w/v)
Actual Factors
C: Retention time (hours) = 1.00
D: Number of leaching steps = 2
Ni removal
B: Solid/liquid ratio (%, w/v)
A: H2SO4 concentration (M)
18
14
10
6
2
1.0
1.5
2.0
2.5
3.0
40
10
20
30
40
50
60
5

d.

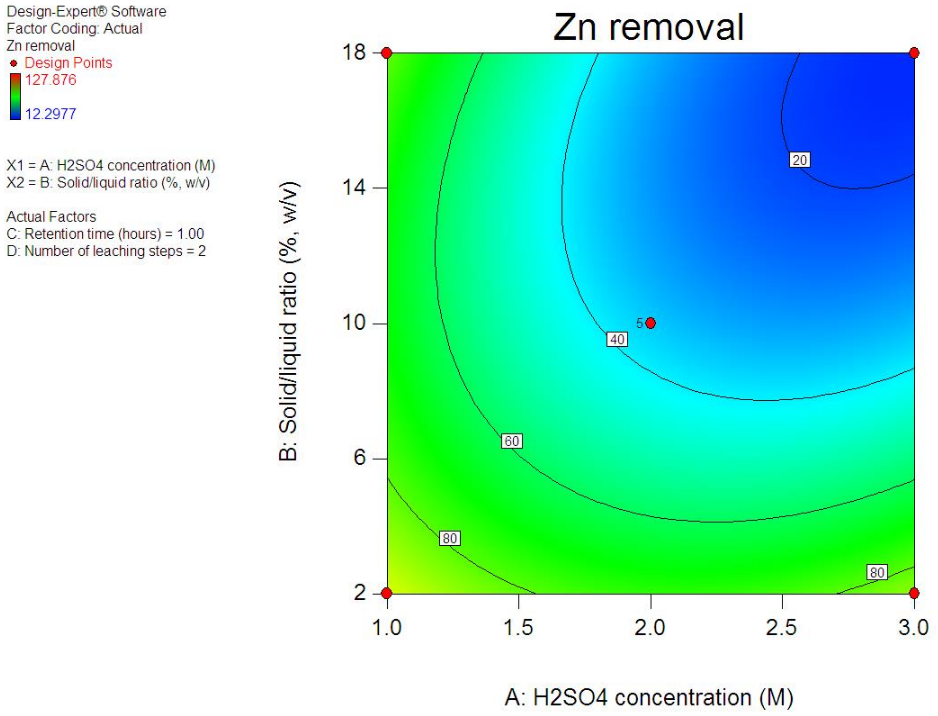
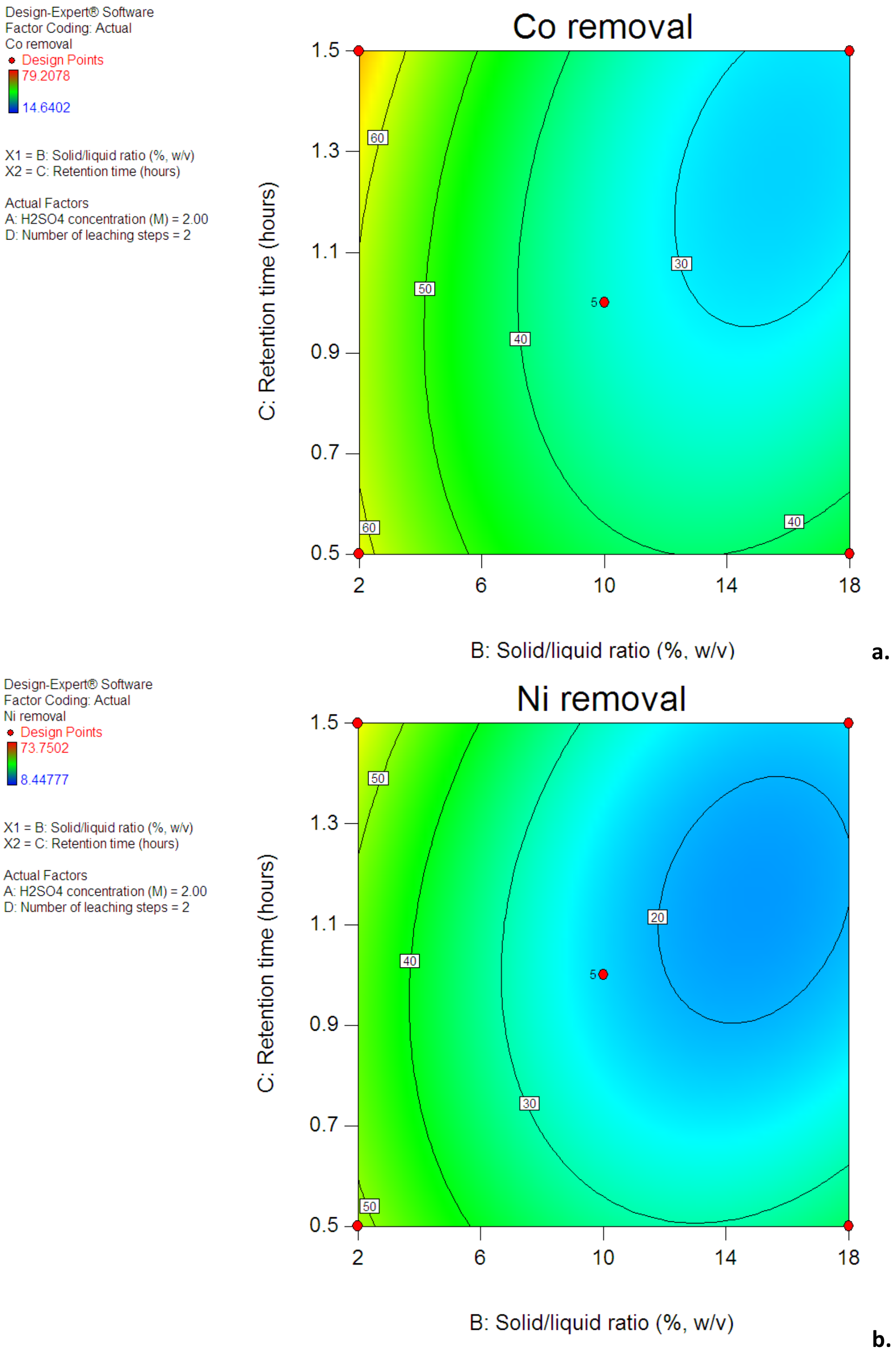


Figure 3.3 Effect of H_2SO_4 concentration and solid/liquid (S/L) ratio on the solubilization of Cd (a.), Co (b.), Mn (c.), Ni (d.) and Zn (e.) from a mixture of spent batteries (t = 60 min, T = 20°C, number of leaching steps = 2)



a.

b.

Figure 3.4 **Effect of retention time and solid/liquid (S/L) ratio on the solubilization of Co (a.) and Ni (b.) from a mixture of spent batteries ([H_2SO_4] = 2.0 M, T = 20°C, number of leaching steps = 2)**

Table 3.1 Metal concentrations (mg/kg) measured in each type of waste batteries and in the mix used for the present experiments

Metals	Alkaline	Zn-C	Ni-MH	Ni-Cd	Li-ion	Li-M	Mixture of battery wastes
Al	1 112 ± 40	875 ± 110	7 372 ± 96	410 ± 98	23 055 ± 5 400	59 260 ± 2 200	2 230 ± 55
Ba	35 ± 18	114 ± 13	25 ± 3	13 ± 4	31 ± 1	56 ± 5	3 620 ± 1 900
Cd	2.6 ± 4.0	1.4 ± 1.0	10 ± 2	209 985 ± 23 400	488 ± 281	22 ± 2	26 370 ± 2 800
Co	11 ± 7	48 ± 3	43 690 ± 342	9 380 ± 850	245 380 ± 14 100	170 ± 15	3 420 ± 185
Cu	124 ± 14	104 ± 25	51 640 ± 8 400	22 ± 1	149 550 ± 635	1 735 ± 45	400 ± 32
Fe	4 700 ± 15	426 ± 182	2 168 ± 284	82 610 ± 140	811 ± 584	230 110 ± 6 400	20 860 ± 2 900
K	54 635 ± 1 300	559 ± 129	28 780 ± 140	< 0.2*	< 0.2*	< 0.2*	35 200 ± 2 500
Li	< 0.8*	< 0.8*	812 ± 360	733 ± 150	29 870 ± 1 400	98 265 ± 2 750	830 ± 177
Mn	361 700 ± 5 400	265 720 ± 24 200	15 915 ± 232	494 ± 30	31 ± 16	513 ± 55	271 400 ± 19 300
Ni	111 ± 27	116 ± 43	503 360 ± 10 800	335 900 ± 41 000	106 ± 20	227 ± 25	61 160 ± 3 300
S	2 830 ± 60	2 270 ± 199	328 ± 78	< 0.2*	480 ± 129	197 110 ± 3 600	< 0.2*
Zn	239 700 ± 12 300	287 160 ± 25 100	12 040 ± 116	1 790 ± 150	72 ± 50	351 ± 50	198 420 ± 14 000
Nd	< 0.8*	< 0.8*	10 910 ± 54	< 0.8*	< 0.8*	< 0.8*	< 0.8*
La	< 0.8*	< 0.8*	60 340 ± 480	< 0.8*	< 0.8*	< 0.8*	< 0.8*
Ce	< 0.8*	< 0.8*	26 780 ± 350	< 0.8*	< 0.8*	< 0.8*	< 0.8*
Total	664 960	557 394	764 170	641 337	449 875	587 819	623 910

** detection limit.*

Table 3.2 **Effect of the different leaching agents and temperature (20°C or 80°C) on the solubilization of metals (removal yields %) from spent batteries after 4 h (S/L = 10%)**

Metals	**Cd**		**Co**		**Li**		**Mn**		**Ni**		**Zn**	
Leaching agents	**20°C**	**80°C**	**20°C**	**80°C**	**20°C**	**80°C**	**20°C**	**80°C**	**20°C**	**80°C**	**20°C**	**80°C**
Oxalic acid (0.5 M)	0.15	0.56	0.14	0.00	28.4	32.5	0.24	0.81	0.05	0.02	0.00	0.35
NH_4Cl (1.0 M)	8.37	3.84	0.00	0.00	5.53	15.1	0.00	0.06	1.67	0.10	5.43	0.31
NH_4Cl (4.0 M)	26.7	55.8	2.93	11.9	7.18	20.4	0.35	3.68	13.9	39.5	16.5	43.5
EDTA (0.125 M)	22.3	29.9	2.23	13.5	6.08	17.6	0.06	0.14	0.79	6.04	22.2	24.7
EDTA (0.25 M)	0.02	46.2	0.00	26.0	-0.21	21.8	0.00	2.38	0.02	15.4	0.00	38.3
NaCl (1.0 M)	0.02	0.36	0.00	0.00	6.32	9.75	0.00	0.92	0.00	0.33	0.00	1.37
NaCl (4.0 M)	2.51	2.91	0.00	0.61	8.49	11.4	0.00	4.38	0.00	1.16	0.00	3.77
Acetic acid (0.5 M)	46.6	52.4	5.95	23.0	9.74	18.1	1.26	7.04	18.0	39.9	41.2	40.4
Acetic acid (2.0 M)	67.8	64.2	43.4	45.0	14.6	33.8	13.7	12.3	72.0	59.7	48.6	51.4
NaOH (0.5 M)	0.01	0.80	6.05	0.78	1.76	2.31	0.00	0.91	0.00	0.52	1.55	3.25
NaOH (2.0 M)	0.03	0.00	8.95	0.18	1.49	2.64	0.01	-0.01	0.00	0.00	21.5	11.6
H_2SO_4 (0.5 M)	25.5	63.2	1.45	39.4	5.70	28.2	0.16	16.0	7.62	49.5	15.6	48.0
H_2SO_4 (2.0 M)	67.5	66.3	50.1	55.9	22.7	40.0	29.9	33.3	67.4	65.1	65.5	61.6
HCl (0.5 M)	29.3	38.4	13.2	19.0	11.8	28.0	5.38	9.39	18.1	27.4	29.5	26.5
HCl (2.0 M)	74.1	63.4	57.8	59.4	27.1	35.1	31.9	34.7	77.0	64.5	71.4	61.2

Table 3.3 Box Behnken experimental design and metal removal efficiencies from battery wastes, chemical product costs and metal revenues

Run	[H_2SO_4] (M)	S/L (% w/v)	Retention time (h)	Nb of leaching steps	Cd removal (%)	Co removal (%)	Mn removal (%)	Ni removal (%)	Zn removal (%)	Metal revenues ($/ton)	Chemical reagent costs (CRC) ($/ton)
1	1	18	1.0	2	85.4	53.2	48.4	52.7	82.1	1125	163
2	1	10	1.5	1	66.0	40.3	48.0	38.5	58.2	890	147
3	2	10	1.0	3	75.9	46.9	71.6	29.6	47.4	925	882
4	2	2	0.5	2	69.2	66.2	58.1	52.8	73.9	1149	2940
5	3	2	1.0	3	74.4	79.2	64.0	73.8	91.2	1476	6615
6	2	10	1.0	2	69.3	39.1	64.1	23.8	38.8	798	588
7	2	18	1.5	2	51.4	31.1	45.5	26.4	38.8	687	327
8	3	10	0.5	2	66.9	36.1	65.1	27.2	49.2	857	882
9	1	18	1.0	3	87.1	56.9	51.0	54.7	84.2	1170	245
10	1	10	1.5	3	73.1	52.2	63.5	47.0	72.4	1120	441
11	2	18	1.5	3	57.0	39.7	51.4	29.4	45.3	782	490
12	2	2	0.5	1	60.1	37.1	53.9	30.2	66.4	872	1470
13	3	10	0.5	3	74.9	50.7	72.8	36.8	64.1	1055	1323
14	1	2	1.0	2	66.9	55.1	65.0	41.2	95.2	1239	1470
15	2	2	1.5	1	61.5	50.8	59.8	39.9	77.9	1071	1470
16	3	2	1.0	2	74.1	77.6	63.8	67.8	89.8	1413	4410
17	2	10	1.0	2	58.0	30.3	59.5	14.5	24.0	616	588
18	2	10	1.0	3	82.6	46.4	79.1	29.3	51.7	986	882
19	2	18	0.5	2	60.4	39.5	-	31.5	46.3	627	327
20	3	18	1.0	1	23.3	14.6	19.5	8.45	12.3	256	245
21	2	2	1.5	3	68.7	76.5	63.2	71.6	93.7	1484	4410
22	2	10	1.0	2	73.2	37.1	67.2	23.8	36.5	799	588

23	3	10	0.5	1	51.5	22.5	45.6	18.0	30.9	578	441
24	3	10	1.5	2	63.5	26.5	60.8	17.7	33.0	679	882
25	2	18	1.5	1	28.9	15.6	24.1	14.8	20.8	372	163
26	2	10	1.0	1	47.9	17.2	35.6	14.7	23.0	457	294
27	2	10	1.0	1	44.7	24.1	42.9	11.3	15.7	450	294
28	2	10	1.0	1	49.5	19.5	38.8	17.2	26.9	514	294
29	2	2	0.5	3	70.4	69.8	59.2	59.7	74.5	1218	4410
30	3	18	1.0	3	47.8	27.7	49.1	14.5	23.0	544	735
31	2	10	1.0	1	55.0	25.6	42.2	20.1	27.1	567	294
32	1	2	1.0	3	71.0	67.9	66.5	55.0	128	1640	2205
33	2	10	1.0	1	53.4	25.2	44.3	17.7	24.8	549	294
34	2	10	1.0	3	71.6	30.4	66.9	20.4	38.9	777	882
35	2	10	1.0	3	70.6	38.6	75.0	19.9	32.7	799	882
36	1	10	0.5	2	90.4	59.6	72.7	57.2	85.9	1328	294
37	3	18	1.0	2	39.7	22.2	39.1	11.1	17.7	428	490
38	3	10	1.5	1	47.0	15.45	42.3	10.2	17.1	431	441
39	2	10	1.0	3	47.8	30.0	28.5	29.9	47.8	965	882
40	1	10	0.5	1	82.2	45.0	52.4	44.5	68.1	1018	147
41	2	18	0.5	1	44.5	26.1		23.7	31.6	367	163
42	2	10	1.0	2	70.9	30.1	66.2	22.0	37.9	776	588
43	1	18	1.0	1	64.8	32.2	29.3	30.2	58.8	707	81.7
44	2	18	0.5	3	64.4	52.9		34.2	51.8	713	490
45	3	10	1.5	3	72.7	43.4	70.0	27.6	47.8	892	1323
46	1	2	1.0	1	53.8	28.4	52.0	21.7	49.3	723	735
47	2	2	1.5	2	68.5	74.4	63.0	64.0	92.1	1404	2940
48	3	2	1.0	1	69.5	62.2	62.2	49.3	86.2	1210	2205
49	2	10	1.0	2	62.6	25.3	55.1	17.9	29.9	638	588
50	1	10	0.5	3	91.2	65.1	76.2	60.9	88.52	1397	441
51	1	10	1.5	2	72.7	50.3	62.5	46.3	71.7	1103	294

Table 3.4 **Adequacy of mathematical models established to predict metals solubilization from a mix of spent batteries**

Metal	R-squared	Adj R-squared	Pred R-square	Adeq Precision
Cd	0.88	0.84	0.82	23.9
Co	0.90	0.87	0.83	24.5
Mn	0.76	0.66	0.63	11.7
Ni	0.90	0.86	0.80	21.1
Zn	0.92	0.89	0.83	21.2

Table 3.5 **Results from ANOVA for response surface models established for the modelling of metals solubilization from a mix of spent batteries (X_1 = [H_2SO_4]; X_2 = Solid/Liquid ratio; X_3 = Retention time; X_4 = Number of leaching steps)**

Metals	**Source**	**Analysis of variance**					
	Model	**Sum of squares**	**Degree of freedom**	**Mean square**	**F value**	**P-value Prob >F**	**Conclusion**
Mn	Model	7125	14	508.9	7.46	<0.0001	Significant
	X_2	1802	1	1802	26.4	<0.0001	Significant
	X_2^2	541.5	1	541.5	7.94	0.0081	Significant
	X_4	3567	2	1784	26.1	<0.0001	Significant
Zn	Model	33559	12	2797	35.9	<0.0001	Significant
	X_1	6020	1	6020	77.3	<0.0001	Significant
	X_2	10642	1	10642	137	<0.0001	Significant
	X_4	4538	2	2269	29.2	<0.0001	Significant
	X_1X_2	2320	1	2320	29.8	<0.0001	Significant
	X_2X_3	456.1	1	456.1	5.86	0.0204	Significant
	X_1^2	3320	1	3320	42.7	<0.0001	Significant
	X_2^2	4277	1	4277	55.0	<0.0001	Significant
	X_3^2	708.1	1	708.1	9.10	0.0045	Significant
Ni	Model	14290	12	1183	27.5	<0.0001	Significant
	X_1	1465	1	1465	34.0	<0.0001	Significant
	X_2	3631	1	3631	84.4	<0.0001	Significant
	X_4	2453	2	1227	28.5	<0.0001	Significant
	X_1X_2	2597	1	2597	60.4	<0.0001	Significant
	X_2X_3	223.0	1	223.0	5.18	0.0285	Significant
	X_1^2	745.5	1	745.5	17.3	0.0002	Significant
	X_2^2	1685	1	1685	39.1	<0.0001	Significant
	X_3^2	709.9	1	709.9	16.5	0.0002	Significant
Cd	Model	9294	13	715.0	21.4	<0.0001	Significant
	X_1	1654	1	1654	49.4	<0.0001	Significant
	X_2	984.5	1	984.5	29.4	<0.0001	Significant
	X_3	379.1	1	379.1	11.3	0.0018	Significant
	X_4	2926	2	1463	43.7	<0.0001	Significant
	X_1X_2	1944	1	1944	58.1	<0.0001	Significant

	X_1X_3	146.2	1	146.2	4.37	0.0436	Significant
	X_1^2	548.7	1	548.7	16.4	0.0003	Significant
	X_2^2	405.2	1	405.2	12.1	0.0013	Significant
Co	Model	14486	10	1449	34.4	< 0.0001	Significant
	X_1	684.5	1	684.5	16.3	0.0002	Significant
	X_2	4640	1	4640	110	< 0.0001	Significant
	X_4	4253	2	2126	50.5	< 0.0001	Significant
	X_1X_2	1761	1	1761	41.8	< 0.0001	Significant
	X_2X_3	306.8	1	306.8	7.28	0.0101	Significant
	X_1^2	381.3	1	381.3	9.05	0.0045	Significant
	X_2^2	1685	1	1685	40.0	< 0.0001	Significant
	X_3^2	410.8	1	410.8	9.75	0.0033	Significant

Table 3.6 **Solutions suggested by the Box Behnken methodology for the optimization of the leaching conditions for metals solubilization from a mixture of spent batteries**

No.	$[H_2SO_4]$ (M)	S/L ratio (%, w/v)	Retention time (h)	Nb of leaching steps	Predicted metal removal yields (%)					Metal revenues ($/t)	Reagent costs (CRC) ($/t)	Desirability
					Cd	Co	Mn	Ni	Zn			
1	1.0	18.0	0.5	3.0	99.9	74.4	64.8	67.7	106	1351	33.6	0.9
2	1.0	17.2	0.5	3.0	99.8	71.9	66.2	65.3	103	1338	-33.1	0.9
3	1.0	18.0	0.5	2.0	94.7	67.2	58.3	64.9	97.5	1256	424	0.8
4	1.0	17.9	0.5	2.0	94.8	66.9	58.5	64.6	97.0	1253	406	0.8
5	1.0	18.0	0.5	2.0	94.3	67.0	58.2	64.6	96.9	1248	424	0.8

4 CHAPITRE 3

MODELING AND OPTIMIZATION OF METALS LEACHING FROM UNSORTED SPENT BATTERIES USING RESPONSE SURFACE METHODOLOGY

Revue : Environmental Technology

Auteurs : Kulchaya Tanong[a], Lucie Coudert[b], Chartier Myriam[c], Guy Mercier[d], Jean-Francois Blais[e*]

[a] Ph.D. student, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-4677, Fax: (418) 654-2600, email: kulchaya.tanong@ete.inrs.ca

[b] Research Associate, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-3793, Fax: (418) 654-2600, email: lucie.coudert@ete.inrs.ca

[c] Research Associate, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-3793, Fax: (418) 654-2600, email: lucie.coudert@ete.inrs.ca

[d] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-2633, Fax: (418) 654-2600, email: guy.mercier@ete.inrs.ca

[e] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-2575, Fax: (418) 654-2600, email: jean-francois.blais@ete.inrs.ca

*Corresponding author:
Tel: (418) 654-2575, Fax: (418) 654-2600
email: jean-francois.blais@ete.inrs.ca

Note

L’étudiante est le premier auteur de cet article. Toutes les manipulations, le traitement des données ainsi que la rédaction ont été effectués par l’étudiante sous la supervision des autres co-auteurs.

Modifications exigées par le comité de lecture de la revue

Les commentaires des réviseurs ont été reçus. Les principales modifications concernant des éclaircissements en ce qui concerne la méthodogie Box Behnken et l’exploitation des résultats issus de l’ANOVA.

4.1 Résumé

Cet article présente un procédé innovant développé pour récupérer les métaux contenus dans un mélange de déchets de piles et de batteries usagées. Différents types de piles/batteries ont été utilisés: alcaline, zinc-carbone (Zn-C), nickel-cadmium (Ni-Cd), hydrure métallique de nickel (Ni-MH), lithium-ion (Li-ion) et lithium métallique (Li-M). Le mélange de déchets de piles et de batteries a été préparé en fonction des proportions de ventes de piles estimée au Canada en 2007. Un plan d'expérience de type Box Behnken a été appliqué pour déterminer les conditions optimales de lixiviation permettant une lixiviation maximale des métaux recherchés à partir d'une solution d'acide sulfurique (H_2SO_4) et d'un agent réducteur métabisulfite de sodium ($Na_2S_2O_5$). Les résultats ont mis en évidence l'effet positif du $Na_2S_2O_5$ sur la lixiviation des métaux, en particulier pour Mn. Le rapport S/L et la concentration en H_2SO_4 sont les principaux facteurs qui influencent la lixiviation des métaux (Zn, Mn, Cd, Ni) présents dans les piles usagées. Les conditions optimales de lixiviation sont les suivantes: une étape de lixiviation, un rapport S/L = 10,9% (p/v), $[H_2SO_4]$ = 1,34 M, quantité de métabisulfite de sodium ($Na_2S_2O_5$) = 0,45 g/g de poudre de piles et batteries et un temps de rétention = 45 min. Dans ces conditions, les rendements d'élimination atteints sont de 94% pour le Mn, 81% pour le Cd, 99% pour le Zn, 96% pour le Co et 68% pour le Ni.

Mots-clés: Mélange des piles usagées, Design Box Behnken, Agent réducteur, Acide sulfurique, Lixiviation

4.2 Abstract

This paper presents an innovative process for the recovery of the valuable metals from a mixture of spent batteries. Different types of batteries, including alkaline, zinc-carbon (Zn-C), nickel cadmium (Ni-Cd), nickel metal hydride (Ni-MH), lithium ion (Li-ion) and lithium metallic (Li-M) batteries, were mixed according to the proportion of the Canadian sales of batteries predicted for 2007. A Box-Behnken design was applied to find the optimum leaching conditions allowing a maximum of valuable metal removals from a mixture of spent batteries in the presence of an inorganic acid and a reducing agent. The results highlighted the positive effect of sodium metabisulfite on the performance of metals removal, especially for Mn. The solid/liquid ratio and the concentration of H_2SO_4 were the main factors affecting the leaching behavior of valuable metals (Zn, Mn, Cd, Ni) present in spent batteries. Finally, the optimum leaching conditions were found as follows: one leaching step, solid/liquid ratio = 10.9%, $[H_2SO_4]$ = 1.34 M, sodium metabisulfite ($Na_2S_2O_5$) = 0.45 g/g of battery powder and retention time = 45 min. Under such conditions, the removal yields achieved 94% for Mn, 81% for Cd, 99% for Zn, 96% for Co and 68% for Ni.

Keywords: Box-Behnken design, Reducing agent, Sulfuric acid, Leaching, Spent batteries.

4.3 Introduction

Over the last decades, the amount of spent batteries discharged to the environment has significantly increased because of their extensive uses in electronic applications, and a large quantity of batteries was disposed in the landfill sites [1]. This disposal option is not an environmental friendly method due to the limited volume of existing landfill sites that are reaching their capacity and to the risks of contamination and the increasingly fees [1-2]. Until now, only a small number of regulations related to the collection and/or the discharge of spent batteries to the landfill sites were in effect in Canada. For the above reasons, the sustainability and stewardship program adopted the Call2Recycle project to restrict the disposal of batteries to the environment and to encourage the reuse of the valuable metals present in spent batteries as a primary source. Spent batteries are not considered hazardous materials even if they contain large amounts of toxic metals. The main metals found in spent batteries are Zn and Mn, mainly found in alkaline and zinc-carbon batteries [3]; Ni and Cd, mainly found in Ni-Cd and Ni-MH batteries [4-5]; and Li, Co and Cu, mainly found in Li-ion and Li primary batteries [6-7]. The presence of toxic metals in spent batteries poses environmental concerns related to their potential risks of dispersion in the environment and their toxic effects on humans and fauna. Indeed, the exposure to high amounts of Ni either by ingestion or skin contact may cause dermatitis, chronic asthma, cardiovascular troubles, lung cancer, etc. [8]. According to several studies, Cd is highly toxic to humans even at low concentrations [9]. Exposure to cobalt at high concentrations may induce erythropoiesis to humans [10]. The toxicity of lithium to humans and to fauna were studied by Aral and Vecchio-Sadus [11]. The results showed that lithium was not considered bioaccumulative and that its toxicity to humans is very low. According to several studies, Zn and Mn are nutrients necessary for living microorganisms; however, they become toxic at certain concentrations [12-13].

Many technologies based on physical, hydrometallurgical and/or pyrometallurgical methods have been proposed to recover the valuable metals from spent batteries [4, 14-15]. Pyrometallurgical processes are one of the most effective processes used to manage and destroy spent batteries. Melin and Svensson [16] developed a process to recover nickel (Ni) and cadmium (Cd) from Ni-Cd batteries using a pyrometallurgical process. A similar process was performed by Delisle *et al.* [17]. In the latter process, Ni-Cd battery powder was fed into a furnace at high temperatures (500 °C – 800 °C and 900 °C – 1000 °C). This process allowed the recovery of 99% of Cd initially present in Ni-Cd battery powder. However, there are some drawbacks related to this management option, including 1) high-energy consumption during operation, 2) emission of toxic gas (CO_2, SO_2 etc.), 3) the need for highly qualified labor and 4) expensive investment costs. For those reasons, the application of pyrometallurgical processes is not suitable in some countries [1, 18]. However, these processes could be used to treat high-grade metals, especially gold and cadmium, because of their high value, while the hydrometallurgical processes, which are relatively easier to operate and less expensive [18], could be applied to recover the low-grade metals such as Zn and Mn from spent batteries.

The application of the hydrometallurgical processes to treat the mixture of spent batteries have been studied by several authors [4, 19-23]. Usually, sulfuric acid (H_2SO_4) was used in these hydrometallurgical processes due to its low cost. Provazi *et al*. [19] have developed a process used for the recovery of the valuable metals from spent batteries. The battery powder is mixed with sulfuric acid (1 M) at room temperature for 24 h. According to these authors, approximately 99% of Ti and Zn, 85% of Ni, 80% of Cd and 90% of Ce were recovered from the leachate at different pH values by Cyanex272. The treatment of mixed batteries was also studied by Frohlich and Sewing [20]. A diluted solution of H_2SO_4 was used as leaching agent, as in the previous study. In the purification step, an ion-exchange resin was applied to remove the mercury and to selectively recover Cd, Cu and Ni from the leachate. Zinc was extracted by solvent extraction using several steps. The study conducted by Buzatu *et al*. [22] concluded that a solution of H_2SO_4 (2 M) allowed the solubilization of 96% of the Zn and 43% of the Mn from the spent alkaline batteries at 60 °C. Other studies were also conducted in the presence of H_2SO_4 as a leaching agent for the recovery of metals from Ni-MH, Ni-Cd and Li-ion batteries [4, 23].

To improve the performances of metal leaching from spent batteries, oxidizing or reducing agents are widely used in hydrometallurgical processes. Among oxidizing agents, H_2O_2 and Fe (III) (due to their strong oxidizing potentials of 1.78 V and 0.77 V, respectively), combined with sulfuric or hydrochloric acids, have been extensively studied to increase the leaching rate of valuable metals from spent batteries [18, 24]. Li *et al*. [21] also studied the leaching performances of the metals contained in alkaline batteries using hydrochloric acid (1-2 M). They found that the leaching rate increased with the acid concentration combined with the use of hydrogen peroxide. Reducing agents such as oxalic acid, glucose, sodium metabisulfite and sulfur dioxide were also examined to improve the dissolution of Mn (IV) from alkaline and/or Zn-C spent batteries [1-2]. Several hydrometallurgical processes have been developed over the last decades to recover valuable metals from spent batteries. However, to the best of our knowledge, none of the hydrometallurgical processes developed at the laboratory or industrial scale are able to recover metals from a mixture of spent batteries comprising of alkaline, Zn-C, Ni-MH, Ni-Cd, Li-ion and Li-M batteries, without sorting of the spent batteries according to their physical and chemical properties.

In the present study, a Box-Behnken methodology was used to determine the influence of operating parameters and to find the optimum conditions for the leaching of valuable metals (Cd, Mn, Ni and Zn) from a mixture of spent batteries in the presence of sulfuric acid and sodium metabisulfite, which was added as a reducing agent. Two series of experiments were performed, and the main factors studied were the solid/liquid ratio, the concentration of sulfuric acid, the concentration of metabisulfite, the concentration of sodium chloride (NaCl), the retention time and the number of leaching steps.

4.4 Materials and methods

4.4.1 Sample characterization

The spent batteries, including alkaline, Zn-C, Li-ion, Li-M, Ni-Cd and Ni-MH batteries, were manually dismantled to remove the plastic and steel case components. Special care was taken to avoid the potential explosion of Li-ion, Li-M and Ni-MH batteries when exposed to oxygen, by freezing these spent batteries using liquid nitrogen. Li-ion, Ni-MH, Ni-Cd and Li-M batteries were uncurled, and a pair of scissors was used to cut the foil encasing them into small pieces. After obtaining the battery powder and the small pieces of paper foil, batteries of all types were mixed according to the following proportions: 68.0% alkaline battery, 15.0% Zn-C, 14.3% Ni-Cd, 1.60% Ni-MH, 0.80% lithium iron sulfide and 0.28% Li-ion. These proportions of spent batteries were established according to the amounts of these batteries that were estimated to be sold in Canada [7].

Non-metallic parts were then removed by screening using a 1 mm- and 2 mm- aperture sieves. The powder was then crushed using a mortar and pestle and ground using a FRITSCH pulverisette (Serial no. 06 2000/01908, Germany). To determine the metallic composition of the mixture of spent batteries, strong oxidizing agents such as perchloric acid ($HClO_4$) and hydrofluoric acid (HF) combined with HNO_3 were used during the digestion process [25]. The retention time of the digestion was prolonged to approximately two to three days. Then, the metals were analyzed by inductively coupled plasma - atomic emission spectroscopy (ICP-AES).

4.4.2 Leaching procedure

In the first series of experiments, desired amounts of battery powder, NaCl and $Na_2S_2O_5$ were transferred in a 500 mL Erlenmeyer. A solution of H_2SO_4 (with a desired normality) was then added into the Erlenmeyer. The battery powder and the leaching solution were then mixed at 250 rpm using an orbital shaker (Barnstead Lab-line, Maxq 4000). The operating parameters (solid/liquid ratio, temperature, acid concentration, amounts of battery powder, amounts of chemicals (NaCl, NaS_2O_5 and H_2SO_4) added) used for the different experiments are described in the section *Experimental Design*. After the leaching step(s), the samples were filter using G6 filters (pore size = 1.5 µm) and preserved onto 5% HNO_3. All tests were carried out at ambient temperature.

4.4.3 Student's t-test

A student's t-test was applied to determine whether the two sets of data were significantly different. This statistical test was used in the present study to identify whether the addition of a reducing agent had a significant influence on the solubilization of valuable metals, especially Mn, from spent batteries. The leaching conditions for these two sets of experiments were as follows: three leaching steps, [H_2SO_4] = 1 M, pulp density = 18% (w/v), T = 20 °C. The sodium metabisulfite was not added during the first series of experiments, which were performed in triplicate, whereas 0.45 g of sodium metabisulfite was added per gram of battery powder during the second series of experiments (n = 3). The variance and the t-value, used for the t-test, were calculated as follows [26].

$$\frac{\overline{y_a}-\overline{y_b}}{S_p\sqrt{\frac{1}{n_a}+\frac{1}{n_b}}} \sim t(n_A+n_B-2)$$

Equation 4.1

$$S_p^2=\frac{\sum_{i=1}^{n_A}(Y_{a,z}-\bar{Y}_a)^2+\sum_{i=1}^{n_B}(Y_{b,z}-\bar{Y}_b)^2}{n_A+n_B-2}$$

Equation 4.2

where

t: student value calculation.

$\bar{y}_i$: *average value of solubilization rate of each metal from three repetitions.*

$Y_{i,z}$: *solubilization rate of each metal in each series.*

n_i: *repetition number of the experimental series (n=3).*

4.4.4 Experimental design

Response surface design is commonly used to model and to analyze engineering problems. This methodology is useful to determine the relationship between several operating factors and the desired response and to find the optimum conditions [27].

Box-Behnken design (BBD) is an independent quadratic design belonging to the family of response surface designs. BBD is a class of rotatable second-order designs based on a three-level incomplete factorial design [28]. In this design, three levels of each factor are defined and coded as low level (-1), middle level (0) and high level (+1) [27]. Among the response surface designs, BBD is slightly more efficient compared to the central composite design and is much more efficient than the three-level full factorial design [28]. Furthermore, the extreme conditions, in which unsatisfactory results can occur, are avoided in BBD [28].

In this research, the application of BBD was conducted by studying the effect of different parameters on the solubilization of metals. Two series of experiments were conducted to improve the solubilization of metals, especially the dissolution of Mn. The selected operating parameters studied during these series of experiments were the solid/liquid ratio, the concentration of H_2SO_4, the amount of reducing agent added, the quantity of NaCl added, the retention time and the number of leaching steps. For the first series of experiments, the minimum, middle and maximum values of each factor were determined as follows:

- Mass of sodium metabisulfite ($Na_2S_2O_5$) added (g/g of battery powder) = 0.00 (low level), 0.48 (middle level) and 0.95 (high level) .
- Acid concentration (M) = 1.00 (low level), 2.00 (middle level) and 3.00 (high level),

- Mass of NaCl added (g/g of battery powder) = 0.00 (low level), 8.78 (middle level) and 17.6 (high level),
- Number of leaching steps = 1 (low level), 2 (middle level) and 3 (high level).

In the present study, $Na_2S_2O_5$ has been chosen as a reducing agent due to its relatively low cost (112 $/t [29]) compared to other reducing agents such as $FeCl_2$ (2,500 $/t [29]) and its ease of operation at laboratory scale compared to SO_2 gas. The mass of $Na_2S_2O_5$ required to solubilize all the Mn present in battery powder was obtained from the stoichiometric reaction of Mn reduction and estimated at 0.48 g $Na_2S_2O_5$/g of battery powder. Therefore, the middle level (0) of the BBD design was fixed at the stoichiometric value estimated to reduce all the Mn initially present in the battery powder. The minimum level (-1) was fixed at 0 g/g of battery powder, meaning that no $Na_2S_2O_5$ was added to determine if the addition of this reducing agent is required and to evaluate its influence on the solubilization of the other metals. The maximum level (+1) was defined as twice the stoichiometric amount of $Na_2S_2O_5$. The low level (-1) of H_2SO_4 concentration was fixed at 1 M, based on the previous experiments where 1 M H_2SO_4, 18% S/L ratio, 30 minutes leaching time at 25 °C were determined as optimum conditions for the solubilization of approximately 86% of Cd, 70% of Co, 30% of Mn, 70% of Ni and 100% of Zn from the mixture of battery powder [30]. From these results, it could be noticed that some metals were still present in the residue, so higher acid concentrations might be useful to improve the solubilization of metals. From the previous reason the concentration of H_2SO_4 was fixed at 1 M, 2 M and 3 M to represent the minimum level (-1), the middle level (0) and the maximum level (+1), respectively. Various amounts of NaCl were added in the leaching solution to improve the dissolution of metals by favoring the formation of chloride complex. A value of 8.78 g/g of battery powder (amount of NaCl roughly needed to complex all the metals initially present in battery powder) was assigned as the middle level (0). The minimum level (-1) was fixed at 0 g/g, meaning that no addition of NaCl was performed to determine if the addition of this chemical is required. The maximum level (+1) was fixed as twice the stoichiometric value defined earlier. The numbers of leaching steps were determined as single leaching step (minimum level) to minimize the consumption of chemicals, as two leaching steps (middle level) and as three leaching steps (maximum level). For this first series of experiments, the solid/liquid ratio and the retention time were fixed at 10% and 30 min, respectively.

For the second series of experiments, the parameters were determined as follows:

- Solid/liquid ratio (% - w/v) = 10% (low level), 15% (middle level) and 20% (high level),
- Concentration of H_2SO_4 (M) = 0.5 (low level), 1.0 (middle level) and 1.5 (high level),
- Mass of $Na_2S_2O_5$ added (g $Na_2S_2O_5$/g of battery powder) = 0.45 (-1), 0.60 (0) and 0.75 (+1),
- Retention time (min) = 15 (-1), 30 (0) and 45 (+1).

The minimum, middle and maximum values of solid/liquid ratio were defined based on the results obtained in the previous experiments [30] where the solid/liquid ratio obtained from the optimum conditions was determined at 18% (w/v). However, when using a solid/liquid ratio of 18%, some metals were still present in the residue after the leaching step. Consequently, the decrease in solid/liquid ratio was necessary. From the previous reason, values of 10%, 15% and 20% (w/v) were assigned to represent the low level (-1), middle level

(0) and high level (+1), respectively. The acid concentration was determined based on the results from the first series of experiments of the present study. In this series of experiments, the concentration of acid was decreased, due to the high costs of neutralizing agent required in the purification steps following the solubilization of metals. The values of $Na_2S_2O_5$ added were determined based on the results of the previous series of experiments. Indeed, the first series of experiments showed the significant effect of $Na_2S_2O_5$ on the solubilization of metals (Cd, Co, Mn and Ni) on the experimental domain. From the previous reason, a value of 0.45 g of $Na_2S_2O_5$/g of battery powder (stoichiometric value) was assigned at the low level (-1), a value of 1.3 times the stoichiometric value was assigned as the middle level (0) and a value of 1.7 times the stoichiometric value was assigned at the high level (+1). The levels of the retention time were fixed based on the previous experiments [30] which showed that the solubilization of the metals was quite rapid and can be done in less than an hour.

For our two series of experiments, the number of experiments determined using the software Expert Design 8.0 was equal to 29, and the number of the central points was equal to 5. After each series of experiments, the removal yields obtained for Cd, Co, Mn, Ni and Zn were determined by measuring the concentration of metals present in the leaching solution using ICP-AES [30]. The results were studied and interpreted by the software to obtain the relationship between the responses and the variables (operating parameters). The polynomial equation modelling the desired response as a function of the operating parameters studied can be written as follow:

$y = \beta_0 + \sum_i^n \beta_i X_i + \sum_i^n \beta_{ii} X_i^2 + \sum_{i<j} \beta_{ij} X_i X_j$ Equation 4.3 [31]

where

y: predicted response.

β_0*: model constant.*

X_i *and* X_j*: symbol for independent variables.*

$\beta_{i,}\beta_j$ *and* β_{ij}*: linear, quadratic and cross-product coefficients, respectively.*

4.5 Results and discussion

4.5.1 Metal composition

The concentrations of the metals measured in the mixture of spent batteries are presented in Table 4.1. The price of these valuable metals in the market [32] and their values in spent batteries are also included. The main metals present in the spent batteries were Mn (42% of the metallic composition), Zn (34%), Ni (10%), Cd (4.3%) and Fe (3.6%). Only 0.1% of Li, 0.1% of Cu and 0.6% of Co were found because of the small amounts of Li-ion and Li-M batteries commercialized in the market and therefore found in the spent batteries stream [7]. Rare earths elements such as lanthanum, cerium and neodymium were also found in Ni-MH batteries; however, the proportion of Ni-MH in the market is small compared to the other types of batteries. For the above reasons, we focused our study on the recovery of the major metals present in spent batteries such as Mn, Zn, Ni and Cd, as their values represented US$ 2510 per ton metric of spent battery powder.

4.5.2 Influence of the addition of a reducing agent on the metal solubilization

Experiments have been performed with the optimum conditions defined in a previous study with and without the addition of a reducing agent (three leaching steps, $[H_2SO_4]$ = 1 M, solid/liquid ratio = 18% (w/v), retention time = 30 min and temperature = 20 °C). The average removal yields obtained without any reducing agent were estimated at 86% for Cd, 70% for Co, 30% for Mn, 70% for Ni and 100% for Zn [30]. For the experiments performed in the presence of sodium metabisulfite, more than 75%, 81%, 76%, 66% and 104% of Cd, Co, Mn, Ni and Zn were removed from spent batteries, respectively. Student's t-test was applied to determine whether the addition of the reducing agent significantly improved the solubilization of metals from spent batteries. The variances and the t-values were calculated for each metal using Equations 4.1 and 4.2. A t-value higher than 2.776 (degrees of freedom = 4, confidence level = 95%) indicated that the mean values of each of the series of experiments were significantly different and that the addition of a reducing agent had a significant impact on the solubilization of the considered metal from spent batteries. After three leaching steps, the t-values obtained were equal to 11 for Cd, 0.8 for Co, 20 for Mn, 4.3 for Ni and 4.3 for Zn. According to these values, the addition of sodium metabisulfite was shown to have a significant influence on the solubilization of Cd, Mn, Ni and Zn from spent batteries (t value > 2.776). Moreover, it appeared that the addition of $Na_2S_2O_5$ significantly improved the dissolution of Mn whereas its effect was slightly negative on the solubilization of Cd, Ni and Zn. The positive influence of $Na_2S_2O_5$ addition on the dissolution of Mn from spent batteries could be due to the reduction of MnO_2

to MnO. The dissolution processes of Mn_2O_3 and Mn_2O_4 present in the battery powder in the presence of sulfuric acid are described in Equations 4.4 and 4.5 [1].

$$Mn_2O_3(\mathrm{s}) + H_2SO_4(\mathrm{aq}) \rightarrow MnSO_4\,(aq) + MnO_2(s) + H_2O \qquad \text{Equation 4.4}$$

$$Mn_3O_4(\mathrm{s}) + 2H_2SO_4(\mathrm{aq}) \rightarrow 2MnSO_4\,(aq) + MnO_2(s) + 2H_2O \qquad \text{Equation 4.5}$$

According to these equations, the dissolution of Mn_2O_3 and Mn_2O_4 leads to the formation of MnO_2, which is insoluble in acidic solutions. Therefore, the addition of a reducing agent is required to reduce MnO_2, which is insoluble, to MnO, which is more soluble due to the possible formation of a soluble complex of manganese sulfate in sulfuric acid media. The amount of reducing agent added was calculated based on the stoichiometry of the reaction described in Equation 4.6 [33].

$$Na_2S_2O_5 + H_2SO_4 + 2MnO_2 \rightarrow SO_4^{2-} + 2MnSO_4 + 2Na^+ + H_2O \qquad \text{Equation 4.6}$$

4.5.3 Optimization of leaching conditions using the Box-Behnken methodology

Two series of experiments were conducted using the BBD methodology to study the influence of operating parameters on the solubilization of metals, especially Mn, from a mixture of spent batteries and to determine the optimal leaching conditions.

4.5.4 Influence of the concentration of H_2SO_4, NaCl and $Na_2S_2O_5$ and the number leaching steps on metal solubilization

In this experiment, the influence of various parameters including the concentration of $Na_2S_2O_5$ (X_1), the concentration of H_2SO_4 (X_2), the concentration of NaCl (X_3) and the number of the leaching steps (X_4) were investigated. Table 4.2 presents the operating factors that have a significant effect on metal solubilization from spent batteries based on the analysis of variance (ANOVA). According to these results, the addition of a reducing agent (X_1) significantly improved the solubilization of all of the metals (except Zn) from spent batteries, whereas the effect of NaCl (X_3) was insignificant for almost all of the valuable metals studied. Moreover, the significant effect of NaCl observed for the solubilization of Cd and Zn was negative, indicating that the addition of NaCl significantly decreased the performance of the leaching process for these metals. Therefore, this parameter was not considered in the next series of experiments.

Figure 4.1 presents the effect of the concentration of H_2SO_4 and $Na_2S_2O_5$ on the solubilization of valuable metals from spent batteries. These results revealed that an increase of $Na_2S_2O_5$ concentration from 0 to 0.95 g/g of battery powder had a positive effect on the removal yields of Co, Mn and Zn, especially for Mn, when the solid/liquid ratio was fixed at 10%. Similar results were obtained in other studies conducted with a low solid/liquid ratio (< 10%), indicating that the addition of a reducing agent ($NaHSO_3$, oxalic acid or glucose) significantly improved the performances of metals leaching [35-37]. According to Meshram *et al.* [35], the use of $NaHSO_3$ allowed the removal of 49.1-77.1% of the Co and 48.5-85.5% of the Mn from Li-ion batteries. Their experimental results also revealed the positive effect of the H_2SO_4 concentration on the performances of metal removal, which was similar to our results. Indeed, an increase of H_2SO_4 concentration (X_2) from 1.0 to 3.0 M led to an increase of the metal removal yields as revealed in Figure 4.1 [35, 38]. The interaction (X_1X_2) of these factors was also significant, indicating that the concentration of both H_2SO_4 (X_2) and $Na_2S_2O_5$ (X_1) had an important effect on the solubilization of metals from spent batteries.

4.5.5 Influence of the solid/liquid ratio (S/L), the concentration of H_2SO_4 and $Na_2S_2O_5$ and the retention time on metal solubilization

A second series of experiments was performed using BBD to determine the effect of H_2SO_4 and $Na_2S_2O_5$ in the absence of NaCl. The influence of various parameters including the solid/liquid ratio (X'_1), the concentrations of H_2SO_4 (X'_2) and $Na_2S_2O_5$ (X'_3) and the retention time (X'_4) and their interactions were investigated. The removal yields obtained during this second series of experiments were in the range of 2 to 96% for Cd, 2-85% for Co, 10-97% for Mn, 2-71% for Ni and 12-99% for Zn.

Table 4.3 presents the correlation coefficients (R^2, adjusted R^2 and predicted R^2) and adequate precision obtained from the ANOVA. According to these results, R^2 values were in the range of 0.88 to 0.96 for all of the metals, indicating that 88-96% of the variations observed for metal removal yields were attributed to the independent variables and that approximately 4-12% of the variations cannot be explained by the mathematical models [39]. These observations are in accordance with the comparison of all predicted values and actual values, presented in Figure 4.2, which shows a good correlation.

The low coefficient of variation (CV) obtained meant that the experiments were accurate and reliable [41]. Generally, the CV values should not exceed 10%. The lowest CV value was obtained for Mn extraction, and the highest value was obtained for Ni extraction (Table 4.3). It can be concluded that the most reliable model was obtained for the solubilization of Mn. High CV values indicated an inadequate mathematical model, resulting from the high variation of the mean value from the replicates [41]. Although the CV values obtained for Cd, Co, Ni and Zn were high, we still consider that all of the mathematical models were significant because their adequate precision values were higher than 4 and their lack of fit were non-significant. An adequate precision value greater than 4 means that the models are favorable [39].

The results of the ANOVA consisting of p-value, sum of squares, mean square, *F*-value and degrees of freedom (df) are presented in Table 4.4. The *p*-values obtained were lower than 0.05 for all of the mathematical models, indicating that they were all significant [39]. According to these results, it appeared that an increase of the concentration of $Na_2S_2O_5$ from 0.45 to 0.75 g/g did not have a significant effect on the solubilization of metals. This could be because the addition of the stoichiometric quantity of $Na_2S_2O_5$ was sufficient to reduce all of the MnO_2 present in our sample to MnO. Therefore, the use of a quantity of $Na_2S_2O_5$ higher than the 0.45 g/g was not required to improve the solubilization of manganese. The retention time (X'_4) did not have a significant effect on metal solubilization, which could be due to the high dissolution rate of metals within the first minutes of each experiment. These results highlighted that only two operating factors; the S/L ratio (X'_1) and the concentration of H_2SO_4 (X'_2) had a positive and significant effects on the solubilization of valuable metals from spent batteries. The influence of the H_2SO_4 concentration on metal solubilization seemed to be important, as presented in Figure 4.3. Indeed, the solubilization of valuable metals was significantly improved with the increase of the acid concentration and the decrease of the solid/liquid ratio. The increase of the solid/liquid ratio led to an increase of the amount of valuable metals that should be removed from spent batteries, leading to a significant decrease of metal solubilization performances [31, 42]. Furthermore, the agitation became less efficient as the S/L ratio increased, reducing the contact between the metals to be solubilized and the leaching agent [34].

The removal yields of Cd, Co, Mn Ni and Zn can be calculated by using Equations 4.7 to 4.11 defined, in terms of the factor coded, by the software Expert Design 8.0. According to these results, the relationship between the response and the variables followed a linear expression for the removal of Cd and Co and a quadratic expression for the removal of Mn, Ni and Zn.

$Cd\ removal\ yield\ (\%) = 36.9 – 25.4\ X'_1 + 33.7\ X'_2 – 5.27\ X'_3 – 0.40\ X'_4$ Equation 4.7

$Co\ removal\ yield\ (\%) = 37.7 – 21.1\ X'_1 + 30.0\ X'_2 – 2.05\ X'_3 + 0.83\ X'_4$ Equation 4.8

$Mn\ removal\ yield\ (\%) = 68.2 – 15.7\ X'_1 + 24.1\ X'_2 – 0.47\ X'_3 – 0.50\ X'_4 – 0.56\ X'_1X'_3 – 0.04\ X'_1X'_4 – 0.76\ X'_2X'_3 – 1.02\ X'_2X'_4 – 2.19\ X'_3X'_4 – 1.08\ X'^2_1 – 10.3\ X'^2_2$ Equation 4.9

$Ni\ removal\ yield\ (\%) = 13.9 – 22.3\ X'_1 + 28.3\ X'_2 – 3.55\ X'_3 + 2.21\ X'_4 – 4.38\ X'_1X'_4 – 6.06\ X'_2X'_3 + 12.3\ X'^2_1 + 10.2\ X'^2_2 + 5.15\ X'^2_3 + 6.18\ X'^2_4$ Equation 4.10

$Zn\ removal\ yield\ (\%)$ = 57.4 – 18.8 X'_1 + 29.8 X'_2 – 4.05 X'_3 – 0.90 X'_4 – 3.49 $X'_1X'_3$ + 1.70 $X'_2X'_3$ – 0.46 $X'_2X'_4$ – 2.38 $X'_3X'_4$ – 8.47 X'^2_2 Equation 4.11

The software Expert Design 8.0 was used to determine the optimal operating conditions taking into account the performances of metal solubilization, the costs of chemical reagents and the potential revenues related to the sales of the metals solubilized defined as described by Tanong *et al.* [43]. Several criteria were imposed for the determination of the optimum leaching conditions: 1) maximized Cd, Co, Mn, Ni and Zn removal yields; 2) maximized revenues (metal price); and 3) minimized costs related to the consumption of chemical products (product price).

The optimum conditions were obtained as follows: one leaching step, solid/liquid ratio = 10.9%, [H_2SO_4] = 1.34 M, 0.45 g $Na_2S_2O_5$ per g of battery powder and retention time = 45 min. From the mathematical models, metals removal yields were estimated at 86% for Cd, 78% for Co, 94% for Mn, 89% for Ni and 90% for Zn under these optimum operating conditions.

Three repetitions were conducted to confirm the optimum conditions and the results are shown in Table 4.5. With these conditions, up to 81% of the Cd, 96% of the Co, 94% of the Mn, 68% of the Ni and 99% of the Zn were removed from spent batteries. The removal yields obtained for Co and Zn were slightly higher than the predicted values, whereas the percentages of Cd and Ni solubilized were lower than the predicted values. The solubilization of manganese was close to the predicted value. The low under- or over-estimation of the different mathematical models established for Cd, Co, Ni and Zn could be due to the lower precision observed for the Cd and Ni models (low R^2 values of 0.89 and 0.88, respectively, and the high

CV values) compared to Mn. The high R^2 values obtained for the model established for Mn showed a high precision of the model. Nevertheless, despite the low variations observed between experimental and predicted values, the optimal leaching conditions identified by the software were validated and will be used in the next purification step.

4.6 Conclusion

A three level Box-Behnken design was shown to be a suitable tool to identify the operating parameters influencing a process and to optimize metal extraction from a mixture of spent batteries. The results revealed that the presence of a reducing agent (sodium metabisulfite), the solid/liquid ratio and the concentration of sulfuric acid were significant parameters affecting the solubilization of valuable metals (Cd, Co, Mn, Ni and Zn) from spent batteries. Indeed, $Na_2S_2O_5$ was proven to be effective in extracting Mn from spent batteries by presumably reducing MnO_2 to MnO. However, the increase of the $Na_2S_2O_5$ concentration beyond the stoichiometric value did not have a significant effect on the solubilization of metals from spent batteries. The best conditions were indentified to be a 45 min-leaching step performed in the presence of sulfuric acid (1.34 M) and $Na_2S_2O_5$ (0.45 g/g) with a solid/liquid ratio fixed at 10.9% (w/v). Under these optimized conditions, more than 81% of the Cd, 96% of the Co, 94% of the Mn, 68% of the Ni and 99% of the Zn were solubilized from spent batteries. From the results obtained in the present study, it appeared that the leaching process developed and optimized represents a promising first step toward the establishment of a pilot scale plant. Indeed, the high metal removal yields obtained for Cd, Co, Mn, Ni and Zn promotes the development and the study of the leaching process at a larger scale to valid the process performances and to evaluate the influence of the variation of the mixture battery powder on the recoveries of valuable metals. However, the presence of various metals in the leach solution will lead to more complex purification processes to allow the selective and efficient recoveries of valuable metals present in the leach solution. However, the use of solvent extraction (green solvent, commercial organic solvent) offers an interesting and simple solution to selectively recover metals from the leach solution, allowing their recoveries even if they are initially present in small amounts. Solvent extraction processes are currently used in the mining industries to selectively recover rare earth elements (light rare earth elements from heavy rare earth elements) from leach solutions. The simplicity of solvent extraction and their efficiency to selectively recover the individual metal (even in the small concentration because of the selective extraction depend strongly on the pH value) present from complex solutions reduced the complexity of the purification, separation and recovery operations. Additional works have been done by our research team to selectively recover the metals from the leach solution using a combination of solvent extraction, selective electrodeposition and precipitation. The results will be published or submitted to publication soon.

4.7 References

[1] Sayilgan E, Kukrer T, Civelekoglu G, Ferella F, Akcil A, Veglio F, Kitis M. A review of technologies for the recovery of metals from spent alkaline and zinc–carbon batteries. Hydromet. 2009;97:158-166.

[2] Muller T, Friedrich B. Development of a recycling process for nickel-metal hydride batteries. J. Power Sources. 2006;158:1498-1509.

[3] Almeida MF, Xara SM, Delgado J, Costa CA. Characterization of spent AA household alkaline batteries. Waste Manag. 2006;26:466-476.

[4] Mantuano DP, Dorella G, Elias RCA, Mansur MB. Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid-liquid extraction with Cyanex 272. J. Power Sources. 2006;159:1510-1518.

[5] Nogueira CA, Delmas F. New flowsheet for the recovery of cadmium, cobalt and nickel from spent Ni-Cd batteries by solvent extraction. Hydromet. 1999;52:267-287.

[6] Li J, Shi P, Wang Z, Chen Y, Chang CC. A combined recovery process of metals in spent lithium-ion batteries. Chemosphere. 2009;77:1132-1136.

[7] RIS international Ltd., Canadian Consumer Battery Baseline Study, Retrieved from: http://www.docstoc.com/docs/79783916/Canadian-Consumer-Battery-Baseline-Study-Final-Report, 2007, Consulted on February 2015.

[8] Denkhaus E, Salnikow K. Nickel essentiality, toxicity, and carcinogenicity. Crit. Rev. Oncol. Hemat. 2002;42:35-56.

[9] Fowler BA. Review monitoring of human populations for early markers of cadmium toxicity. Toxicol. Appl. Pharmacol. 2009;238:294–300.

[10] Tolan NV, Sierra RJ, Moyer TP. Evidence against implant-derived cobalt toxicity: Case report and retrospective study of serum cobalt concentrations in an orthopedic implant population. Clin. Biochem. 2015;48:130–134**.**

[11] Aral H, Sadus AV. Toxicity of lithium to humans and the environment—A literature review. Ecotoxicol. Environ. Safety. 2008;70:349-356.

[12] WHO. Chapter 6.8 Manganese. World Health Organization, Technical report, 2001, 13 p.

[13] Nriagu J. Zinc toxicity in humans. School of Public Health, University of Michigan, USA, 2007, 7 p.

[14] Huang K, Li J, Xu Z. A novel process for recovering valuable metals from waste nickel-cadmium batteries. Environ. Sci. Technol. 2009;43:8974-8978.

[15] Cheret D, Santen S. Battery recycling. US7169206B2, 2007, 6 p.

[16] Melin L, Svensson VH. Process for the recovery of metals from the scrap from nickel-cadmium electric storage batteries. US4401463, 1983, 5 p.

[17] Delisle RJ, Martin HE, Wilkerson A. Device and process for the recovery of cadmium and nickel. US5437705, 1995, 7 p.

[18] Yazici EY, Deveci H. Extraction of metals from waste printed circuit boards (WPCBs) in H_2SO_4-$CuSO_4$-NaCl solution. Hydromet. 2013;139:30-38.

[19] Provazi K, Campos BA, Espinosa DCR, Tenorio JAS. Metal separation from mixed types of batteries using selective precipitation and liquid-liquid extraction techniques. Waste Manag. 2011;31:59-64.

[20] Frohlich S, Sewing D. The BATENUS process for recycling mixed battery waste. J. Power Sources. 1995;57:27-30.

[21] Li YQ, Xi GX, The dissolution mechanism of cathodic active materials of spent Zn-Mn batteries in HCl. J. Hazard. Mater. 2005;127:244-248.

[22] Buzatu T, Popescu G, Birloaga I. Saceanu S. Study concerning the recovery of zinc and manganese from spent batteries by hydrometallurgical processes. Waste Manag. 2013;33:699-705.

[23] Nan JM, Han DM, Yang MJ, Cui M, Hou XL. Recovery of metal values from a mixture of spent lithium-ion batteries and nickel-metal hydride batteries. Hydromet. 2006;84:75-80.

[24] Sun L, Qiu KQ. Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries. Waste Manag. 2012;32:1575-1582.

[25] Van Loon JC. Selected methods of trace metal analysis: biological and environmental samples, John Wiley & Sons, Inc., USA, 1985.

[26] Mercier G. Disponibilité des métaux dans les sols et prévision du rendement d’enlèvement par des techniques minéralurgiques, Ph.D. thesis, Université Laval, Québec, QC, Canada, 2000, 293 p.

[27] Aslan N, Cebeci Y. Application of Box–Behnken design and response surface methodology for modeling of some Turkish coals. Fuel. 2007;86:90-97.

[28] Ferreira SLC, Bruns RE, Ferreira HS, Matos GD, David JM, Brandao GC, da Silva EGP, Portugal LA, dos Reis PS, Souza AS, dos Santos WNL. Box-Behnken design: An alternative for the optimization of analytical methods. Anal. Chim. Acta. 2007;597:179–186.

[29] Tanong K, Coudert L, Mercier G, Blais J.F. Preliminary study for the recovery of metals from a mixture of various spent batteries by hydrometallurgy process. J.Environ. Manag. Submitted in February 16th, 2016.

[30] Zhang ZY, Peng ZJ, Srinivasakannan C, Zhang Z, Zhang L, Fernández Y, Menéndez JA. Leaching zinc from spent catalyst: Process optimization using response surface methodology. J. Hazard. Mater. 2010;176:1113-1117.

[31] InvestmentMine, Retrieved from: http://www.infomine.com/investment/metal-prices/manganese, 2014, Consulted on February 2015.

[32] Owusu G. Process development studies for the hardshell ore deposit, Wildcat Silver Corporation, 2009, 157 p.

[33] Nayl AA, Elkhashab RA, Badawy SM, El-Khateeb MA. Acid leaching of mixed spent Li-ion batteries. Arabian J. Chem. In press, 2014, doi:10.1016/j.arabjc.2014.04.001.

[34] Meshram P, Pandey BD, Mankhand TR. Hydrometallurgical processing of spent lithium ion batteries (LIBs) in the presence of a reducing agent with emphasis on kinetics of leaching. Chem. Eng. J. 2015;281:418-427.

[35] Sahoo RN, Naik, PK, Das SC. Leaching of manganese from low-grade manganese ore using oxalic acid as reductant in sulphuric acid solution. Hydromet. 2001;62:157-163.

[36] Furlani G, Moscardini E, Pagnanelli F, Ferella F, Vegliò F, Toro L. Recovery of manganese from zinc alkaline batteries by reductive acid leaching using carbohydrates as reductant. Hydromet. 2009; 99:115-118.

[37] Parhi PK, Sethy TR, Rout PC, Sarangi K. Selective dissolution of copper from copper-chromium spent catalyst by baking–leaching process. J. Ind. Eng. Chem. 2015;21:604–609.

[38] Mannan S, El-Razi AF, Alam MZ. Optimization of process parameters for the bioconversion of activated sludge by *Penicillium corylophilum*, using response surface methodology. J. Environ. Sci. 2007;19:23–28.

[39] Garai D, Kumar V. Enhancement of specific activity of xylanase produced by Ca-alginate entrapped cells of *Aspergillus candidus*: Optimization by Box–Behnken design. Biocatal. Agric. Biotechnol. 2013;2:12–20.

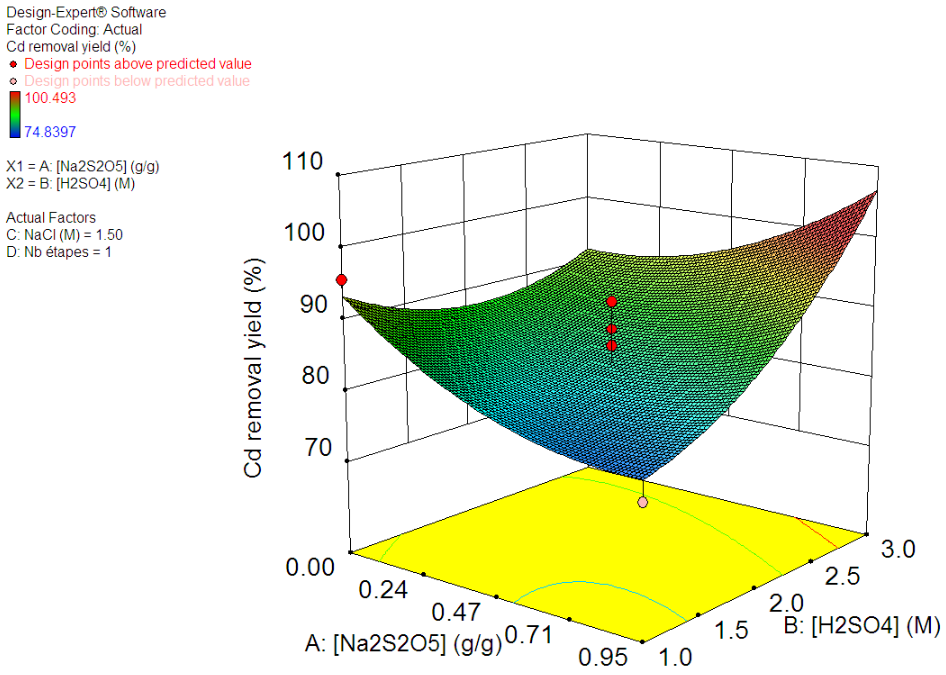
[40] Mocellin J, Mercier G, Morel JL, Blais JF, Simonnot MO. Factors influencing the Zn and Mn extraction from pyrometallurgical sludge in the steel manufacturing industry. J. Environ. Manag. 2015;158:48-54.

[41] Moradkhani D, Rasouli M, Behnian D, Arjmandfar H, Ashtari P. Selective zinc alkaline leaching optimization and cadmium sponge recovery by electrowinning from cold filter cake (CFC) residue. Hydromet. 2012;115-116:84–92.

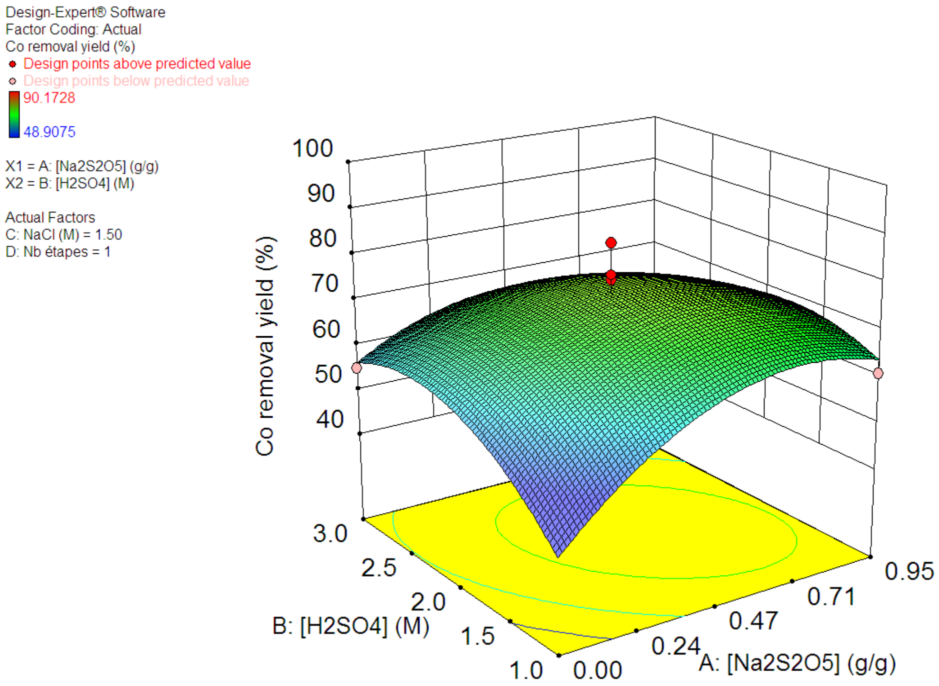
[42] Tanong K. Récupération des métaux à partir des déchets de piles mélangées, Technical report, Institut National de la Recherche Scientifique, Québec, QC, Canada, 2015, 145 p.

4.8 List of figures

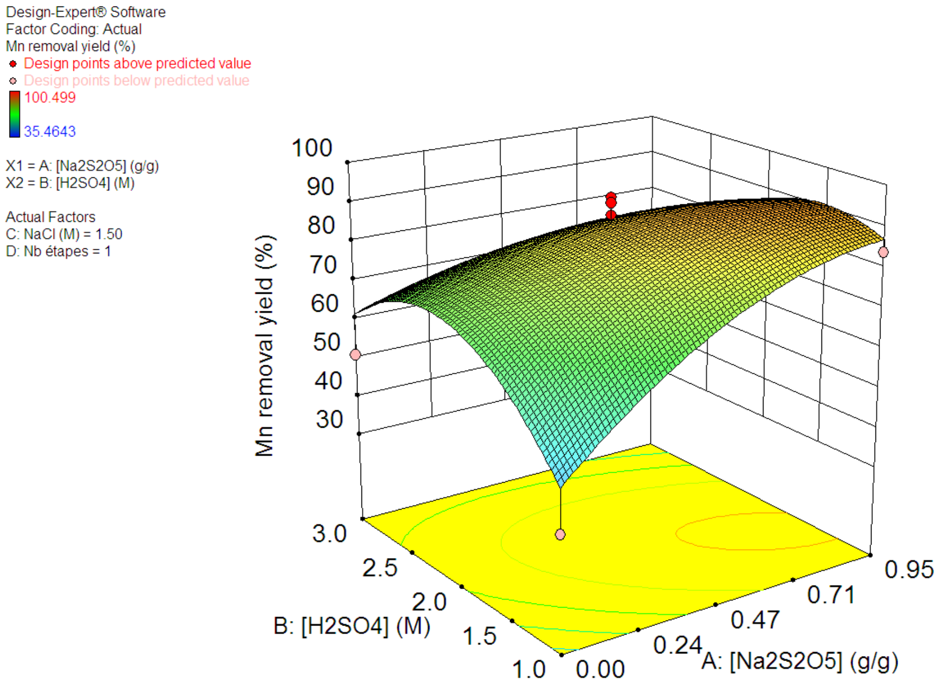
4.9 List of tables


Design-Expert® Software
Factor Coding: Actual
Cd removal yield (%)
Design points above predicted value
Design points below predicted value
100.493
74.8397
X1 = A: [Na2S2O5] (g/g)
X2 = B: [H2SO4] (M)
Actual Factors
C: NaCl (M) = 1.50
D: Nb étapes = 1
Cd removal yield (%)
110
100
90
80
70
0.00
0.24
0.47
0.71
0.95
A: [Na2S2O5] (g/g)
1.0
1.5
2.0
2.5
3.0
B: [H2SO4] (M)

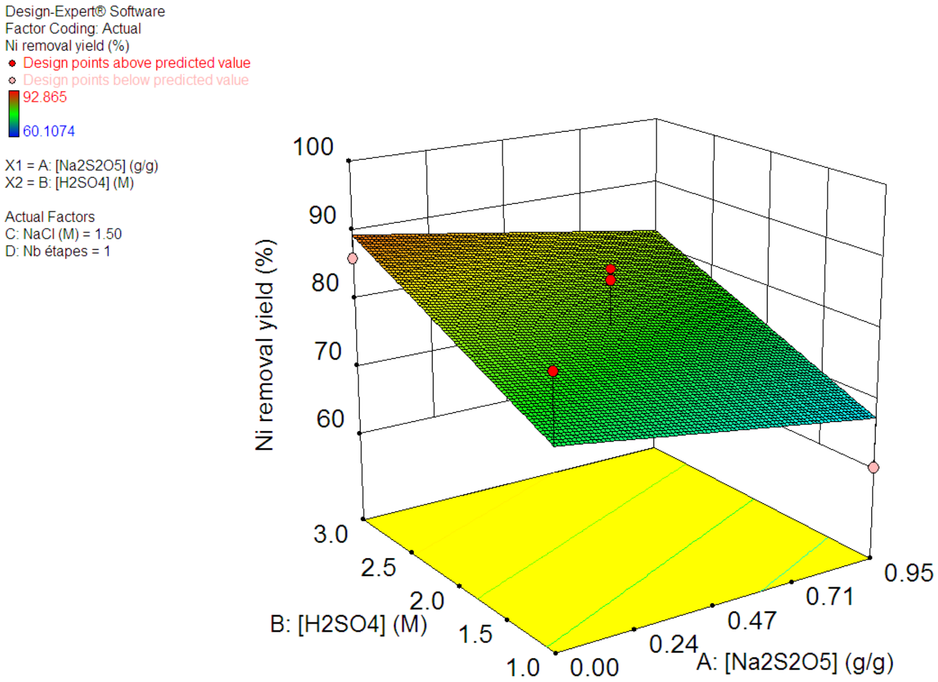
a.


Design-Expert® Software
Factor Coding: Actual
Co removal yield (%)
Design points above predicted value
Design points below predicted value
90.1728
48.9075
X1 = A: [Na2S2O5] (g/g)
X2 = B: [H2SO4] (M)
Actual Factors
C: NaCl (M) = 1.50
D: Nb étapes = 1
Co removal yield (%)
100
90
80
70
60
50
40
3.0
2.5
2.0
1.5
1.0
B: [H2SO4] (M)
0.00
0.24
0.47
0.71
0.95
A: [Na2S2O5] (g/g)

b.


Design-Expert® Software
Factor Coding: Actual
Mn removal yield (%)
● Design points above predicted value
○ Design points below predicted value
100.499
35.4643
X1 = A: [Na2S2O5] (g/g)
X2 = B: [H2SO4] (M)
Actual Factors
C: NaCl (M) = 1.50
D: Nb étapes = 1
Mn removal yield (%)
100
90
80
70
60
50
40
30
B: [H2SO4] (M)
3.0
2.5
2.0
1.5
1.0
A: [Na2S2O5] (g/g)
0.00
0.24
0.47
0.71
0.95

c.


Design-Expert® Software
Factor Coding: Actual
Ni removal yield (%)
● Design points above predicted value
○ Design points below predicted value
92.865
60.1074
X1 = A: [Na2S2O5] (g/g)
X2 = B: [H2SO4] (M)
Actual Factors
C: NaCl (M) = 1.50
D: Nb étapes = 1
Ni removal yield (%)
100
90
80
70
60
B: [H2SO4] (M)
3.0
2.5
2.0
1.5
1.0
A: [Na2S2O5] (g/g)
0.00
0.24
0.47
0.71
0.95

d.

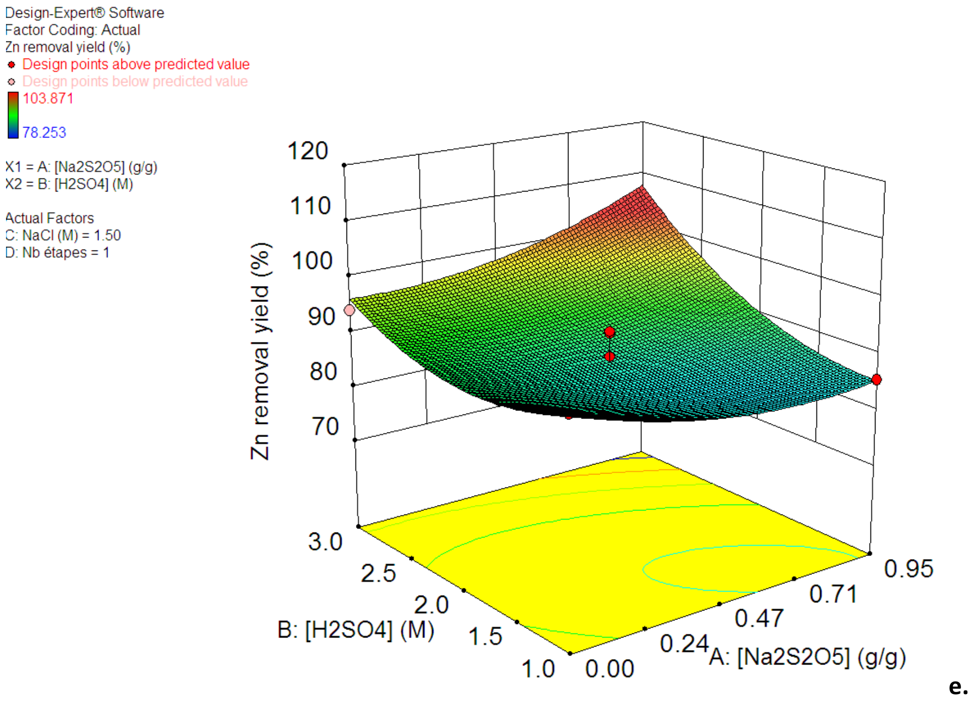
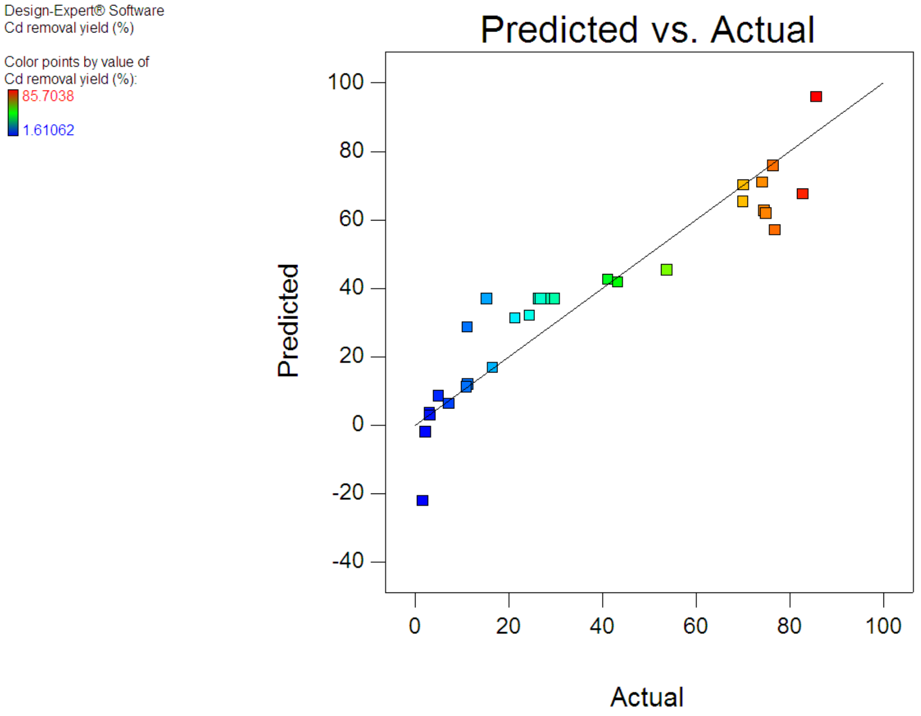
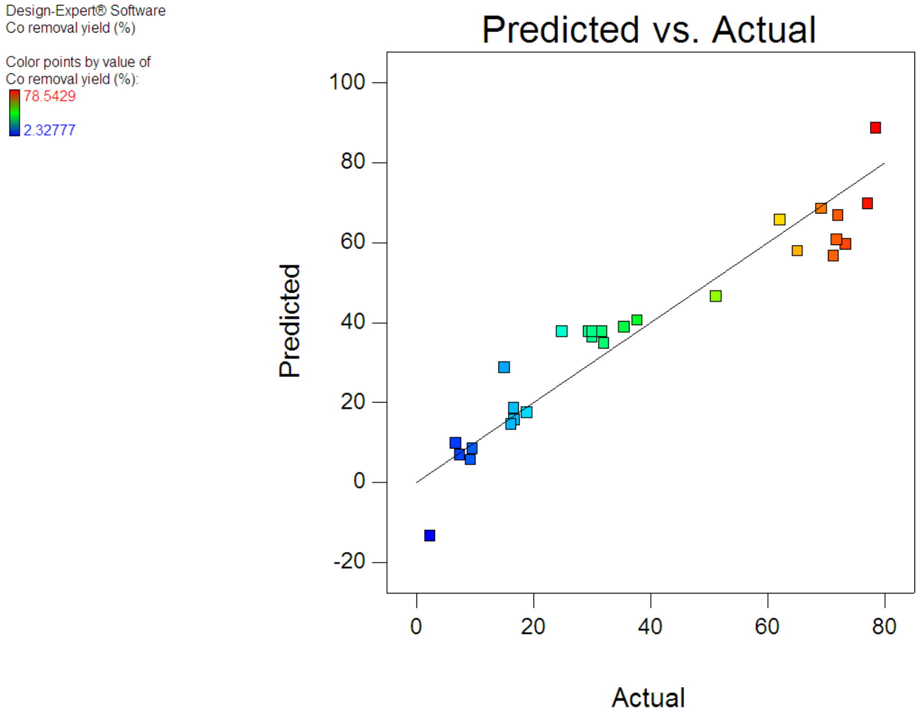


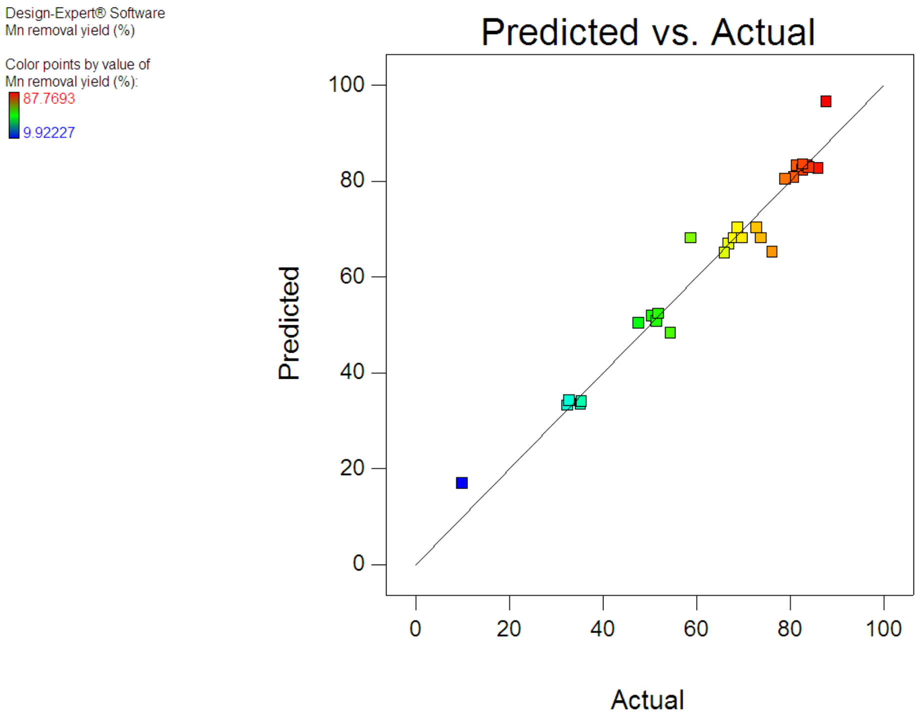
Figure 4.1 Effect of sodium metabisulfite concentration and H_2SO_4 concentration on the solubilization of Cd (a.), Co (b.), Mn (c.), Ni (d.) and Zn (e.) from a mixture of spent battery powder (one leaching step, retention time = 30 min, solid/liquid ratio = 10%, NaCl = 8.78 g/g, T = 20°C)


Design-Expert® Software
Cd removal yield (%)
Color points by value of
Cd removal yield (%):
85.7038
1.61062
Predicted vs. Actual
Predicted
Actual
100
80
60
40
20
0
-20
-40
0
20
40
60
80
100

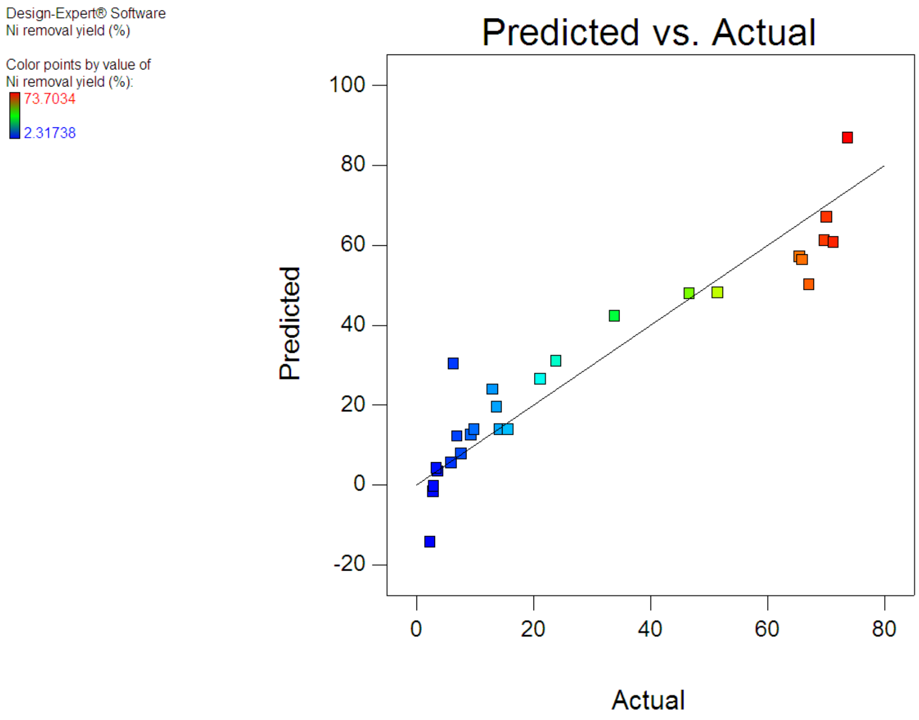
a.


Design-Expert® Software
Co removal yield (%)
Color points by value of
Co removal yield (%):
78.5429
2.32777
Predicted vs. Actual
Predicted
Actual
100
80
60
40
20
0
-20
0
20
40
60
80

b.


Design-Expert® Software
Mn removal yield (%)
Color points by value of
Mn removal yield (%):
87.7693
9.92227
Predicted vs. Actual
Predicted
Actual
0
20
40
60
80
100
0
20
40
60
80
100

c.


Design-Expert® Software
Ni removal yield (%)
Color points by value of
Ni removal yield (%):
73.7034
2.31738
Predicted vs. Actual
Predicted
Actual
-20
0
20
40
60
80
100
0
20
40
60
80

d.

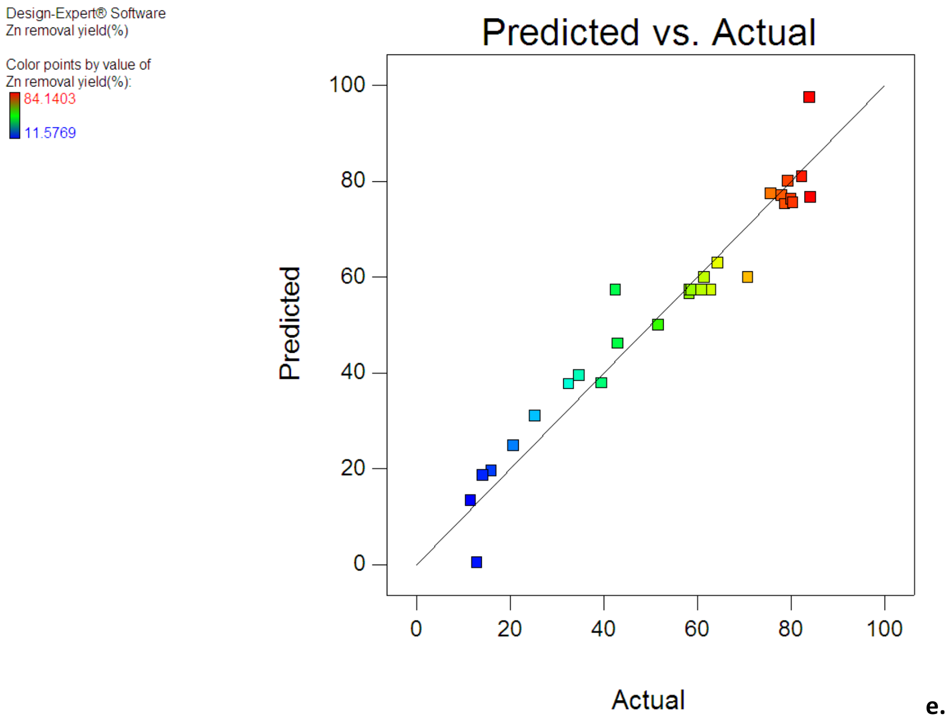
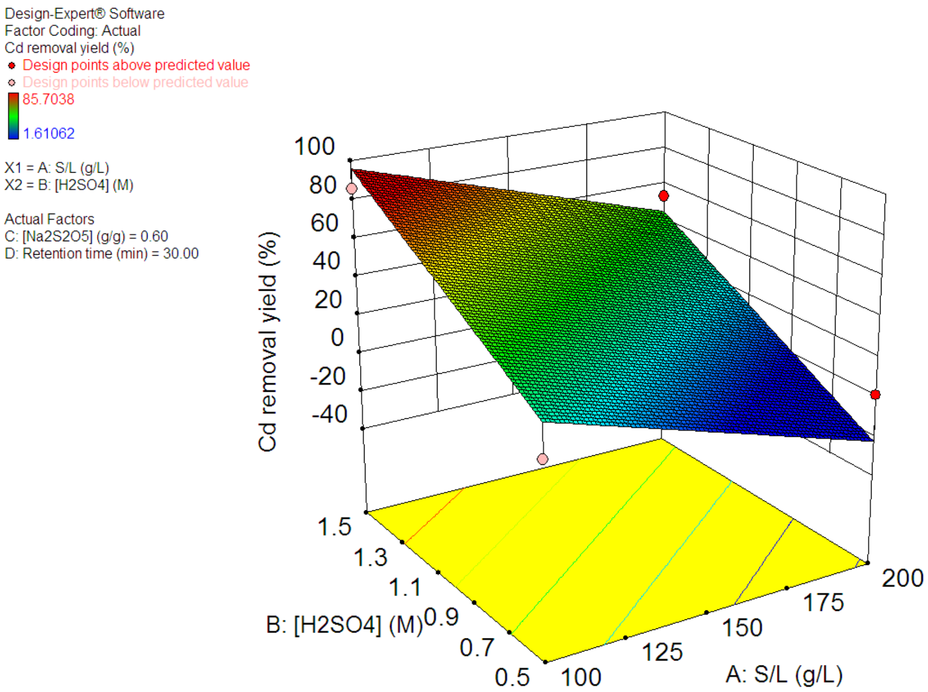
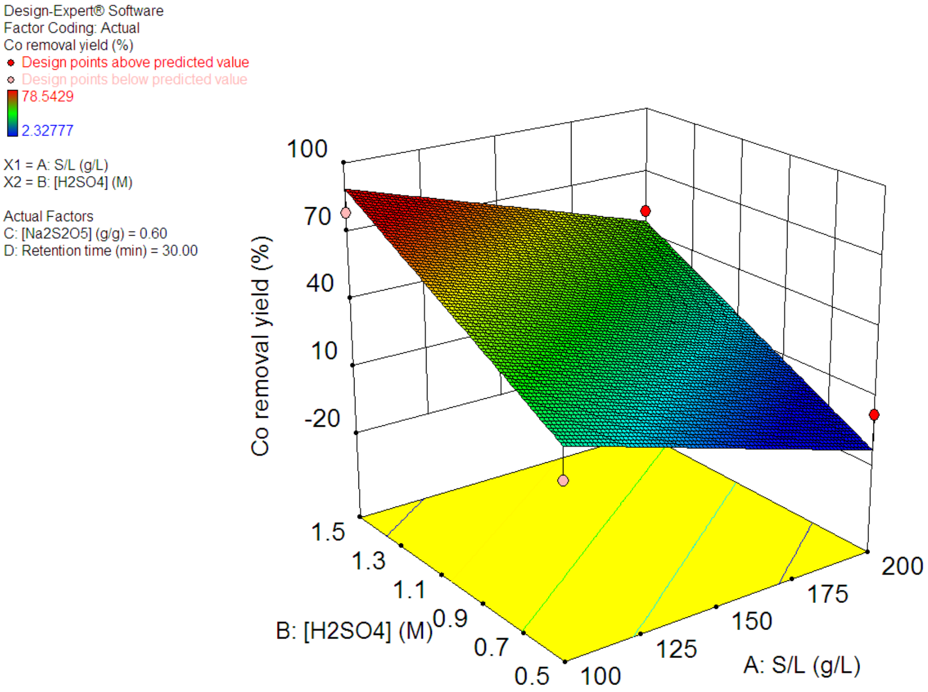


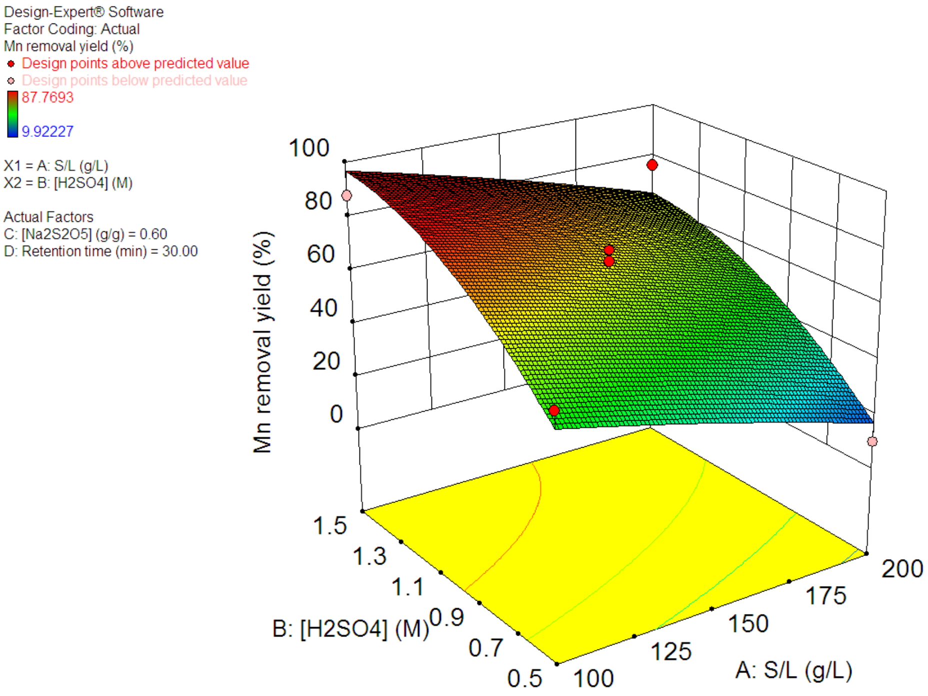
Figure 4.2 **Relationship between predicted values and actual values defined for the mathematical models established for Cd (a.), Co (b.), Mn (c.), Ni (d.) and Zn (e.) during the second series of BBD experiments**


Design-Expert® Software
Factor Coding: Actual
Cd removal yield (%)
● Design points above predicted value
○ Design points below predicted value
85.7038
1.61062
X1 = A: S/L (g/L)
X2 = B: [H2SO4] (M)
Actual Factors
C: [Na2S2O5] (g/g) = 0.60
D: Retention time (min) = 30.00
Cd removal yield (%)
100
80
60
40
20
0
-20
-40
B: [H2SO4] (M)
1.5
1.3
1.1
0.9
0.7
0.5
A: S/L (g/L)
100
125
150
175
200

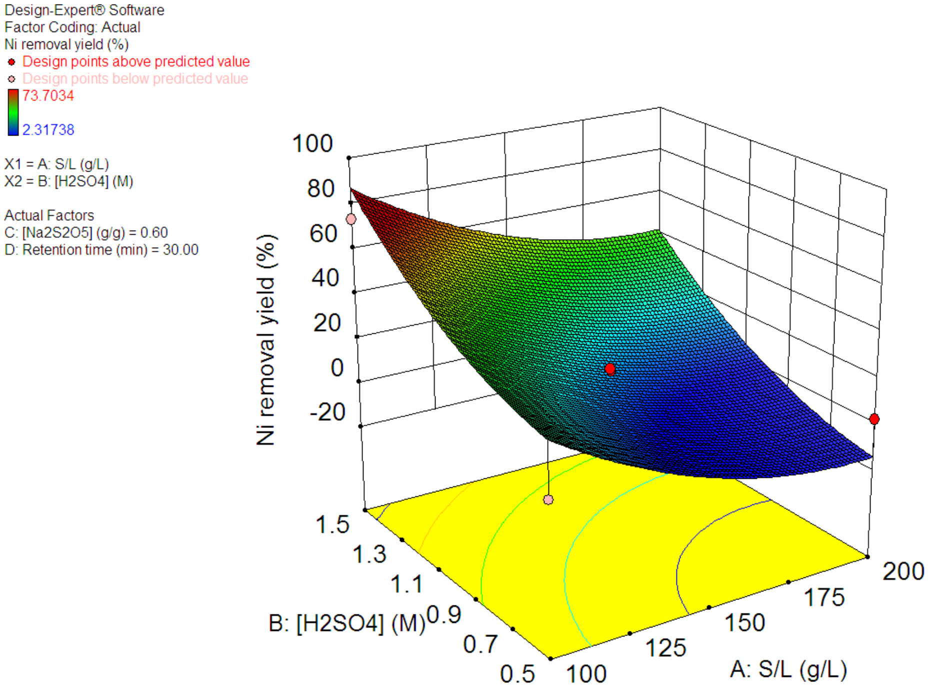
a.


Design-Expert® Software
Factor Coding: Actual
Co removal yield (%)
● Design points above predicted value
○ Design points below predicted value
78.5429
2.32777
X1 = A: S/L (g/L)
X2 = B: [H2SO4] (M)
Actual Factors
C: [Na2S2O5] (g/g) = 0.60
D: Retention time (min) = 30.00
Co removal yield (%)
100
70
40
10
-20
B: [H2SO4] (M)
1.5
1.3
1.1
0.9
0.7
0.5
A: S/L (g/L)
100
125
150
175
200

b.


Design-Expert® Software
Factor Coding: Actual
Mn removal yield (%)
Design points above predicted value
Design points below predicted value
87.7693
9.92227
X1 = A: S/L (g/L)
X2 = B: [H2SO4] (M)
Actual Factors
C: [Na2S2O5] (g/g) = 0.60
D: Retention time (min) = 30.00
100
80
60
40
20
0
Mn removal yield (%)
1.5
1.3
1.1
0.9
0.7
0.5
B: [H2SO4] (M)
100
125
150
175
200
A: S/L (g/L)

c.


Design-Expert® Software
Factor Coding: Actual
Ni removal yield (%)
Design points above predicted value
Design points below predicted value
73.7034
2.31738
X1 = A: S/L (g/L)
X2 = B: [H2SO4] (M)
Actual Factors
C: [Na2S2O5] (g/g) = 0.60
D: Retention time (min) = 30.00
100
80
60
40
20
0
-20
Ni removal yield (%)
1.5
1.3
1.1
0.9
0.7
0.5
B: [H2SO4] (M)
100
125
150
175
200
A: S/L (g/L)

d.

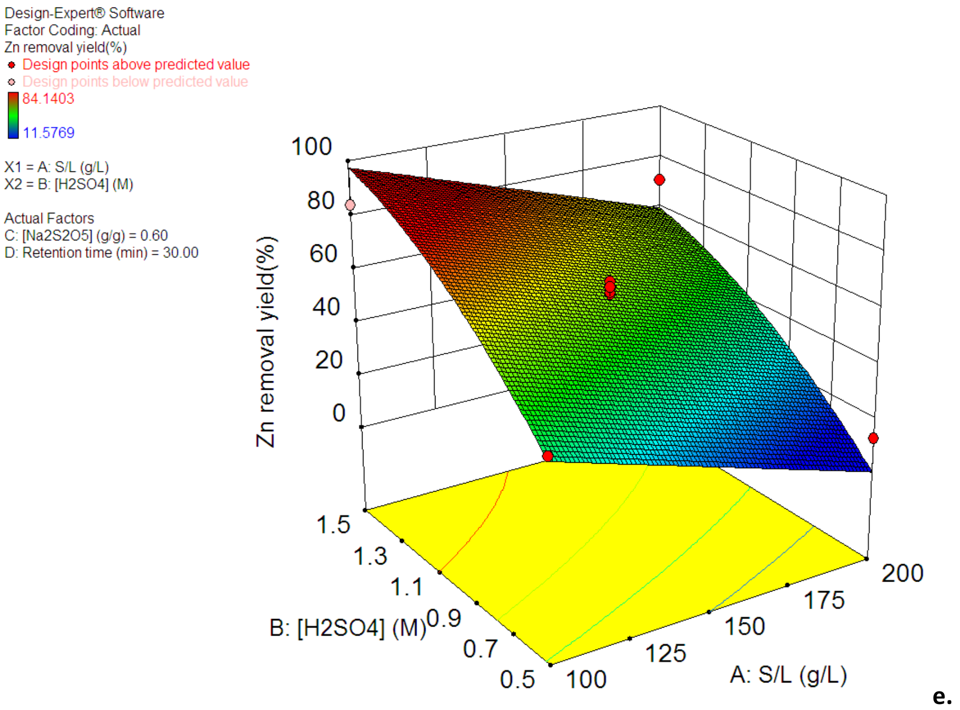


Figure 4.3 Effect of S/L ratio and H_2SO_4 concentration on the solubilization of Cd (a.), Co (b.), Mn (c.), Ni (d.) and Zn (e.) from a mixture of spent battery powder (one leaching step, retention time = 30 min, $Na_2S_2O_5$ = 0.6 g/g of battery powder, T = 20 °C)

Table 4.1 Metals composition in the mixture of waste batteries (mg/kg)

Metals	Metals content (mg/kg)	Metals proportion (%)	Value on market (US$/kg metal) [31]	Value of metals present in a mixture of spent batteries powder (US$/t.m. of spent battery powder)
Al	2 340 ± 190	0.39	1.83	4.28
Ba	3 470 ± 170	0.58	NA*	NA
Ca	681 ± 217	0.11	NA	NA
Cd	25 900 ± 2 300	4.32	3.90	101
Co	3 660 ± 430	0.61	14.90	54.4
Cu	403 ± 169	0.07	4.47	1.80
Fe	21 300 ± 1 400	3.55	0.05	1.06
K	22 000 ± 3 600	3.67	0.29	6.38
Li	812 ± 304	0.14	24.20	19.6
Mg	195 ± 38	0.03	NA	NA
Mn	253 800 ± 29 700	42.3	2.30	584
Ni	62 400 ± 8 200	10.4	21.80	1 360
Ti	534 ± 14	0.09	4.20	2.24
Zn	202 000 ± 9 800	33.7	2.30	465
Total	600 000	100		2 600

**NA = non applicable.*

Table 4.2 **Results of an optimization by using Box Behnken for the experimental studying the variation of $Na_2S_2O_5$ concentration (X_1), the effect of H_2SO_4 concentration (X_2), the variation of NaCl concentration (X_3) and the numbers of leaching steps (X_4) on the dissolution of metals**

Metals	**Source**	**Analysis of variance**					
	Model	**Sum of squares**	**Degree of freedom**	**Mean square**	**F value**	**P-value Prob >F**	**Conclusion**
Cd[a]	X_1	95.75	1	95.75	4.99	0.0319	Significant
	X_2	115.9	1	115.9	6.05	0.0190	Significant
	X_3	147.4	1	147.4	7.69	0.0088	Significant
	X_4	337.1	2	168.5	8.80	0.0008	Significant
	X_1X_2	381.8	1	381.8	19.9	<0.0001	Significant
	X_2X_3	193.0	1	193.0	10.1	0.0031	Significant
	X_1^2	201.0	1	201.0	10.5	0.0026	Significant
	X_2^2	266.5	1	266.5	13.9	0.0007	Significant
Co[b]	X_1	416.3	1	416.3	9.02	0.0048	Significant
	X_2	239.9	1	239.9	5.20	0.0285	Significant
	X_4	377.4	2	188.7	4.09	0.0249	Significant
	X_1X_2	481.3	1	481.3	10.4	0.0026	Significant
	X_2X_3	822.1	1	822.1	17.8	0.0002	Significant
	X_1^2	1 671	1	1 671	36.2	<0.0001	Significant
	X_2^2	1 194	1	1 194	25.9	<0.0001	Significant
	X_3^2	563.0	1	563.0	12.2	0.0013	Significant
Mn[c]	X_1	1 192	1	1 192	13.9	0.0010	Significant
	X_2	637.2	1	637.2	12.6	0.0134	Significant
	X_1X_2	1 952	1	1 952	20.6	<0.0001	Significant
	X_2X_3	3 556	1	3 556	37.5	<0.0001	Significant
	X_1^2	946.8	1	946.8	9.98	0.0003	Significant
	X_2^2	3 655	1	3 655	38.5	<0.0001	Significant
	X_3^2	430.5	1	430.5	4.54	0.0395	Significant
Ni[d]	X_1	248.4	1	248.4	9.01	0.0047	Significant
	X_2	204.8	1	204.8	7.43	0.0097	Significant
	X_4	515.2	2	257.6	9.34	0.0005	Significant
	X_1X_3	366.8	1	366.8	13.3	0.0008	Significant
	X_2X_3	215.1	1	215.1	7.80	0.0081	Significant
	X_2X_4	198.4	2	99.22	3.60	0.0371	Significant

Zn[e]	X_2	322.7	1	322.7	27.8	<0.0001	Significant
	X_3	124.5	1	124.5	10.7	0.0024	Significant
	X_4	216.0	2	108.0	9.31	0.0006	Significant
	X_1X_2	150.7	1	150.7	13.0	0.0010	Significant
	X_1X_3	390.2	1	390.2	33.6	<0.0001	Significant
	X_1^2	123.1	1	123.1	10.6	0.0025	Significant
	X_2^2	315.3	1	315.3	27.2	<0.0001	Significant

[a]: *$R^2 = 0.71$, $R^2_{adj} = 0.61$, Adeq precision = 11.2.*

[b]: *$R^2 = 0.76$, $R^2_{adj} = 0.68$, Adeq precision = 12.1.*

[c]: *$R^2 = 0.78$, $R^2_{adj} = 0.73$, Adeq precision = 12.2.*

[d]: *$R^2 = 0.64$, $R^2_{adj} = 0.55$, Adeq precision = 11.5.*

[e]: *$R^2 = 0.79$, $R^2_{adj} = 0.72$, Adeq precision = 12.3.*

Table 4.3 **The model adequacy analysis of the experimental studying the effect of H_2SO_4 concentration (y1), reactions times (y2), sodium metabisulphide concentration (y3) and solid/liquid (S/L) ratio (y4) on the dissolution of metals**

Metal	R-squared	Adj R-squared	Pred R-square	CV (%)	Adeq Precision
Cd	0.88	0.86	0.83	30.3	25.4
Co	0.91	0.89	0.86	22.3	29.3
Mn	0.96	0.93	0.91	8.16	23.9
Ni	0.89	0.83	0.74	38.6	15.3
Zn	0.94	0.91	0.88	13.4	22.9

Table 4.4 **Results of an optimization by using Box Behnken for the experimental studying the effect of H_2SO_4 concentration (y1), reactions times (y2), sodium metabisulphide concentration (y3) and solid/liquid (S/L) ratio (y4) on the metals dissolution**

Metal	**Source**	**Analysis of variance**					
	Model	**Sum of squares**	**Degree of freedom**	**Mean square**	**F value**	**P-value Prob >F**	**Conclusion**
Cd	Model	21 674	4	5 418	43.4	< 0.0001	Significant
	X'_1	7 725	1	7 725	61.8	< 0.0001	Significant
	X'_2	13 614	1	13 614	109	< 0.0001	Significant
Co	Model	16 204	4	4 051	57.3	< 0.0001	Significant
	X'_1	5 343	1	5 343	75.5	< 0.0001	Significant
	X'_2	10 803	1	10 803	153	< 0.0001	Significant
Mn	Model	10 721	11	974.6	36.3	< 0.0001	Significant
	X'_1	2 965	1	2 965	111	< 0.0001	Significant
	X'_2	6 996	1	6 996	261	< 0.0001	Significant
	X'^{2}_{2}	726.7	1	727.0	27.1	< 0.0001	Significant
Ni	Model	17 498	10	1 750	15.2	< 0.0001	Significant
	X'_1	5 976	1	5 976	51.8	< 0.0001	Significant
	X'_2	9 639	1	9 639	83.5	< 0.0001	Significant
	X'^{2}_{1}	976.9	1	976.9	8.46	0.0094	Significant
	X'^{2}_{2}	669.9	1	669.9	5.80	0.0269	Significant
Zn	Model	15 678	9	1 742	33.3	< 0.0001	Significant
	X'_1	4 231	1	4 231	80.9	< 0.0001	Significant
	X'_2	10 652	1	10 652	204	< 0.0001	Significant
	X'^{2}_{2}	505.0	1	504.9	9.65	0.0058	Significant

Table 4.5 **Performances of the metal solubilization from a mixture of spent battery powder using the optimal leaching conditions (S/L = 10.9%, [H_2SO_4] = 1.34 M, [$Na_2S_2O_5$] = 0.45 g/g of battery powder and reaction time = 45 min)**

Assays	**Metals solubilization (%)**				
	Cd	**Co**	**Mn**	**Ni**	**Zn**
1	78.7	90.3	90.4	63.5	98.7
2	83.9	100	98.6	69.8	100
3	81.1	97.9	92.9	72.0	100
Average	81.2	96.1	94.0	68.4	99.6

5 CHAPITRE 5

RECOVERY OF ZN FROM UNSORTED SPENT BATTERIES USING SOLVENT EXTRACTION AND ELECTRODEPOSITION

Revue : Journal of Environmental Engineering

Auteurs : Kulchaya Tanong[a], Lan Huong Tran[b], Lucie Coudert[c], Guy Mercier[d], Jean-Francois Blais[e*]

[a] Ph.D. student, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-4677 ext. 4473, Fax: (418) 654-2600, email: kulchaya.tanong@ete.inrs.ca

[b] Research Associate, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-2550, Fax: (418) 654-2600, email: lan.huong.tran@ete.inrs.ca

[c] Research Associate, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-3793, Fax: (418) 654-2600, email: lucie.coudert@ete.inrs.ca

[d] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-2633, Fax: (418) 654-2600, email: guy.mercier@ete.inrs.ca

[e] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-2575, Fax: (418) 654-2600, email: jean-francois.blais@ete.inrs.ca

*Corresponding author:
Tel: (418) 654-2575, Fax: (418) 654-2600,
email: **jean-francois.blais@ete.inrs.ca**

Note

L’étudiante est le premier auteur de cet article. Toutes les manipulations, le traitement des données ainsi que la rédaction ont été effectués par l’étudiante sous la supervision des autres co-auteurs.

Modifications exigées par le comité de lecture de la revue

Les commentaires des réviseurs n’ont pas été reçus.

5.1 Résumé

Cette étude porte sur la récupération sélective du zinc (Zn) à partir d'une solution de lixiviation de piles et batteries usagées. Dans cet article, seules les étapes de précipitation, d'extraction par solvant des métaux ont été étudiées. D'après les résultats obtenus, l'extraction par solvant à l'aide de Cyanex 272 a permis l'élimination sélective du zinc de la solution synthétique contenant des concentrations élevées en métaux: (Zn ~19,4 g/L; ~23,4 g Mn/L, Cd ~3,27 g/L, Ni ~3,19 g/L et Co ~0,25 g/L). D'après les résultats, le procédé d'extraction par solvant permet de récupérer 98 ± 8% du Zn initialement présent dans la solution de lixiviation dans les conditions suivantes: deux étapes d'extraction en présence d'une solution organique faite de Cyanex 272 (30%, v/v) et de tributylphosphate (TBP – 2%, v/v) dans du kérosène, pH = 2,2, Ratio phase organique/phase aqueuse (O/A) = 2/1 et T = 50°C. Le Zn présent dans la phase organique a été ensuite récupéré en utilisant 0,4 M H_2SO_4 avec un rapport O/A fixé à 1/2. Cette étape a permis de récupérer 82 ± 1% du Zn initialement présent dans la phase organique. Par la suite, 82 ± 7% du Zn présent dans la solution aqueuse a été récupéré par électrodéposition après 3 h à pH 2, avec une densité de courant fixée à 360 A/m^2.

Mots-clés: Déchets des piles non triées, Précipitation, Électrodéposition, Extraction par solvant, Cyanex 272, Zinc.

5.2 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 synthetic 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 98 ± 8% 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 H_2SO_4 with an O/A ratio fixed at 1/2. This stripping step allowed for the recovery of 82 ± 1% of the Zn initially present in the organic phase. Subsequently, 82 ± 7% 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/m^2.

Keywords: Unsorted spent battery, Precipitation, Electrodeposition, Solvent extraction, Cyanex 272, Zinc.

5.3 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 ($Zn-MnO_2$) sold in Canada, only 4.7 million units were recycled [1]. 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. In 2014, the quantities of spent batteries recycled were estimated at 79 % for alkaline battery, 2 % for lithium battery, 0.7 % for Zinc-carbon battery, 9.4 % for nickel-cadmium battery, 6.5 % for lithium ion battery and 2.5 % for nickel-metal hydride battery [2].

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 [2]. According to Bonhomme *et al.* [3], 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 effect in Canada, the government applied the Extended Producers Responsibility Program to the management of primary and secondary spent batteries, which means the battery's producers take part in the battery recycling process [2]. Moreover, a non-profit organization named "Call2Recycle" was created by the Canadian Government to collect and promote the recycling of spent batteries at no cost for the municipalities, industries and consumers [4]. This project was adopted by the government of Canada 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 [4]. 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 [5]. Several researchers have shown the effectiveness of inorganic acids (H_2SO_4, HCl) and/or reducing agents (oxalic acid, carbohydrates, H_2O_2, SO_2/NH_3) in efficiently solubilizing the valuable metals present in spent batteries [6-11]. 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 [12]. 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 [12]. 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. However the organic solvent is considered as the substance which is volatile and toxic so the operation in the closed system would be necessary in order to avoid those problems.

Solvent extraction was first applied in a hydrometallurgical process in 1947 for the Manhattan project [13]. 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 [14]. 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. Indeed, Frohlich *et al.* [6] have developed the BATENUS process that enables recycling of unsorted spent batteries, including Zn-C, alkaline, lithium and Ni-Cd batteries. This process, developed in 1995, involves pre-treating the mixture of spent batteries using mechanical processes. The metals contained in the black powder obtained from this pre-treatment were then leached in the presence of sulfuric acid. Various chemical processes, such as ion exchange and solvent extraction, were then applied to separate each valuable metal from the leach liquor. The performance of the process was not specified in the published paper. Provazi *et al*. [15] 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_2SO_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 extraction efficiencies higher than 88%. According to Innocenzi and Veglio [16], 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 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.* [18] 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 aim of this work was to selectively recover the Zn from a PLS emerging from the recycling of unsorted spent batteries (alkaline, Zn-C, Li-ion, Ni-Cd, Ni-MH). This PLS contained high amounts of metals (Zn, Fe, Cd, Mn, Ni, Co, etc.). First, this work focused on the selective recovery of Zn from the PLS by comparing the performances of the selective precipitation and solvent extraction methods. The influence of solvent extraction parameters (pH, diluent concentration, phase modifier concentration, reaction time, etc.) was also investigated. The second aspect of this research focused on the recovery of Zn by electrodeposition.

5.4 Background

5.4.1 Solvent extraction mechanisms

Cyanex 272 is an ester organic solvent formed by the reaction of an alcohol with inorganic acid [12]. 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 5.1 [19].

Équation 5-1 $$\mathbf{Zn^{2+} + 2\ RH \leftrightarrow ZnR_2 + 2\ H^+}$$

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 [20]. 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 pHs ranging from 0.5 to 8.0 follows this sequence: $Fe^{3+} > V^{4+} > Zn^{2+} > Al^{3+} > Cu^{2+} > Mn^{2+} > Co^{2+} > Mg^{2+} > Ca^{2+} > Ni^{2+}$ [21]. 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 5.2 [22].

Equation 5-2 $$D_M = \frac{[M_{org}]}{[M_{aq}]}$$

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

The separation factor between two metals was calculated using Equation 5.3 [12].

Equation 5-3 $$\beta_{A/B} = \frac{[D_{MA}]}{[D_{MB}]}$$

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 slope analysis was conducted to determine the stoichiometric coefficient of the extractant. Equation 5.4 was used to obtain this value, and it was further revealed from the combination of the Equations 5.5 and 5.6 [23].

Equation 5-4 $$\log D_M = n \log \left[0.6 - n\, [M]_{org}\right] + \log K + 2\ pH$$

Where D_M represents the distribution coefficient, n represents the stoichiometric coefficient of the extractant, $[M_{org}]$ represents the concentration of metal in the organic phase and K represents the equilibrium constant.

Equation 5-5 $$\log D_M = \log K + 2\ pH + n \log [RH]_{eq}$$

Where D_M represents the distribution coefficient, K represents the equilibrium constant, n represents the stoichiometric coefficient of the extractant and $[RH]_{eq}$ represents the concentration of organic solvent at equilibrium (Equation 5.6).

Equation 5-6 $[RH]_{eq} = 0.6 - n\,[M_{org}]$

Where n represents the stoichiometric coefficient of the extractant, $[M_{org}]$ represents the concentration of metal in the organic phase.

To obtain the stoichiometry value of Cyanex 272, the n value could first be determined using the “trial and error” method deduced from Equation 5.4 [23]. 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.* [24]. 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 [25]. From the literature, it appeared that the tributylphosphate (TBP) modifier interacts with metals and allows for the formation of adducts by replacing water molecules [20]. 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 [24].

5.4.2 Electrodeposition

In electrochemical processes, the displacement of electrons is supplied by electron-donating species. Considering the standard electrode potential E^0 of the couple Zn^{2+}/Zn^0 (E^0 = - 0.76 V), which is lower than the electrode potential of water decomposition (E^0 = 0.00 V), the ions Zn^{2+} will be reduced and deposited on the cathode during the electrodeposition process as revealed by Equation 5.7 [26]. Parasite reactions related to the decomposition of water will occur at the cathode (Equation 5.8) and at the anode (Equation 5.9), decreasing the performances of Zn^{2+} ions reduction [26].

Cathodic reactions:

Equation 5-7 $\mathbf{Zn^{2+} + 2\,e^- \leftrightarrow Zn_{(s)},\ E_0 = -0{,}76\ V}$

Equation 5-8 $\mathbf{2\,H^+ + 2\,e^- \leftrightarrow H_{2(g)},\ E_0 = 0.00\ V}$

Anodic reaction:

Equation 5-9 $\mathbf{2\,H^+ + 2\,e^- + \frac{1}{2}\,O_{2(g)} \leftrightarrow H_2O_{(l)},\quad E_0 = -1.229\ V}$

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 [27]. This parameter indicates the current actually used for depositing the Zn^{2+} ions from the total current applied [28]. Thus, an electrodeposition process with higher current efficiency (CE) shows the greater performances of the deposition of the metal of interest [27].

Equation 5-10 $$CE=\frac{w'}{w}\times 100$$

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.

5.4.3 Preparation of the pregnant leach solution

5.4.3.1 Preparation of pregnant leach solution 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-ion, 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, 107 g of the black powder was mixed with 1 L of the leaching solution containing 1.34 M H_2SO_4 (Fisher, Canada) and 48 g of sodium meta-bisulfite ($Na_2S_2O_5$ – Fisher, Canada). After 45 min at room temperature, the solid was separated from the pregnant leach solution by filtration. The composition of the PLS obtained from the leaching process was characterized using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian 725-ES) apparatus. The PLS was used for the experiments carried out on the selective precipitation of metals to validate assays with the synthetic PLS.

5.4.3.2 Preparation of the synthetic PLS

Synthetic PLS was prepared based on the characterization results of the PLS emerging from the leaching of metals from unsorted spent batteries -According to the results, the metallic species present in the PLS in small amounts (less than 1% of Ca, Li, Cu, Al, etc.) were neglected for the preparation of the synthetic pregnant leach solution. The synthetic solution was used for all 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 $ZnSO_4.7H_2O$, $MnSO_4.H_2O$, $CdSO_4.H_2O$, $CoSO_4.7H_2O$ and K_2SO_4 (Laboratoire MAT, Canada) were dissolved in distilled water to prepare a synthetic PLS. Concentrated H_2SO_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 $FeSO_4.7H_2O$ (Laboratoire MAT, Quebec, Canada) was not added because the Fe was already removed by precipitation at pH = 4. However, a defined quantity of

$FeSO_4.7H_2O$ 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 and from the organic phase using a selective stripping method.

5.4.4 Precipitation

For the first series of solvent extraction experiments, Fe was selectively removed from the PLS by precipitation after the addition of H_2O_2 to oxidize Fe^{2+} ions to Fe^{3+} ions and the addition of NaOH until pH = 4.00 to precipitate Fe as $Fe(OH)_3$. Various amounts of H_2O_2, corresponding to 100%, 125% and 200% of the stoichiometric amount required to oxidize all of the Fe present in PLS, were added to compare the Fe removal efficiencies. Filtration on fiber filter (G6-glass 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 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 was continuously mixed at 250 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 at 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 and 12. 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. However, for the second series of experiments, a NaOH solution was stepwise added to the PLS until pH = 4.00 and a powder of

Na_2CO_3 (Fisher, Canada) was then used to increase the pH to precipitate the metals as carbonates.

For all of these experiments, the residual concentrations of metals present in the supernatant were measured by collecting the supernatant obtained after filtration (1.5-µm pore size) followed by analysis by ICP-AES.

5.4.5 Solvent extraction

5.4.5.1 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; 5% (v/v) TBP (tributylphosphate, 97%, Sigma Aldrich, Canada) and 75% (v/v) kerosene (Recochem. Inc., Canada).

5.4.5.2 Solvent extraction procedure

Solvent extraction experiments were carried out in 250-mL beakers at 50°C. 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 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), equilibration time (5, 10, 20, 30 and 60 min) and [TBP] (0, 2 and 5% (v/v)), 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_2SO_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. The residual concentrations of metals were determined by collecting 1 mL of aqueous phase and diluting this sample 10 times in HNO_3 5% to avoid the precipitation of metals before analysis by ICP-AES.

5.4.5.3 Stripping procedure of the organic solvent

The organic phase emerging from the solvent extraction step and containing the metals 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_2SO_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 pHs lower than the optimal pH for Zn extraction. For this reason, a solution of H_2SO_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.

5.4.6 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 deposit of Zn obtained. The purity of Zn powder was also evaluated by scanning electron microscope (SEM).

5.4.7 Analytical techniques

The aqueous samples were analyzed by ICP-AES (Inductively coupled plasma - atomic emission spectroscopy, Varian 725-ES). 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% HNO_3 before analysis. The aqueous samples emerging from the solvent extraction experiments were preserved in 5% HNO_3 before analysis.

The purity of Zn deposits following the 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.

5.5 Results and discussion

5.5.1 Characterization of the Pregnant Leach Solution (PLS) and the synthetic solution

Table 5.1 presents the characteristics of the PLS resulting from the leaching process (H_2SO_4 + $Na_2S_2O_5$) applied to unsorted spent batteries (alkaline, Zn-C, Ni-Cd, Ni-MH, Li-ion and lithium iron) used for the precipitation experiments. This table also shows the composition of the synthetic solution used for the solvent extraction assays. According to these results, the composition of both the PLS and the synthetic solution were quite similar, except for the concentration of Fe (0.53 g/L in PLS versus 0.005 g/L in synthetic solution). Indeed, the Fe ions were removed by selective precipitation before they were reintroduced into the PLS during the solvent extraction process, which explains why the concentration of Fe was lower in the synthetic solution. Initially, the PLS contained 28 ± 2 g Mn/L, 20 ± 2 g Zn/L, 3.2 ± 0.2 g Cd/L, 3.5 ± 0.3 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 (4.6 ± 0.1 g K/L) was due to the use of KOH as the electrolyte in the production of alkaline batteries.

5.5.2 Metal selective recovery using precipitation

5.5.2.1 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 5.2 presents the metal removal yields obtained at pH = 4.0

depending on the amounts of H_2O_2 added to the PLS (100%, 125% and 200% of the stoichiometry value required to oxidize all ferrous ions present in the PLS). According to these results, an increase in the amount of H_2O_2 added from 100% to 125% led to an increase in the removal of Fe from 69 ± 12% to 92 ± 2%, whereas its increase from 125% to 200% did not lead to an increase in Fe removal yield. The highest Fe removal efficiencies were obtained with the addition of 125% of the stoichiometry value of H_2O_2. According to these results, the precipitation of Fe as ferric hydroxide ($Fe(OH)_3$) when using 125% of H_2O_2 stoichiometry at pH = 4.0 was highly efficient, reaching 92% removal of Fe. Under these operating conditions, we noticed that only 2.8% of Co, 3.3% of Mn, 2.7% Ni, 3.1% of Cd and 4.3% of Zn were removed from the PLS, which was quite favorable for the selective recovery of these valuable metals, especially Zn.

5.5.2.2 Precipitation of metal as hydroxides

A second series of experiments was conducted to determine if the valuable metals present in the PLS could be selectively removed from the solution by successive additions of a solution of NaOH to precipitate the metals as hydroxides (Equation 5.11).

Equation 5-11 $\mathbf{M^{2+} + 2\ OH^- \rightarrow M(OH)_2}$

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

Figure 5.1 presents the residual concentrations of the metals initially present in the PLS, including Zn measured in the supernatant after precipitation at different pHs 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 Figure 5.1a, the precipitation of Zn started at pH = 4 and was complete at pH = 8. From the results presented in Figure 5.1a and Figure 5.1b, 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 6 (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.

5.5.2.3 Precipitation of metal carbonates

As the selective recovery of the Zn present in PLS 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 Na_2CO_3. The objective of this third series of experiments was to determine if Zn can be selectively recovered from the PLS as zinc carbonate (Equation 5.12).

Equation 5.5-12 $x\,M^{z+}_{(aq)} + y\,CO_3^{2-}{}_{(aq)} \leftrightarrow M_x(CO_3)_{y(s)}$

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

Figure 5.1c and Figure 5.1d present the residual concentrations of the metals initially present in the PLS, including Zn, measured in the supernatant after precipitation at different pHs using NaOH and Na_2CO_3. 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 PLS (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 conditions. According to these results, the selective precipitation of Zn as carbonates from the PLS was not efficient at pHs near 5. Notably, most of the metals present in the PLS 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_2CO_3 due to the large amounts of Mn, Ni and Cd initially present in the PLS. Similar results were found in the study conducted by Provazi *et al.* [15] 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_2O_2 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, solvent extraction was studied as an alternative option. These results will be discussed in the following section.

5.5.3 Solvent extraction

In the following section, all of the results were expressed for the treatment of one liter of synthetic sulfate 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.

5.5.3.1 Extraction pH isotherm

Figure 5.2 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 (19.4 g) was extracted, whereas almost all of the Zn initially present in the synthetic 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 Figure 5.2, 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.* [29] and Rickelton [30] 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.* [29], 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 Figure 5.2, the highest Zn extraction rates were obtained at pH values between 3.0 and 3.5. However, according to a personal discussion with the Cyanex 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 (Figure 5.2) 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). 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*. [29] and Nathsarma and Devi [31]. Therefore, solvent extraction conditions in this stage were chosen as follows: T = 50°C, O/A ratio = 2/1, 20% vol. Cyanex 272 and 2% vol. TBP in kerosene, residence time = 10 min, and pH = 2.2.

5.5.3.2 Effect of TBP concentration

The effect of the TBP concentration on the extraction efficiencies was studied, and the results are revealed in Table 5.3. 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°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% (10.6 g), 60% (11.6 g) and 49% (9.54 g), respectively, while approximately 3.0% (0.70 g), 9.2% (2.15 g) and 6.3% (1.47 g) of Mn were co-extracted in the organic phase. Eskandari and Najafabadi [32] 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, 60% 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, 2.2 g of Mn and 0.31 g of Ni were co-extracted.

5.5.3.3 Effect of reaction time

Table 5.4 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 5.4, the equilibrium of Zn extraction was achieved within 10 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 PLS. After 10 min, the standard deviation obtained from the three repetitions experiments of Mn^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} extractions were not different from their average values (extraction yields), indicating that the system was stable for these compounds. The effect of contacting time on solvent extraction efficiency was also studied by Gupta *et al*. [33], 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 efficacy. Generally, the equilibrium of a solvent extraction process can be achieved in a short period of time (< 5 mins), which was also confirmed by the study of Hereijgers *et al.* [34]. 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 Fatmehsari *et al.* [35].

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

Table 5.5 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 5.2, 5.3, 5.4 and 5.5. 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 [35]. 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.* [37] 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.* [38] 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 (PLS: 8.65 g/L Zn^{2+}, 3.15 g/L Mn^{2+}, 10 min extraction time at 22°C).

Figure 5.3 presents the plot of the log D_M - n log [0.6-n[M]org] versus the pH for different stoichiometry values (n) of 2, 3 and 4 deduced from Equation 5.4. From the results presented in Figure 5.3, a value of 2 for the stoichiometric coefficient of the extractant ($n = 2$) gave a satisfactory agreement between the values of pH and the values of the log D_M - n log [0.6-n$[M]_{org}$] with an R^2 value of 0.99. Therefore, two moles of Cyanex 272 were needed to transfer one mole of Zn^{2+} from the PLS to the organic phase, as previously described in the literature [34,39].

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 the PLS to the organic phase without co-extracting other metals in huge amounts.

5.5.3.5 Effect of the extraction stage number

Three extraction stages were conducted to determine the effectiveness of Zn extraction from the PLS. Table 5.6 shows the residual amounts of Zn present in the PLS obtained after each stage of extraction. The Zn extraction efficiencies from the PLS 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.

5.5.3.6 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 PLS 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 (PLS). Therefore, the above operating conditions were applied to the PLS in triplicate to verify the effectiveness and the reproducibility of the solvent extraction process we developed. Moreover, these additional experiments were performed on the PLS 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 PLS. The results obtained are summarized in Table 5.7. According to these results, it was found that approximately 72.0% of the Zn were extracted from the PLS after 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% (14.3 g) whereas 98.8% of Fe (0.21 g), 7.13% of Cd (0.30 g), 2.35% of Co (0.01 g), 4.12% of Mn (1.61 g) and 7.28% of Ni (0.34 g) were also co-extracted with Zn during its transfer to the organic phase.

5.5.3.7 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_2SO_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 and are presented in Table 5.8. 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_2SO_4 concentrations of 0.15 M and 0.40 M, respectively. According to these results, an increase in the concentration of H_2SO_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_2SO_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_2SO_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 $ZnSO_4$ for electrodeposition and the second stripping was applied for Fe removal. The results presented in Table 5.8 showed that only the Zn was transferred to the stripping solution during the first stripping step performed at 0.4 M H_2SO_4. The Fe presents in the organic phase was then stripped using 1.0 M of H_2SO_4 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.

5.5.4 Zn electrodeposition

Figure 5.4 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 mainly contains Zn (19 $\pm$ 1 g/L), Mn (23 $\pm$ 1 g/L), Cd (3.3 $\pm$ 0.1 g/L), Ni 3.2 $\pm$ 0.1 g/L), Co (0.25 $\pm$ 0.01 g/L), and Fe (0.53 $\pm$ 0.05 g/L). Electrodeposition experiments were carried out on the stripping solution obtained from the experiments conducted in the previous section to recover the Zn. Figure 5.5 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 H_2SO_4 from unreacted sulfate ions and hydrogen ions dislodged during water decomposition [27]. 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 $ZnSO_4$ 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 MnO_2 rather than being deposited on the cathode [40]. 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 64 ± 7%, 82 ± 2%, and 48 ± 5% for the experiments carried out at pH = 2.0, 2.5 and 3.0, respectively after 180 min. The current efficiencies (CE) were also calculated according to the Equation 5.10 and were estimated at 51.3%, 40.3% and 22.3% for pH = 2.0, 2.5 and 3.0, respectively. These results indicate 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 MEB-EDS to determine its composition. The result from the EDS analysis presented in Figure 5.6 showed that there was only Zn in the metallic powder.

5.6 Conclusions

In this study, the Zn initially present in a PLS containing high amounts of Mn, Cd, Ni, Co, and Fe (28 ± 2 g Mn/L, 20 ± 2 g Zn/L, 3.2 ± 0.2 g Cd/L, 3.5 ± 0.3 g Ni/L, 0.26 ± 0.02 g Co/L and 0.53 ± 0.05 g Fe/L) 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 PLS. 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°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 should also be considered in further works.

5.7 Aknowledgments

The authors acknowledge the Natural Sciences and Engineering Research Council of Canada for the financial support to this research (grant RGPIN-2014-04794).

5.8 References

[1] RIS International, Canadian Consumer Battery baseline Study, Environment Canada, Canada, 2007, 90 p.

[2] Klaassen P & Lagourgue D, 2012, Available at this address: http://www.cw2rc.ca/Portals/0/2015%20Presentations/DL%20PK%20FINAL%20v2.pdf Consulted on December 2016.

[3] R. Bonhomme, P. Gasper, J. Hines, J.P. Miralda, Economic feasibility of a novel alkaline battery recycling process. Rapport technique, Worcester Polytechnic Institute, Worcester, MA, USA, 2013, 95 p.

[4] Call2Recycle, 2012, Available at this adress: http://www.call2recycle.ca/british-columbia. Consulted on April 2016.

[5] E.Y. Yazici, H. Deveci, Extraction of metals from waste printed circuit boards (WPCBs) in H_2SO_4-$CuSO_4$-NaCl solutions, Hydrometallurgy 139 (2013) 30-38.

[6] F. Ferella, I. De Michelis, F. Beolchini, V. Innocenzi, F. Veglio, Extraction of zinc and manganse from alkaline and zinc-carbon batteries by citric-sulphuric solution, Int. J. Chem. Eng. (2010) Article ID 659434, 13 p.

[7] S. Frohlich, D. Sewing, The BATENUS process for recycling mixed battery waste, J. Power Sources 57 (1995) 27-30.

[8] G. Furlani, E. Moscardini, F. Pagnanelli, F. Ferella, F. Veglio, L. Toro, Recovery of manganese from zinc alkaline batteries by reductive acid leaching using carbohydrates as reductant, Hydrometallurgy 99 (2009) 115-118.

[9] Y.Q. Li, G.X. Xi, The dissolution mechanism of cathodic active materials of spent Zn-Mn batteries in HCl, J. Hazard. Mater. 127 (2005) 244-248.

[10] E. Sayilgan, T. Kukrer, F. Ferella, A. Akcil, F. Veglio, M. Kitis, Reductive leaching of manganese and zinc from spent alkaline and zinc-carbon batteries in acidic media, Hydrometallurgy 97 (2009) 73-79.

[11] G. Senanayake, S.M. Shin, A. Senaputra, A. Winn, D. Pugaev, J. Avraamides, J.S. Sohn D.J. Kim, Comparative leaching of spent zinc-manganese-carbon batteries using sulfur dioxide in ammoniacal and sulfuric acid solutions, Hydrometallurgy 105 (2010) 36-41.

[12] F. Habashi, Textbook of hydrometallurgy Métallurgie Extractive, Québec, Québec, Canada, 1999, 689 p.

[13] M.B.J.G Freitas, V.C. Pegoretti, M.K. Pietre, Recycling manganese from spent Zn-MnO_2 primary batteries, J. Power Sources 164 (2007) 947-952.

[14] P.A. Tasker, Ion exchange and solvent extraction: Supramolecular aspects of solvent extraction, Taylor and Francis Group, New-York, NY, USA, 2014, 273 p.

[15] K. Provazi, B.A. Campos, D.C. Espinosa, J.A. Tenorio, Metal separation from mixed types of batteries using selective precipitation and liquid-liquid extraction techniques, Waste Manag. 31 (2011) 59-64.

[16] V. Innocenzi, F. Veglio, Separation of manganese, zinc and nickel from leaching solution of nickel-metal hydride spent batteries by solvent extraction, Hydrometallurgy 129 (2012) 50-58.

[17] Y.J. Park, D.J. Fray, Separation of zinc and nickel ions in a strong acid through liquid-liquid extraction. J. Hazard. Mater. 163 (2009) 259-265.

[18] R.K. Biswas, M.A. Habib, A.K. Karmakar, S. Tanzin, Recovery of manganese and zinc from waste Zn-C cell powder: Mutual separation of Mn(II) and Zn(II) from leach liquor by solvent extraction technique, Waste Manag. 51 (2015) 149-156.

[19] M.T. Coll, A. Fortuny, C.S. Kedari, A.M. Sastre, Studies on the extraction of Co(II) and Ni(II) from aqueous chloride solutions using Primene JMT-Cyanex 272 ionic liquid extractant. Hydrometallurgy 125 (2012) 24-28.

[20] J. Rydberg, M. Cox, C. Musikas, G.R. Choppin, Solvent extraction principles and practice – Second edition, Revised and Epanded. CRC Press, Boca Raton, FL, USA, 2004, 480 p.

[21] Cytec, Cyanex 272 extractant, Cytec Industries Inc., 2008, 16 p. Available at: https://www.cytec.com/sites/default/files/datasheets/CYANEX%%20272%%20Brochure.pdf, Consulted on April 2016.

[22] G. Owusu, Selective extractions of Zn and Cd from Zn-Cd-Co-Ni sulphate solution using di-2-ethylhexyl phosphoric acid extractant, Hydrometallurgy 47 (1998) 205-215.

[23] D. Darvishi, D.F. Haghenas, E. Keshavarz Alamdari, Extraction of Zn, Mn and Co from Zn-Mn-Co-Cd-Ni containing solution using D2EHPA, Cyanex 272 and Cyanex 302, Int. J. Eng. 24 (2011) 183-192.

[24] M. Hutton-Ashkenny, D. Ibana, K.R. Barnard, Reagent selection for recovery of nickel and cobalt from nitric acid nickel laterite leach solutions by solvent extraction, minerals Eng. 77 (2015) 42-51.

[25] R.K. Jha, K.K. Gupta, P.G. Kulkarni, P.B. Gurba, P. Janardan, R.D. Changarani, P.K. Dey, P.N. Pathak, V.K. Manchanda, Third phase formation in the extration of U(VI), Th (IV) and Pu (IV) by n,n-dialkyl aliphatic amides, Symposium on Emerging Trends in Separation Science and Technology (SESTEC-2006), Mumbai, India, 2006, 5 p.

[26] A.C. Scott, R.M. Pitblado, G.W. Barton, A mathematical model of a zinc electrowinning cell, Proceedings of the Twentieth International Symposium on the Application of Computers and Mathematics in the mineral Industries, Volume 2: Metallurgy, Johannesburg, South Africa, 1987, pp. 51-62.

[27] N. Almeida MF, Xara SM, Delgado J & Costa CA (2006) Characterization of spent AA household alkaline batteries. Waste Manag 26(5):466-476.

[28] J. Carrillo-Abad, M. Garcia-Gabaldon, I. Ortiz-Gandara, E. Bringas, A.M. Urtiaga, I. Ortiz, V. Perez-Herranz, Selective recovery of zinc from spent pickling, baths by the combination of membrane-based solvent extraction and electrowinning technologies, Separation Purification Technology 151 (2015) 232-242.

[29] A.L. Salgado, A.M.O. Veloso, D.D. Pereira, G.S. Gontijo, A. Salum, M.B. Mansur, Recovery of zinc and manganese from spent alkaline batteries by liquid-liquid extraction with Cyanex 272, J. Power Sources 115 (2003) 367-373.

[30] W.A. Rickelton, The removal of cadmium impurities from cobalt-nickel solutions by precipitation with sodium diisobutyldithiophosphinate, Hydrometallurgy 50 (1998) 339-344.

[31] K.C. Nathsarma, N. Devi, Separation of Zn(II) and Mn(II) from sulphate solutions using sodium salts of D2EHPA, PC88A and Cyanex 272, Hydrometallurgy 84 (2006) 149-154.

[32] SH. Eskandari and M.R. Najafabadi, Effect of TBP on Zn solvent extraction from chloride media by D2EHPA, Available at: http://hmpjournal.znu.ac.ir/Portals/0/Cache/2015-2-6.pdf, Consulted on April 2016.

[33] B. Gupta, P. Malik, A. Deep, Extraction of uranium, thorium and lanthanides using Cyanex 923: Their separations and recovery from monazite, J. Radioanalytical & Nuclear Chemistry 251 (2002) 451-456.

[34] J. Hereijgersa, T. Vandermeersch, N. Van Oeteren, H.Verelst, H. Song, D. Cabooter, T. Breugelmans, W. De Malsche, Separation of Co(II)/Ni(II) with Cyanex 272 using a flat membrane microcontactor: Extraction kinetics study, J. Membrane Sci. 499 (2016) 370-378.

[35] D.H. Fatmehsari, D. Darvishi, S. Etemadi, A.R.E. Hollagh, E.K. Alamdari, A.A. Salardini, Interaction between TBP and D2EHPA during Zn, Cd, Mn, Cu, Co and Ni solvent extraction: A thermodynamic and empirical approach, Hydrometallurgy 98 (2009) 143-147.

[36] T. Hosseini, F. Rashchi, E. Vahidi, N. Mostoufi, Investigating the synergistic effect of D2EHPA and Cyanex 302 on zinc and manganese separation, Separation Science & Technology 45 (2010) 1158–1164.

[37] X.P. Chen, B. Xu, T. Zhou, D.P. Liu, H. Hu, S.Y. Fan, Separation and recovery of metal values from leaching liquor of mixed-type of spent lithium-ion batteries, Separation & Purification Technology 144 (2015) 197-205.

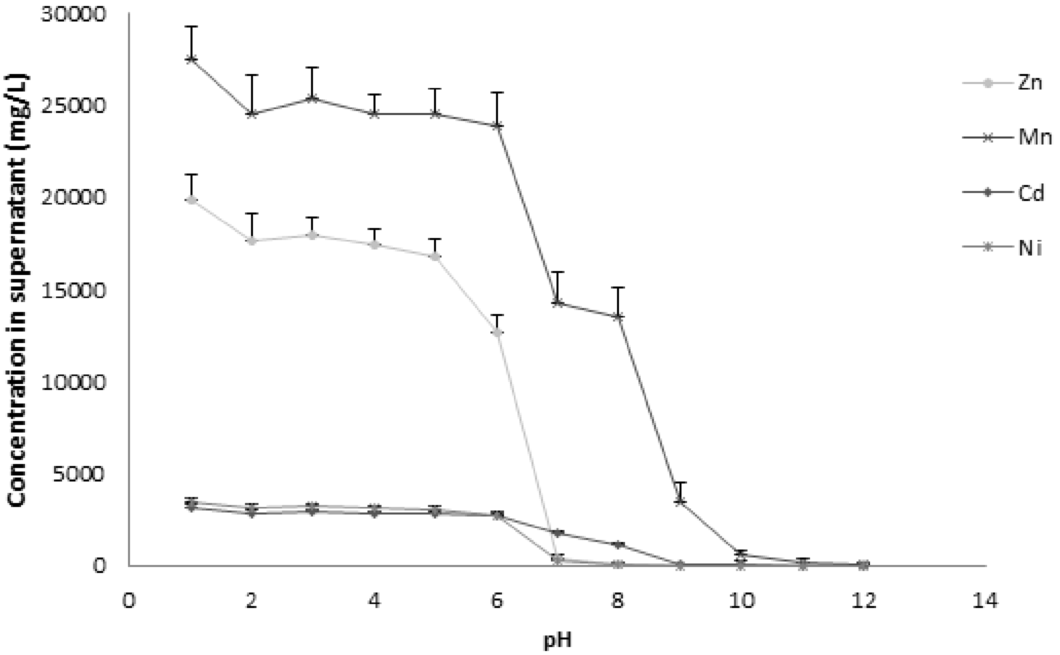
[38] I.Y. Fleitlikh, G.L. Pashkov, N.A. Grigorieva, L.K. Nikiforova, O.A. Logutenko, Zinc extraction from sulfate media with bis(2,4,4-trimethylpentyl)dithiophosphinic acid in the absence and in the presence of electron donor additives, Hydrometallurgy 110 (2011) 73-78.

[39] A. Yilmaz, G. Arslan, A. Tor, I. Akin, Selectively facilitated transport of Zn(II) through a novel polymer inclusion membrane containing Cyanex 272 as a carrier reagent, Desalination 277 (2011) 301-307.

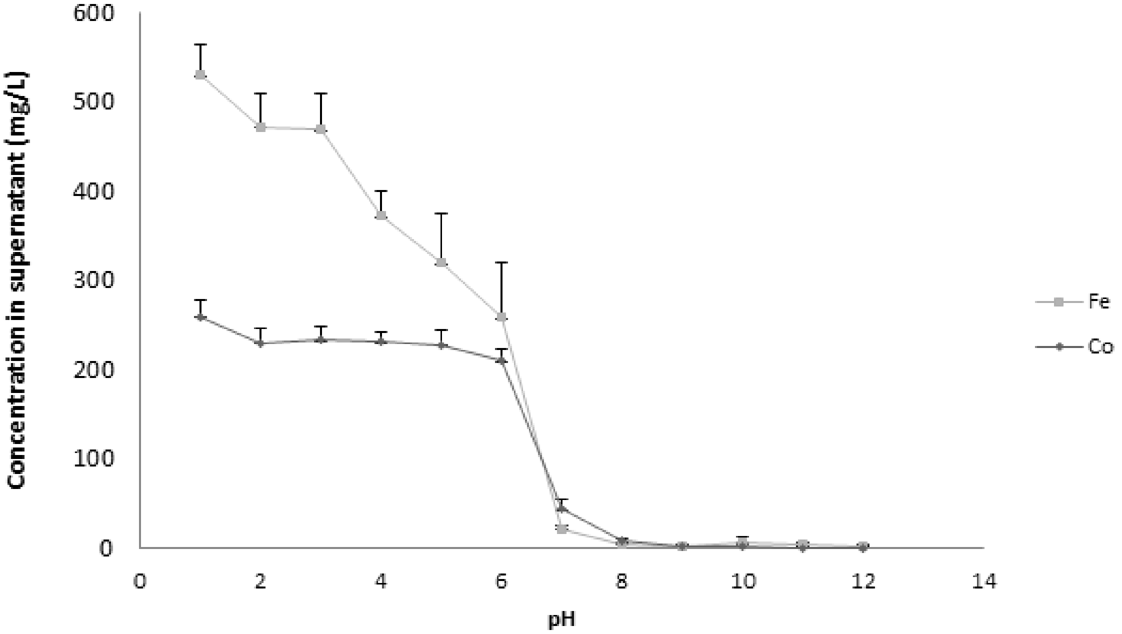
[40] C. Poinsignon, Procédé de traitement de piles usagée par électrolyse, Grenoble, France, 1994.

5.9 List of figures

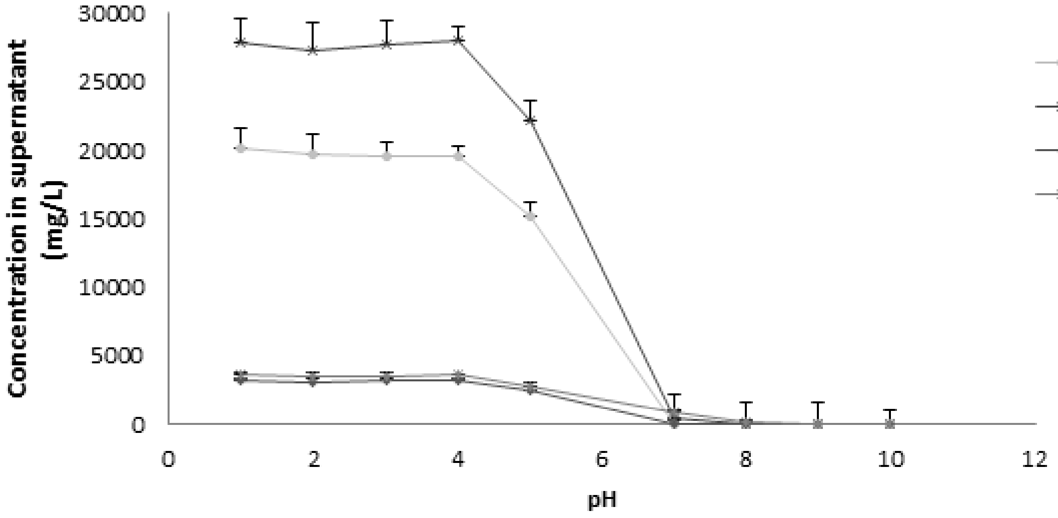
5.10 List of tables


Concentration in supernatant (mg/L)
30000
25000
20000
15000
10000
5000
0
0
2
4
6
8
10
12
14
pH
Zn
Mn
Cd
Ni

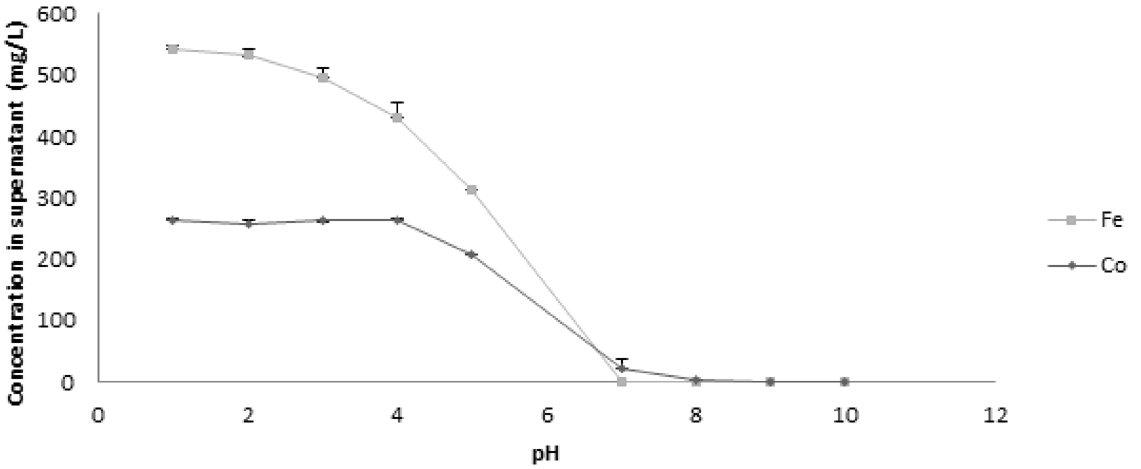
a.


Concentration in supernatant (mg/L)
600
500
400
300
200
100
0
0
2
4
6
8
10
12
14
pH
Fe
Co

b.



c.



d.

Figure 5.1 **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+Na_2CO_3 (c., d.) at 25°C**

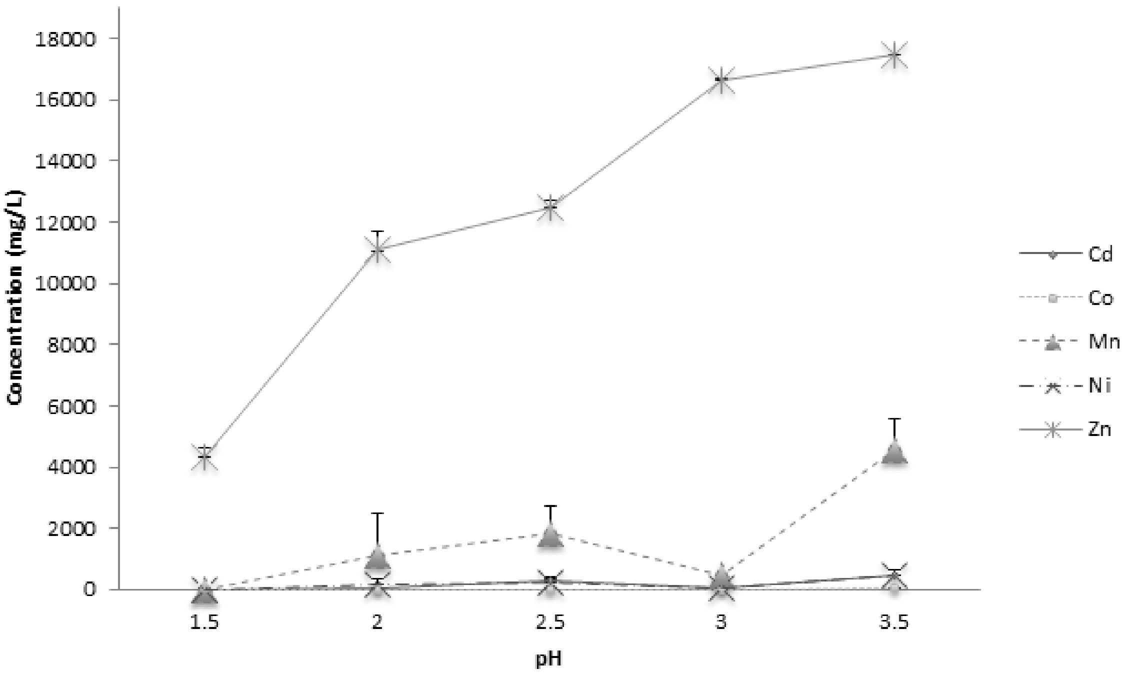


Figure 5.2 **Amounts of Zn, Mn, Cd, Co and Ni extracted in the organic phase after solvent extraction using Cyanex 272 (20%, v/v) at different pHs (single extraction stage; T = 50°C, O/A ratio = 2/1, [TBP] = 2% (v/v), residence time = 10 min)**

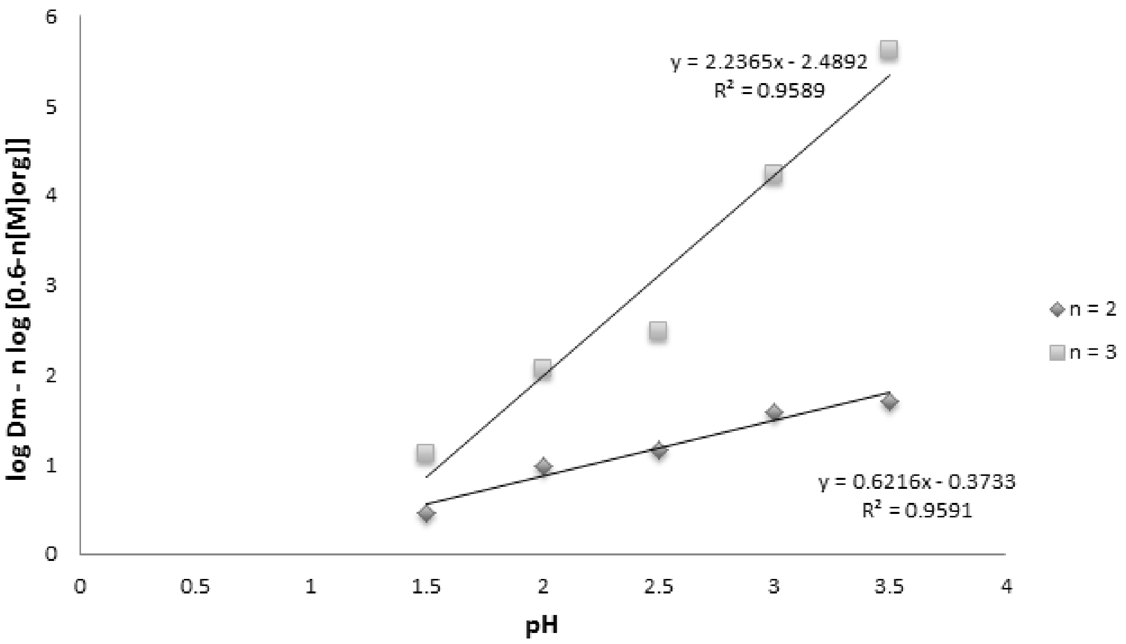
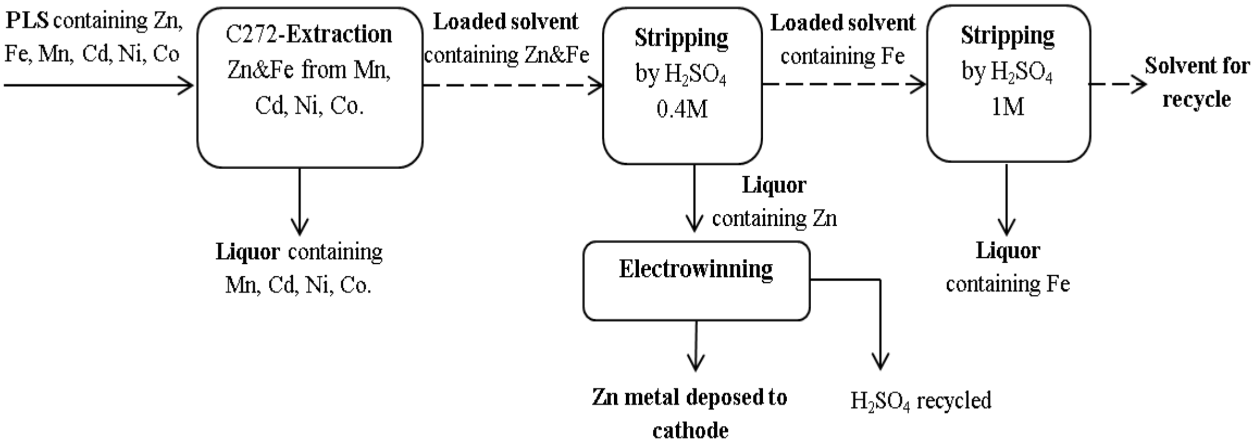


Figure 5.3 Plot of log Dm - n log [0.6-n[M]org] versus pH for the aqueous phase (single extraction stage; T = 50°C; O/A ratio = 2/1; [Cyanex 272] = 20% (v/v) in kerosene; [TBP] = 2% (v/v); residence time = 10 min)



**** 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***

Figure 5.4 **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**

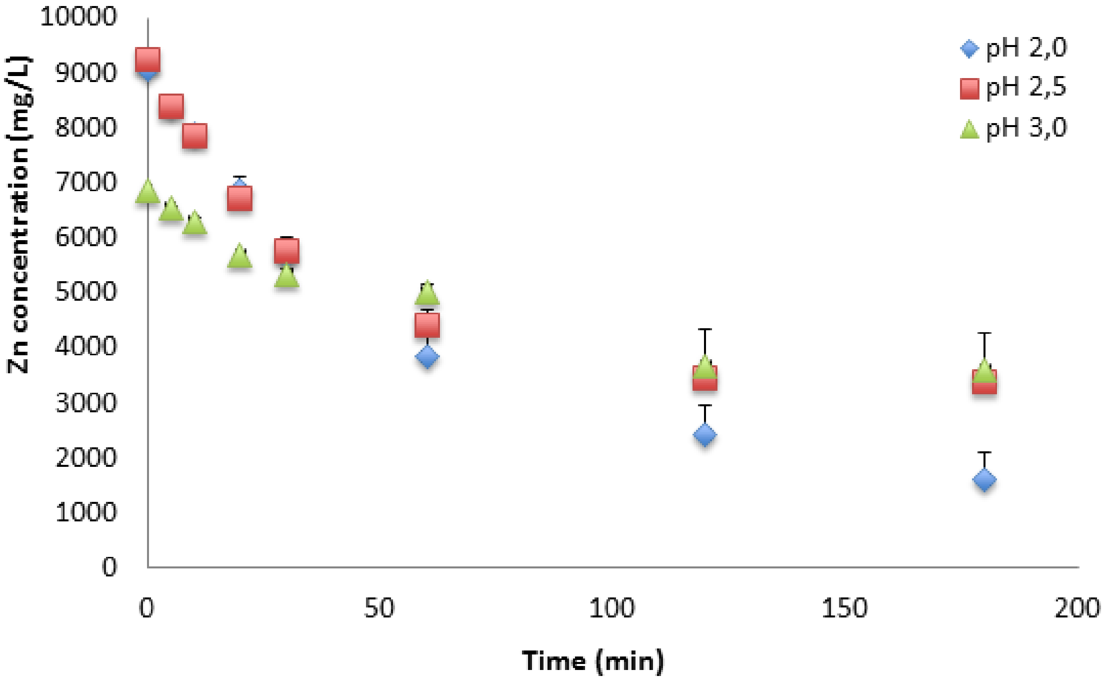


Figure 5.5 Kinetic of Zn electrodeposition observed at different pH values (current density = 360 A/m^2, agitation rate = 300 rpm, T = 25°C, residence time = 180 min)

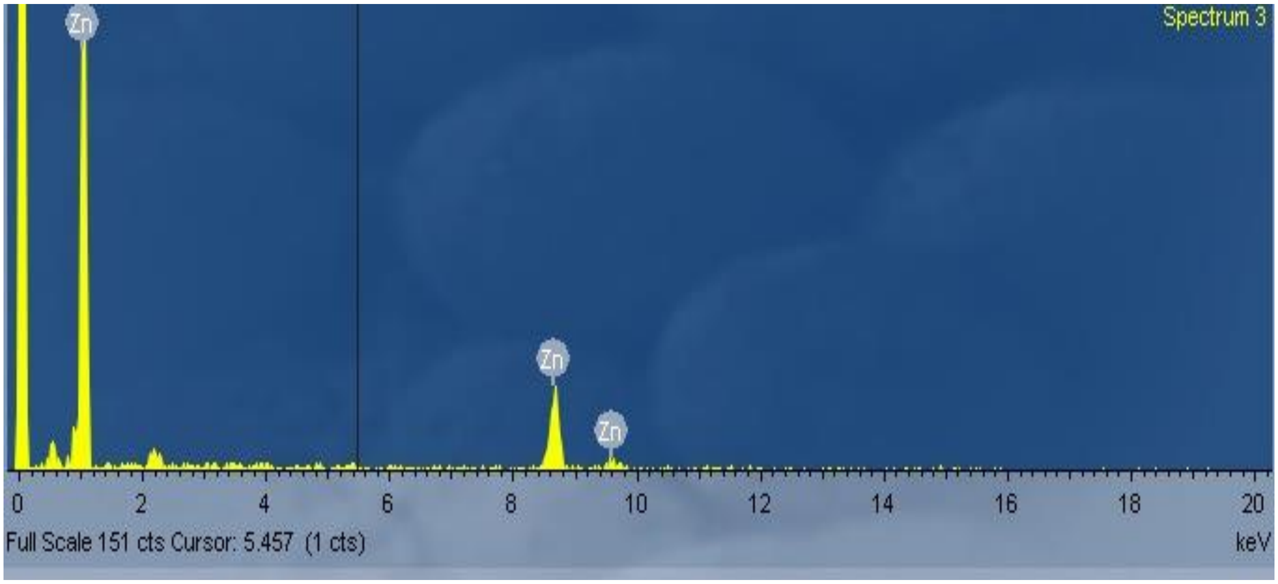


Figure 5.6 **Composition of the metallic powder emerging from the electrodeposition process using MEB-EDS**

Table 5.1 **Characteristics of unsorted spent batteries pregnant leaching solution and synthetic solution used for precipitation and solvent extraction assays, respectively**

Composition elements (g/L)	Pregnant leaching solution	Synthetic solution
Major metals		
Cd	3.7 ± 0.2	3.3 ± 0.1
K	4.6 ± 0.1	3.6 ± 0.1
Mn	28 ± 2	23 ± 1
Ni	3.5 ± 0.3	3.2 ± 0.1
Zn	20 ± 2	19 ± 1
Na	18 ± 7	5.2 ± 0.6
S	5.0 ± 0.1	30 ± 1
Minor metals		
Al	0.08 ± 0.01	0.08 ± 0.01
Ca	0.05 ± 0.01	0.29 ± 0.15
Co	0.26 ± 0.02	0.25 ± 0.01
Fe	0.53 ± 0.05	0.01 ± 0.00
Mg	0.01 ± 0.01	0.08 ± 0.02

Table 5.2 **Selective recovery of Fe from a solution containing Zn (20 ± 2 g/L), Mn (28 ± 2 g/L), Cd (3.7 ± 0.2 g/L), Ni (3.5 ± 0.3 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_2O_2**

Mass of H_2O_2 (added)	**Precipitation efficiencies (%)**		
	100% S*	**125% S**	**200% S**
Major metals			
Zn	6.9 ± 1.4	4.3 ± 1.7	6.7 ± 4.2
Mn	7.8 ± 0.1	3.3 ± 1.4	5.2 ± 2.6
Cd	7.2 ± 1.6	3.1 ± 1.6	5.0 ± 2.8
Ni	6.5 ± 1.2	2.7 ± 1.6	4.7 ± 2.2
Minor metals			
Fe	69.3 ± 12.3	92.4 ± 1.8	88 ± 6
Co	5.51 ± 1.41	2.78 ± 1.23	5.1 ± 2.7

** S: Stoichiometric value of H_2O_2 required to oxidize all the Fe^{2+} ions present in the PLS to Fe^{3+} ions.*

Table 5.3 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^oC, $[Zn]_0$ = 19 ± 1 g/L, $[Mn]_0$ = 23 ± 1 g/L, $[Cd]_0$ = 3.3 ± 0.1 g/L, $[Ni]_0$ = 3.2 ± 0.1 g/L and $[Co]_0$ = 0.25 ± 0.01 g/L)

TBP concentration (%)	**Extraction efficiency (%)**		
	0	**2**	**5**
Major metals			
Zn	54.4 ± 3.1	59.7 ± 6.1	49.2 ± 2.1
Mn	2.98 ± 0.18	9.20 ± 4.45	6.26 ± 2.04
Cd	3.05 ± 0.02	9.96 ± 4.47	7.22 ± 2.06
Ni	2.98 ± 0.18	9.66 ± 4.38	6.91± 2.22
Minor metals			
Co	2.17 ± 0.04	10.9 ± 1.5	5.73 ± 1.67

Table 5.4 **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^oC, $[Zn]_0$ = 19 ± 1 g/L, $[Mn]_0$ = 23 ± 1 g/L, $[Cd]_0$ = 3.3 ± 0.1 g/L, $[Ni]_0$ = 3.2 ± 0.1 g/L, and $[Co]_0$ = 0.25 ± 0.01 g/L)**

Residence time (min)	**Extraction efficiencies from the synthetic solution (%)**				
	5	**10**	**20**	**30**	**60**
Major metals					
Zn	62.6 ± 4.4	60.0 ± 0.4	60.7 ± 0.1	60.0 ± 0.5	60.9 ± 0.7
Mn	12.1 ± 10.6	3.70 ± 1.19	3.96 ± 0.61	2.58 ± 0.91	2.75 ± 0.77
Cd	11.3 ± 11.0	2.38 ± 0.83	2.72 ± 0.46	1.23 ± 0.67	1.40 ± 0.77
Ni	11.8 ± 11.0	2.95 ± 1.16	3.18 ± 0.60	1.73 ± 0.96	1.92 ± 0.90
Minor metals					
Co	11.8 ± 9.6	3.02 ± 0.88	2.24 ± 0.32	1.57 ± 1.11	3.57 ± 1.38

Table 5.5 **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 ± 1 g/L, $[Mn]_0$ = 23 ± 1 g/L, $[Cd]_0$ = 3.3 ± 0.1 g/L, $[Ni]_0$ = 3.2 ± 0.1 g/L, and $[Co]_0$ = 0.25 ± 0.01 g/L)**

pH	D_{Zn}	D_{Mn}	D_{Cd}	$\beta_{Zn/Mn}$	$\beta_{Zn/Cd}$
1.5	0.33	0.01	0.01	56.9	61.1
2.0	1.54	0.00	0.01	353	110
2.5	2.35	0.04	0.07	57.4	34.2
3.0	40.5	0.08	0.06	538	643
3.5	330	0.90	0.77	366	431

Table 5.6 **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 ± 0.8 g/L, $[Mn]_0$ = 23 ± 1 g/L, $[Cd]_0$ = 3.3 ± 0.1 g/L, $[Ni]_0$ = 3.2 ± 0.1 g/L, and $[Co]_0$ = 0.25 ± 0.01 g/L)**

Nb of stages	**Amounts of metals present in the aqueous phase (g)**		
	1	**2**	**3**
Major metals			
Zn	6.14 ± 0.96	0.16 ± 0.13	0.01 ± 0.01
Mn	23.4 ± 1.2	22.5 ± 1.8	21.3 ± 1.9
Cd	3.22 ± 0.16	3.15 ± 0.22	3.05 ± 0.22
Ni	3.03 ± 0.16	2.97 ± 0.21	2.89 ± 0.19
Minor metals			
Co	0.241 ± 0.012	0.236 ± 0.030	0.230 ± 0.030

Table 5.7 **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)**

Nb of extraction stage	**Initial**	**Residual concentration in aqueous phase (g/L)**	
		1	**2**
Major metals			
Zn	20 ± 2	5.0 ± 0.8	0.29 ± 0.13
Mn	28 ± 2	26 ± 2	26 ± 1
Cd	3.7 ± 0.2	2.9 ± 0.3	2.9 ± 0.3
Ni	3.5 ± 0.3	3.0 ± 0.2	3.1 ± 0.3
Minor metals			
Fe	0.53 ± 0.05	0.32 ± 0.03	0.04 ± 0.02
Co	0.26 ± 0.02	0.26 ± 0.01	0.26 ± 0.02

Table 5.8 **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 H_2SO_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_2SO_4; t = 10 min; T = 50°C) for the recovery of Fe**

[H_2SO_4]	**Initial amount in organic phase**	**Metal amounts in the stripping solution (g)**		
		0.15 M	**0.40 M**	**1.00 M**
Zn	20	13 ± 0	16 ± 0.	0.02 ± 0.00
Fe	0.44	n.a.*	0.19 ± 0.18	0.10 ± 0.00

**n.a.:* *In this case, metal concentration was not investigated.*

6 CHAPITRE 6

SELECTIVE RECOVERY OF CD (II), MN (II) AND NI (II) FROM UNSORTED SPENT BATTERIES USING SOLVENT EXTRACTION AND ELECTRODEPOSITION

Revue : Hydrometallurgy

Auteurs : Kulchaya Tanong[a], Lan Huong Tran[b], Lucie Coudert[c], Guy Mercier[d], Jean-Francois Blais[e*]

[a] Ph.D. student, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-4677, Fax: (418) 654-2600, email: kulchaya.tanong@ete.inrs.ca

[b] Research Associate, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-2550, Fax: (418) 654-2600, email: lan.huong.tran@ete.inrs.ca

[c] Research Associate, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-3793, Fax: (418) 654-2600, email: lucie.coudert@ete.inrs.ca

[d] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-2633, Fax: (418) 654-2600, email: guy.mercier@ete.inrs.ca

[e] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, Qc, Canada, G1K 9A9, Phone: (418) 654-2575, Fax: (418) 654-2600, email: jean-francois.blais@ete.inrs.ca

*Corresponding author: Tel: (418) 654-2575, Fax: (418) 654-2600,

email: jean-francois.blais@ete.inrs.ca

Note

L’étudiante est le premier auteur de cet article. Toutes les manipulations, le traitement des données ainsi que la rédaction ont été effectués par l’étudiante sous la supervision des autres co-auteurs.

Modifications exigées par le comité de lecture de la revue

Les commentaires des réviseurs n’ont pas été reçus.

6.1 Résumé

Cet article traite de la récupération sélective du Cd, du Co, du Mn et du Ni présents dans une solution de lixiviation enrichie (PLS). Pour parvenir à récupérer ces métaux, différents procédés hydrométallurgiques ont été utilisés comme l'extraction par solvant, la précipitation et l'électrodéposition. Dans un premier temps, les métaux présents initialement dans les piles usagées et non triées ont été lessivés en utilisant une solution de H_2SO_4 et un agent réducteur ($Na_2S_2O_5$). La solution PLS a été mélangée avec le Cyanex 272 pour extraire séléctivement le Zn(II) à partir de la solution contenant du Cd(II), Mn(II), Co(II) et Ni(II). Ensuite, le Mn(II) et le Cd(II) ont été extraits de la solution aqueuse en utilisant une solution organique contenant 30% (v/v) d'acide di-2-éthylhexyl-phosphorique (D2EHPA -agent d'extraction), 5% (v/v) de tributylphosphate (TBP) dilué dans du kérosène. Les conditions optimales pour extraire le Cd et le Mn sont les suivantes: deux étapes d'extraction, un ratio organique/aqueuse (O/A) égal à 2/1, un pH de 2,6 à 2,9 à 50°C. Une étape de lavage à l'aide de H_2SO_4 (1,2 M) avec un rapport O/A de 4/1 a ensuite été effectuée, suivie par une étape de dépôt électrolytique pour récupérer sélectivement 99,7% du Cd. Ensuite, une solution de Na_2CO_3 a été utilisée pour précipiter le Mn(II) sous forme de $MnCO_3$. La solution appauvrie en Zn, Mn et Cd a été mélangée avec la solution organique contenant 10% (v/v) de Cyanex 272, 2% (v/v) de TBP dans du kérosène (O/A = 2/1, pH 5,0-6,0) afin d'éliminer le Co, le Cd et le Mn résiduels. À la fin, la solution riche en Ni a été traitée par précipitation pour former du carbonate de nickel.

Mots clés: Extraction par solvant, D2EHPA, Cyanex 272, Électrodéposition, Précipitation, Piles usagées

6.2 Abstract

This study addressed the selective recovery of Cd, Co, Mn and Ni from a pregnant leach solution (PLS) using solvent extraction, electrodeposition and precipitation. The metals initially present in unsorted spent batteries were leached using H_2SO_4 and a reducing agent. The PLS was mixed with Cyanex 272 to extract Zn(II) from the Cd(II), Mn(II), Co(II) and Ni(II) solution selectively. Next, Mn(II) and Cd(II) were extracted using 30% (v/v) di-2ethylhexyl-phosphoric acid (D2EHPA) combined with 5% (v v^{-1}) tributylphosphate (TBP) diluted in kerosene. Optimal experimental conditions were determined to include two stages of extraction, an organic/aqueous (O/A) ratio of 2/1, and a pH of 2.6 to 2.9 at 50°C. The solution was then stripped using H_2SO_4 (1.2 M) with an O/A ratio of 4/1 and electrodeposition was used to recover 99.7% of Cd selectively. Precipitation using Na_2CO_3 was applied to recover $MnCO_3$. Finally, up to 100% of the Ni(II) present in the Zn-, Mn-, Cd- and Co-depleted PLS from the solvent extraction (10% (v v^{-1}) Cyanex 272 and 2% (v v^{-1}) TBP in kerosene, O/A ratio of 2/1, pH of 5.0-6.0) were recovered by precipitation as carbonates.

Keywords: Solvent extraction; D2EHPA; Cyanex 272; Electrodeposition; Precipitation; Spent batteries

6.3 Introduction

In Canada, the “polluter pays” principle is applied to divert spent batteries from landfill sites and to recycle the valuable metals present as raw materials in various industries (RISInternational, 2007). In 2010, alkaline batteries were the most consumed batteries in the Province of Quebec (108,225,000 units), followed by Zn-C batteries (37,541,000 units) and lithium batteries (7,007,000 units) (Roberge, 2010). The consumption of secondary cells (rechargeable batteries) were less important in that year, with 5,214,000 units of Ni-Cd batteries sold, followed by Ni-MH batteries (2,442,000 units) and Li-ion batteries (999,000 units) (Roberge, 2010). Based on the service life of both primary and secondary batteries, the number of spent batteries discarded in the Province of Quebec in 2015 was estimated at 3,092 t for alkaline batteries, 974 t for Zn-C batteries, 114 t for lithium batteries, 772 t for Ni-Cd batteries, 171 t for Ni-MH batteries, 90 t for small sealed lead batteries and 54 t for Li-ion batteries (Roberge, 2010). However, a gradual decrease in the production of Ni-Cd batteries is expected as they are considered hazardous waste; they are to be replaced by Ni-MH batteries, Li-ion batteries or sodium-ion batteries (Charette, 2014). While Ni-Cd batteries are supposed to be completely replaced in the coming decades, there will still be a need to treat them when they reach their end of life. Moreover, Cd has great potential to be recycled within photovoltaic film applications, so its recovery would be more economically and environmentally practical than its discharge into landfill sites (Rudnik and Nikiel, 2007).

A review of the numerous studies that have solubilized the valuable metals present in spent batteries reveals that hydrometallurgical processes are highly efficient (Biswas et al., 2015;

Buzatu et al., 2013; Meshram et al., 2016), environmentally friendly and economically attractive due to their low energy consumption and their low greenhouse gas emissions compared to pyrometallurgical processes. In this study, the use of both inorganic acid leaching and solvent extraction followed by chemical and/or electrochemical processes was demonstrated effectively to recover significant amounts of multiple metals while also enabling high metal selectivity and maintaining purity.

6.4 Solvent extraction application and mechanism

6.4.1 Solvent extraction stage

Cyanex 923 is an organic extractant composed of four trialkylphosphine oxides: trioctylphosphine oxide, dioctylmonohexylphosphine oxide, dihexylmonooctylphosphine oxide and trihexylphosphine oxide (Larsson et al., 2012). The mechanism of metal extraction from a chloride medium is described in Equation 6.1 (Reddy and Priya, 2006).

$$\mathbf{x\ M^{n+}_{(aq)} + y\ H^{+}_{(aq)} + z\ Cl^{-}_{(aq)} + w\ S_{(org)} \leftrightarrow (H_yM_xCl_z)^{n+y-z}\ w\ S_{(org)}} \qquad \textbf{(Equation 6.1)}$$

Where M^{n+} is the metal ion present in the aqueous phase and S is the ligand concentration present in the organic phase.

This organic solvent was used to selectively recover Cd(II) from Ni(II) and Co(II) in a pregnant leach solution (PLS) derived from a hydrometallurgical process applied to spent Ni-MH batteries (Larsson et al., 2012). Gupta et al. (2001) studied the selective recovery of Cd(II) from a mixed electrolyte containing Al(III), Mn(II), Co(II), Ni(II), Cu(II), Hg(II) and Pb(II) in HCl (2 M). After 5 min at 25°C in the presence of Cyanex 923 (0.2 M, O/A ratio = 1), 99% of Cd(II) was selectively recovered from the organic phase while 99% of Mn(II) remained in the aqueous phase (Gupta, 2001).

Cyanex 272 and D2EHPA are phosphorus organic extractants that allow the selective extraction of metals from the PLS via cation-exchange mechanisms (Equation 6.2) through their phosphinic [R_2PO-OH] (Cyanex 272) and phosphoric [$(RO)_2PO-OH$] (D2HEPA) group functions.

$$M^{n+} + n\,HA \leftrightarrow MA_n + n\,H^+ \qquad \text{(Equation 6.2)}$$

Where HA is the extractant (D2EHPA or Cyanex 272) and M^{n+} is the metal.

The selective separation of metals using a specific extractant depends on various factors such as the constant of stability, the enthalpy of formation, the soft-base characteristics of both metals and extractant, the pH of the solution, etc.

These extractants were widely applied to selectively extract Zn(II) from leaching solutions containing various metals. Pereira et al. (2007) studied the use of D2EHPA to selectively recover Zn(II) from a solution containing Cd(II), Co(II), Fe(II), Pb(II), Ca(II), mg(II), Mn(II) and Ni(II) at pH = 2.5. According to these authors, the sequence of metal extraction obtained at pH = 2.5 was as follows: Zn(II) > Fe(II) > Pb(II) ~ Ca(II) ~ Mn(II) ~ Cd(II) > mg(II) ~ Co(II) ~ Ni(II). Their results highlighted that all Zn could be extracted using 20% (v v^{-1}) D2EHPA at pH = 2.5 (O/A ratio of 1/1 for 10 min at 28^{o}C). When using Cyanex 272, 50% of Zn(II) was extracted at pH ~ 1.78 (20% (v v^{-1}) Cyanex 272, O/A ratio of 1/1 at 50°C) from the 5.24 g Zn L^{-1} and 6.69 g Mn L^{-1} feeding solution, while 50% of Mn(II) was extracted at a pH of approximately = 3.78 (Salgado, 2003). Based on the above information, Zn can be separated from Mn at a pH of approximately = 2 ($\Delta pH_{1/2}=pH_{1/2,Mn}-pH_{1/2,Zn}$).

Tsakiridis and Agatzini-Leonardou (2004) tested Cyanex 272 to selectively recover Co(II) from a feeding solution containing Ni (3.80 g L^{-1}), Mg (5.75 g L^{-1}) and Co (0.63 g L^{-1}). According to their results, all Co(II) and Mg(II) were selectively extracted at pH ~ 5.5 when an organic phase composed of 20% (v v^{-1}) Cyanex 272 and 5% (v v^{-1}) TBP diluted in Exxsol D-80 at 40°C was applied.

The metal extraction selectivity of D2EHPA obtained with increasing pH in a solution containing sulfates was defined as follows: Fe(II) > Zn(II) > Mn(II) > Cd(II) > Cu(II) > Mg(II) > Co(II) > Ni(II) (Cheng, 2000). Thus, D2EHPA can be applied to simultaneously extract Mn(II) and Cd(II) from a sulphate leaching solution while Co(II) and Ni(II) are left in the aqueous phase. According to several studies, both Cyanex 272 and D2EHPA are phosphorus extractants that selectively remove Co(II) over Ni(II) from leaching solutions because of their preference for the molecular structure of Co(II) over Ni(II) (Gloe et al., 2014). Indeed, the electron pairs of oxygen atoms bind with Co(II) to form a tetrahedral structure while they bind with Ni(II) to form an octahedral structure. Due to the difference in the structural formation of the metal-phosphorus extractant complex (Gloe, 2014), Co is supposed to be easily separated from Ni when using Cyanex 272 or D2EHPA (Best et al., 2016). The application of these solvents could allow the selective recovery of Co(II) from a solution containing both Co(II) and Ni(II) through the careful control of the solution's pH. The separation ratio of Co/Ni is higher when Cyanex 272 is used compared to D2EHPA because the presence of a lower number of oxygen atoms in the structure of Cyanex 272 increases the difference in the separation pH between Co and Ni by 0.5 (Hubicki and Hubicka, 1996).

6.4.2 Scrubbing stage

After the solvent extraction, the solvent was scrubbed to remove unwanted metals (impurities). A solution containing a salt of the metal of interest was mixed with the loaded organic phase to replace the unwanted metals (impurities) with the metal of interest. For example, the use of Cyanex 272 at pH = 5.0 allows the selective recovery of Co from an aqueous phase that contains a Co/Ni ratio of about 26/1. If the loaded solvent was mixed with an aqueous solution containing 40 g Co L^{-1}, the Co/Ni ratio in the scrubbed solvent could reach a value greater than 1400/1 (Cytec, 2008). Equation 6.3 describes the reaction within the scrubbing stage, which was performed to remove Ni from the organic phase that initially contained both Co and Ni.

$$(R_2PO\text{-}O)_2Ni + (R_2PO\text{-}O)_2Co + CoSO_4 \leftrightarrow 2\ (R_2PO\text{-}O)_2Co + NiSO_4 \qquad \text{(Equation 6.3)}$$

The amount of Ni(II) eliminated from the organic phase and replaced by Co(II) in the scrubbing solution was obtained by the mass balance described in Equation 6.4.

$$[Ni^{2+}]_{org\text{-}i} \times V_{org} = [Ni^{2+}]_{org\text{-}f} \times V_{org} + [Ni^{2+}]_{scrub} \times V_{scrub} \qquad \text{(Equation 6.4)}$$

Where $[Ni^{2+}]_{org-i}$ is the concentration of Ni present in the organic phase before scrubbing, $[Ni^{2+}]_{org-f}$ is the residual concentration of Ni present in the organic phase after scrubbing, $[Ni^{2+}]_{scrub}$ is the concentration of Ni present in the scrubbing solution after scrubbing, V_{org} is the volume of the organic solvent and V_{scrub} is the volume of the scrubbing solution.

The aim of this work was to selectively recover Cd(II), Mn(II) and Ni(II) from a PLS derived from a recycling process developed to remove valuable metals from unsorted spent batteries (alkaline, Zn-C, Li-ion, Ni-Cd, Ni-MH). The metals initially present in unsorted spent batteries (alkaline, Zn-C, Ni-Cd, Ni-MH, Li-ion and lithium iron) were leached in the presence of H_2SO_4 and a reducing agent. The PLS obtained from this leaching contained large amounts of metals (Zn, Cd, Mn and Ni etc.). In a previous study, Zn and Fe were selectively recovered using solvent extraction (Cyanex 272) followed by the electrodeposition of Zn (Fig. 6.1). First, the present study compared the performance of Cyanex 272 and D2EHPA in the selective recovery of Mn and Cd from the PLS. The performance of each solvent extraction step, including extraction, scrubbing and stripping, was investigated. Second, this research focused on the selective recovery of Cd(II) by electrodeposition and Mn(II) as carbonates by precipitation. Third, this research addressed the selective recovery of Co(II) and Ni(II) using solvent extraction followed by the precipitation of Ni as carbonates.

6.5 Material and methods

6.5.1 Preparation of the synthetic pls and organic phases

6.5.1.1 Preparation of the synthetic PLS

The synthetic PLS was prepared based on the characterization of the aqueous solution emerging from the solvent extraction carried out to remove Zn, as described in Fig. 6.1. This solution contained large amounts of Mn(II), Cd(II) and Ni(II) and small amounts of Zn(II) and Co(II). Analytical grade powders of $ZnSO_4.7H_2O$, $MnSO_4.H_2O$, $CdSO_4.H_2O$, $CoSO_4.7H_2O$ and K_2SO_4 (Laboratoire MAT, Quebec, Quebec, Canada) were dissolved in distilled water to prepare the synthetic PLS. Concentrated H_2SO_4 was then used to adjust the pH of the solution to approximately 2.5.

For the Cyanex 923 solvent extraction experiment, a synthetic solution was prepared by dissolving $CdCl_2$ and $MnCl_2$ (Laboratoire MAT) in distilled water. The Cd and Mn solutions were prepared according to their concentrations in the effluent from the D2EHPA stripping step, and the pH of the solution was adjusted using HCl acid.

In the electrodeposition experiment, $CdSO_4$ and $MnSO_4$ (Laboratoire MAT) were dissolved in distilled water and the pH was adjusted using H_2SO_4 acid. The metal concentrations in these experiments were prepared according to the metal composition of the effluent from the D2EHPA stripping experiment as well as the experiment mentioned above.

Fig. 6.2 illustrates the method used to explore the selective recovery of valuable metals (Zn, Cd, Mn and Ni) from unsorted spent batteries, including Cyanex 272, Cyanex 923 and D2EHPA extraction, precipitation and electrodeposition.

6.5.1.2 Preparation of the organic phases

The Cyanex 272 extractant used in this study was provided by Cytec Canada Inc. (Niagara Falls, Ontario, Canada). This extractant was composed of 85% bis (2,4,4-trimethylpentyl) phosphinic acid and had a specific gravity of 0.92 g cm^{-3} at 24°C. The organic phase was prepared before each series of solvent extraction experiments in a 1-L glass tank by mixing 30% (v v^{-1}) Cyanex 272, 2% (v v^{-1}) TBP (tributylphosphate, 97%, Sigma Aldrich, Canada) and 68% (v v^{-1}) of kerosene (Recochem Inc., Canada).

The extractant D2EHPA was provided by Sigma-Aldrich (Oakville, Ontario, Canada). This extractant was composed of 97% bis (2-ethylhexyl) phosphate. D2EHPA had a specific gravity of 0.965 g cm^{-3} at 25°C. The organic phase was prepared by mixing 30% (v v^{-1}) D2EHPA, 5% (v v^{-1}) TBP and 65% (v v^{-1}) kerosene.

Cyanex 923 was provided by Cytec Canada Inc. to investigate the removal of Cd. The results of this experiment were compared to those of the electrodeposition method as indicated in Fig. 6.2. 93% of this extractant was comprised of four trialkylphosphine oxides. Cyanex 923 had a specific gravity of 0.88 g cm^{-3} at 25°C. The Cyanex 923 organic phase was prepared in a 1-L glass tank by mixing 1 part (v v^{-1}) Cyanex 923 with 9 parts (v v^{-1}) kerosene. The electrodeposition method was selected instead of the Cyanex 923 solvent extraction method because of its ease of operation and reduced need to adjust the pH.

6.5.2 Solvent extraction

Solvent extraction generally occurs in three steps: organic extraction, scrubbing and stripping. During organic extraction, the selected metal is transferred from an aqueous phase to an organic phase. Scrubbing is applied if any impurities were co-extracted with the preferred metal into the organic phase. Unwanted metals can be eliminated from the organic phase by combining it with an aqueous solution containing high quantities of the preferred metal. Stripping is applied to recover the selected metal from the organic phase by mixing the organic solvent with an acidic solution, particularly when D2EHPA or Cyanex 272 is used as the organic solvent.

For every assay, including extraction, stripping and scrubbing, the experiments were carried out in 250 mL-capacity beakers at 50°C. During each stage, the organic and aqueous phases were mixed using a Teflon-covered stirring bar at approximately 400 rotations per minute (rpm) for 10 min. Thereafter, the aqueous and organic phases were transferred to a separating funnel to separate the aqueous solution from the organic solvent. After each extraction, stripping or scrubbing event, a sample of the aqueous solution was drawn and preserved in a 5% (v v^{-1}) HNO_3 solution for analysis.

6.5.3 Extraction of Cd and Mn from the PLS containing Cd, Mn, Co and Ni

The ability of various organic solvents (Cyanex 272 and D2EHPA) to recover Cd(II) and Mn(II) from a PLS solution containing Cd(II), Mn(II), Ni(II) and Co(II) was compared. The maximum organic loading capacity was fixed at approximately 65% to avoid the precipitation of metals while the O/A ratio was set at 2/1 and the initial concentrations of Cd and Mn in the PLS were held constant at 3.75 ± 0.51 g Cd L^{-1} and 26.3 ± 2.9 g Mn L^{-1}. Thus, the amount of Cyanex 272 and D2EHPA needed to completely extract all of the Cd(II) and Mn(II) present in PLS was estimated at 29.2% and 27.2% (v v^{-1}), respectively. The amounts of Cyanex 272 and D2EHPA used to prepare the organic phases were fixed at 30% (v v^{-1}) based on these factors. The performance of Cyanex 272 (30%, v v^{-1}) was tested at pH values ranging from 3.0 to 4.0; the efficiency of D2EHPA (30%, v v^{-1}) was tested at pH values ranging from 2.0 to 2.5. The most appropriate solvent was then chosen and the influence of various parameters (extraction stage, O/A ratio, etc.) was investigated.

6.5.4 Scrubbing of the impurities present in the Cd- and Mn-loaded organic solution

Scrubbing was only applied to the loaded organic solution derived from the D2EHPA extraction due to the presence of certain impurities (Ni and Co). The loaded organic solution, which contained large amounts of Cd(II) and Mn(II) and traces of Ni and Co, was mixed with a scrub solution that initially contained 12.5 g Cd L^{-1} and 19.7 g Mn L^{-1} (Fig. 6.3). The scrubbing experiments were conducted with fixed O/A ratios of 10/1 and 20/1, respectively. After the O/A separation was complete, the aqueous phase was recycled into the scrubbing process. The Mn-and Cd-enriched organic phase (Cd- and Mn-scrubbed organic solution) was then stripped to recover the Cd(II) and Mn(II) from the organic phase and transfer these metals to the aqueous phase.

6.5.5 Stripping of Cd and Mn present in the Cd- and Mn-scrubbed organic solution

The Cd- and Mn-scrubbed organic phase obtained from the scrubbing stage outlined above was then stripped to recover Cd(II) and Mn(II). As seen in Fig. 6.2, two methods were performed to recover Cd(II) and Mn(II) and compared:

- In the first method, an HCl solution (1 M and 2 M) was used to form a metallic complex than could be transferred in the aqueous phase. Then, the aqueous phase, which contained both Cd(II) and Mn(II) in a chloride media, was collected; and a solvent extraction using Cyanex 923 was performed to selectively extract Cd(II) from Mn(II). The experimental conditions used during the Cyanex 923 extraction were as follows: one extraction using Cyanex 923 (5% and 10%, v v^{-1}) diluted in kerosene, O/A ratio = 1/1, pH < 1.
- In the second method, different H_2SO_4 solutions (0.4 M and 1.2 M) were used to obtain a sulfate solution that could be used directly in the electrodeposition of Cd. Different O/A ratios (2/1 and 4/1) were also tested to determine the most favorable operating conditions. After the recovery of Cd in the aqueous phase, electrodeposition was performed to selectively recover the Cd, and then the substance was precipitated to recover the Mn as carbonates.

6.5.6 Electrodeposition of Cd from the aqueous phase containing Cd(ii) and Mn(ii)

The electrochemical reactions related to the electrodeposition of Cd^{2+} are described in Equations 6.5 and 6.6 (Moradkhani et al., 2012):

Cathodic reaction:

$Cd^{2+} + 2e^{-} \rightarrow Cd_{(s)}$ (Equation 6.5)

Anodic reaction:

$4\ H^{+} + 4\ e^{-} + O_2 \rightarrow 2\ H_2O$ (Equation 6.6)

In the presence of Mn(II) in the solution, oxidation of Mn^{2+} ions occurred at the anode, as shown in Equation 6.7 (Mahon and Alfantazi, 2014):

$Mn^{2+} + 2\ H_2O \rightarrow MnO_2 + 4\ H^{+} + 2\ e^{-}$ (Equation 6.7)

A synthetic solution was prepared for the electrodeposition experiments based on the composition of the stripped aqueous solution that emerged from the D2EHPA organic solvent extraction. This solution contained approximately 4.3 g Cd L^{-1} and 27 g Mn L^{-1}. The electrodeposition experiments were carried out in a 500 mL-capacity reactor made of acrylic at ambient temperature. A stainless steel electrode was used as the cathode and had a surface area of approximately 110 cm^2 available for the deposition of Cd. A Ti/IrO_2 electrode was used as the anode. The distance between the electrodes was 1 cm. Each electrodeposition experiment was performed on 500 mL of the aqueous solution derived from the stripping step of the D2EHPA solvent extraction process. No alkaline solution was added during the electrodeposition process to control the pH; and the final pH was measured at the end of each experiment. Once introduced into the reactor, the solution was continuously mixed with a recirculation pump. The current density was fixed at 180 and 360 A m^{-2} to determine the most favorable conditions for the electrodeposition of Cd. The electrochemical experiments were conducted for 6 h, and a 1 mL sample was collected after 10, 20, 45, 60, 90, 150, 240 and 360 min. The residual concentrations of Cd were measured in each sample to evaluate the performance of the electrodeposition of Cd. At the end of the electrodeposition, the cathode was rinsed with an exact volume of a HNO_3 solution (5%, v v^{-1}) to determine the purity of the deposit obtained and the nature of the impurities present.

6.5.7 Extraction of Co from Zn-, Mn- and Cd-depleted pls containing Co and Ni

The Zn-, Mn- and Cd-depleted PLS derived from the D2EHPA extraction stage was subjected to Cyanex 272 extraction to separate Co(II) from Ni(II). The organic phase was composed of Cyanex 272 (10%, v v^{-1}) and TBP (5%, v v^{-1}) diluted in kerosene (85%, v v^{-1}). The experimental conditions used during the Cyanex 272 extraction were as follows: O/A ratio of 1/2, equilibrium pH in the range of 5.0 - 5.5. Next, the Co-loaded organic phase was stripped using H_2SO_4 (0.4 M) with an O/A ratio of 2/1. The Zn-, Mn-, Cd- and Co-depleted PLS was then precipitated to obtain Ni.

6.5.8 Precipitation of Mn and Ni as pure carbonates

6.5.8.1 Precipitation of Mn as carbonates

The Mn(II) present in the aqueous solution obtained after the electrodeposition of Cd (Fig. 6.2) was precipitated as carbonates after the addition of Na_2CO_3 (Na_2CO_3 powder, Sigma Aldrich). All assays were conducted in triplicate and used 200 mL of the aqueous solution each. During the precipitation, the solution was continuously mixed at 250 rpm using a magnetic agitator and a Teflon-coated stirring bar. First, an NaOH solution (10 g L^{-1}) was added to adjust the pH to around 7. Then, an Na_2CO_3 powder was added to allow the precipitation of Mn as $MnCO_3$. The amount of Na_2CO_3 added was calculated based on the stoichiometry of the reaction of Mn precipitation as carbonates. Then, the $MnCO_3$ precipitate was washed three times using distilled water with a solid/liquid ratio of 10% (w v^{-1}) to remove impurities.

6.5.8.2 Precipitation of Ni as carbonates

The Ni(II) present in the Zn-, Mn-, Cd- and Co-depleted PLS obtained from the Cyanex 272 solvent extraction was precipitated as carbonates through the addition of Na_2CO_3. The same procedure developed for the precipitation of Mn was applied to precipitate Ni. However, due to the difficulty of precipitating $NiCO_3$, the amount of Na_2CO_3 added was three times the stoichiometry of the reaction of Ni precipitated as carbonates. The $NiCO_3$ precipitate was then washed twice using distilled water with an S/L ratio of 10% (w v^{-1}) to remove impurities.

6.5.9 Analytical methods

The pH was measured using a Fisher Scientific pH meter (model Accumet AR15), which was calibrated before each series of experiments using a certified buffered solution (pH = 2.00, 4.00 and 7.00).

The concentration of each valuable metal studied in the aqueous samples derived from the extraction, electrodeposition and precipitation of the solvents was analyzed using ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy, Varian, Vista-Pro).

6.6 Results and discussion

6.6.1 Characterization of the synthetic PLS

The Zn-depleted PLS used in the Cyanex 272 and D2EHPA extraction experiments was prepared according to the metal composition in the solution obtained from the leaching process in a previous study (Tanong et al., 2016a,b). The initial pH of the Zn-depleted PLS was estimated at 2.5, and the solution initially contained 3.8 ± 0.5 g Cd L^{-1}, 26 ± 3 g Mn L^{-1}, 0.28 ± 0.03 g Co L^{-1}, 3.3 ± 0.4 g Ni L^{-1} and 0.3 ± 0.2 g Zn L^{-1} (Tanong et al., 2016a,b).

A synthetic PLS was prepared at the beginning of each series of experiments. Therefore, the initial concentration of valuable metals (Cd, Co, Mn, Ni and Zn) varied slightly from one series to the next. The initial concentrations of the metals of interest were measured within the synthetic PLS prior to each series of experiments. In the following sections, all results are expressed in terms of one liter of the Zn-depleted PLS (synthetic solution), even if the experiments were actually performed on smaller volumes.

6.6.2 Comparison of the ability of Cyanex 272 and D2EHPA to remove Mn(II) and Cd(II) from a Zn-depleted PCS

The first series of solvent extraction experiments was conducted using a Cyanex 272 extractant at pH = 3.0, 3.5 and 4.0 and a D2EHPA extractant at pH = 2.0 and 2.5 in order to compare these extractants' ability to recover Cd(II) and Mn(II) from the Zn-depleted PLS. Table 6.1 presents the initial levels of valuable metals (Mn, Cd, Ni) and impurities (Zn, Co) present in the Zn-depleted PLS, along with the residual concentrations of these metals present in the aqueous solution derived from the Cyanex 272 extraction.

These results indicate that only small amounts of both Cd (6.0%) and Mn (19.8%) were extracted from the Zn-depleted solution at pH 3.0 and 11.7% of Cd and 35.5% of Mn were extracted at pH = 3.5 using Cyanex 272. The highest extraction yields were observed at pH = 4.0, with more than 18.3% of Cd and 47.0% of Mn removed from the Zn-depleted PLS. These results show that an increase in pH led to an improvement in the quantity of Cd and Mn extracted from the Zn-depleted PLS and transferred to the organic phase. An increase in the pH above 4.0 was not tested due to the precipitation of the metals. Moreover, it appeared that the increase in the pH from 3.0 to 4.0 during the Cyanex 272 extraction led to an increase in the amount of Ni transferred to the organic phase (considered an impurity at this stage) from 0.08 to 0.15 g.

The use of D2EHPA as an extractant resulted in an increase in the extraction yield from 41.4% to 44.9% and from 60.7% to 64.1% for Cd and Mn, respectively, when the pH of the solution was increased from 2.0 to 2.5. These results were in accordance with the observations made by

Haghshenas Fatmehsari et al. (2009). Indeed, these authors showed that 60% of Cd(II) and 40% of Mn(II) could be extracted at pH = 2.3 from an aqueous solution using D2EHPA (20% (v v^{-1}) D2EHPA + 10% (v v^{-1}) TBP, O/A ratio of 1/1) while Co(II) and Ni(II) remained in the aqueous phase.

Comparing the ability of Cyanex 272 and D2EHPA to remove Cd(II) and Mn(II) from the Zn-depleted PLS indicates that D2EHPA is likely more efficient. Indeed, approximately 47.0% of Mn(II) was extracted at pH = 4.0 when Cyanex 272 was used, whereas more than 64.2% of the metal was extracted at pH = 2.5 when D2EHPA was employed. Moreover, the extraction of Mn(II) and Cd(II) occurred more readily at low pH levels when D2EHPA was used compared to Cyanex 272 because the strong acidic characteristics of the D2EHPA functional group favor the cationic exchange between Cd^{2+} and Mn^{2+} ions present in the aqueous solution and the protons present in the extractant (Rodrigues and Mansur, 2010). Therefore, the pH of the solution plays an important role in the efficient extraction of metals from a solvent. It is important to maintain the pH of the solution during the extraction step by adding alkaline or acidic compounds to the solution. Our results indicate that D2EHPA was better able to remove Cd(II) and Mn(II) from the solvent while using less NaOH to increase the pH of the solution (equilibrium pH of 2.0-2.5 for D2EHPA versus 4.5 for Cyanex 272). Moreover, the low equilibrium pH required during the D2EHPA extraction process inhibited the precipitation of the metals of interest and the formation of a third phase during the aqueous/organic separation step.

6.6.3 Influence of operating parameters on Mn(II) and Cd(II) recovery from the Zn-depleted PLS using D2EHPA

6.6.3.1 Effect of D2EHPA extraction on the recovery of Mn(II) and Cd(II) from the Zn-depleted PLS

Table 6.2 shows the experimental conditions and the residual concentrations of Cd(II) and Mn(II) present in the aqueous phase derived from the D2EHPA extraction process (30% (v v^{-1}) D2EHPA, 5% (v v^{-1}) TBP in kerosene, O/A of 2/1) depending on the O/A ratio used in the second extraction and the equilibrium pH of the solution. The Zn-depleted PLS used for this series of experiments initially contained 0.30 g Co, 3.24 g Ni, 3.76 g Cd and 26.7 g Mn. Compared to the first series of experiments, a second extraction was added to increase the Cd(II) and Mn(II) loading capacity of the organic phase.

A comparison of the results obtained at pH = 2.0 and 2.5 (Tables 6.1 and 6.2) indicates that the Cd(II) and Mn(II) loading capacity of the organic phase increased with the addition of a second extraction. Indeed, the metal content within the organic phase increased from 1.56 g to 2.41 g for Cd and 16.1 to 22.4 g for Mn at pH = 2.0 and from 1.69 to 3.12 g for Cd and 17.1 to 25.0 g for Mn at pH = 2.5. After the first extraction, the amount of Cd and Mn remaining in the aqueous phase was estimated at 2.07 g and 9.57 g, respectively, for the experiments conducted at pH = 2.5 (Table 6.1). The determination of the stoichiometry mass value indicated that an O/A ratio of 1/1 was required to extract the remaining amounts of Cd and Mn in the aqueous phase at pH = 2.5. As indicated by the results in Table 6.2, an increase in the loading capacity of both Cd(II) and Mn(II) within the organic phase was observed when an O/A ratio of 1/1 (2.36 g of Cd and 20.87 g of Mn loaded in the organic phase) increased to 2/1 (3.12 g of Cd and 25.03 g of Mn loaded in the organic phase). Similar results were observed in the study conducted by Mellah *et al.* (Mellah and Benachour, 2006). In their study when the O/A ratio increased from 1/8 to 1/1, the efficiency of Cd(II) extraction increased from 27% to 61% (pH = 2.0, 0.5 M D2EHPA, 0.5×10^{-3} M Cd(II) in PLS at 25°C). Therefore, an O/A ratio of 2/1 was selected for the two extraction stages.

According to the results presented in Table 6.2, an increase of the equilibrium pH improved the Cd(II) and Mn(II) extraction from the Zn-depleted PLS. These observations were in accordance with the results obtained by (Cortina et al., 1995) and (Yong, 2000). Therefore, additional experiments were conducted at pH = 2.7 (two extraction stage, O/A ratio of 2/1). When the equilibrium pH was increased to 2.7, higher Cd(II) and Mn(II) extraction efficiencies were observed compared to the experiments carried out at pH = 2.0 and 2.5 (Table 6.2). Almost all of the Cd (3.56 g) and Mn (26.32 g) initially present in the Zn-depleted PLS were transferred to the organic phase with the following experimental conditions: two stages of extraction, 30% ($v\ v^{-1}$) DEHPA + 5% ($v\ v^{-1}$) TBP, O/A ratio of 2/1 for the 1st and 2nd stage of extraction, equilibrium pH = 2.7. Indeed, up to 95.2% of Cd(II) and 98.5% of Mn(II) were transferred to the organic phase at pH = 2.7. However, high amounts of Ni (0.58 g) and Co (0.12 g) were co-extracted in the organic phase. Indeed, approximately 40.0% of Co(II) and 17.9% of Ni(II) initially present in the Zn-depleted PLS were transferred to the organic phase.

6.6.3.2 Performances of D2EHPA scrubbing stage on the removal of impurities from the Cd- and Mn-loaded organic phase

The Cd(II)- and Mn(II)-loaded organic phase was mixed with a scrub solution that contained $CdSO_4$ (12.6 g L^{-1}) and $MnSO_4$ (19.7 g L^{-1}). The O/A ratios tested during the scrubbing stage were equal to 10/1 and 20/1 and the initial pH of the scrub solution was fixed at $\sim$ 2.2. After an intensive mixing, the Co(II) and Ni(II) ions initially present in the organic phase were replaced by the Mn(II) or Cd(II) ions initially present in the scrubbing solution. The amounts of metals eliminated from the organic phase (D2EHPA) after the scrubbing phase were obtained as shown in Table 6.3. These amounts were estimated for 4 L of the Cd(II)- and Mn(II) loaded organic solution (two extraction steps performed onto 1 L of Zn-depleted PLS with an O/A of 2/1 each).

The results were expressed for experiments conducted on 4 L of a Cd(II)- and Mn(II)-loaded organic solution that initially contained 2,451 mg Cd, 46 mg Co, 22,570 mg Mn and 432 mg Ni. The metals concentrations in organic phase were a little bit lower comparing with the metals concentrations in D2EHPA organic solvent in the previous section due to the lower pH equilibrium after extraction (<3.0) (Table 6.2). The author did not redo the experiment due to the different in the metals concentration were not significant. After the scrubbing step, the amounts of Cd present in the organic phase increased from 2,451 mg (initial) to 3,845 mg and 3,343 mg (final) for the experiments conducted with an O/A ratio of 10/1 and 20/1, respectively. The amounts of Mn present in the organic phase decreased from 22,570 mg (initial) to 22,043 mg (final) for the experiments conducted with an O/A ratio of 10/1 as well as for the experiments performed with an O/A ratio of 20/1, a decrease in the amounts of Mn(II) present in the organic phase was observed (initial amount of 22,570 mg versus final amount of

22,071 mg). The diminution of the amount of Mn present in the organic phase was considered negligible. The results showed that, only Cd(II) replaced Ni(II) and Co(II) ions in the organic phase when the O/A ratio of 20/1 and 10/1 were applied. When using an O/A ratio of 10/1, approximately 14 mg of Co and 153 mg of Ni were removed from the Cd(II)- and Mn(II)-loaded organic phase. According to these results, approximately 30% of the Co(II) and 35% of the Ni(II) initially contained in the Cd(II)- and Mn(II)-loaded organic phase were transferred to the aqueous solution during the scrubbing experiments conducted with an O/A ratio of 10/1. The pH equilibrium obtained after the scrubbing stage was equal to 2.31. The pH of the solution used during the scrubbing steps should be controlled than those used for the extraction steps to prevent the back extraction of the desired metals to the aqueous phase and the transfer of the metallic impurities to the organic phase. At the O/A ratio of 20/1, the removal efficiencies were obtained for Co (46%) and Ni (25). With these operational conditions, approximately 21 mg of Co and 105 mg of Ni were removed from the Cd(II)- and Mn(II)-loaded organic phase that initially contained 46 mg of Co and 432 mg of Ni. The pH equilibrium obtained after the scrubbing stage was equal to 2.31. The removal efficiencies of Co and Ni for the two essays were not really distinct; therefore, an O/A ratio of 20/1 was retained for the rest of the experiments.

According to the study carried out by Nogueira and Demas (1999), the Ni(II) was successfully removed from the organic phase containing Ni(II) and Co(II) using a scrubbing step (Nogueira, 1999). Padhan *et al.* (Padhan et al., 2014) scrubbed an Mn(II)-enriched organic solution to remove Co(II) by using an $MnSO_4$ solution (0.1 M) as the scrubbing agent. According to their results, 40 mg of Co(II) were removed from the organic phase, which initially contained 43 mg of Co with an O/A ratio of 1/1. These earlier studies prove that scrubbing is an effective method to remove impurities such as Co(II) present in organic phases. However, the scrubbing efficiencies found in our study were not as high as expected, and only small proportion of the impurities were eliminated. Additional research is necessary to improve scrubbing's ability to remove Co and Ni completely from the organic phase.

6.6.3.3 Ability of D2EHPA stripping using HCl and Cyanex 923 solvent extraction to selectively recover Cd (first method)

The organic phase containing Cd(II) and Mn(II) and derived from the scrubbing step discussed above was mixed with an HCl solution (1 M or 2 M) to simultaneously recover Cd and Mn in the aqueous phase. Table 6.4 presents the results obtained from the stripping experiments performed using the different concentration of HCl. Because Cyanex 923 effectively extracted the metals in complex forms, HCl could be applied to obtain a chloro-complex solution.

Approximately 96.3 and 99.7% of Mn(II) and 88.1% and 89.9% of Cd(II) initially present in the organic phase were transferred to the aqueous phase with the addition of 1 M and 2 M of HCl, respectively. The amounts of impurities transferred to the aqueous phase were slightly higher when using 2 M of HCl compared to 1 M of HCl (0.38 g of Ni with 2 M of HCl versus 0.29 g with 1 M of HCl). Thus, 1 M HCl was used during the stripping step to reduce the amounts of impurities transferred to the Mn- and Cd-laden aqueous phase; this also reduced the costs associated with the consumption of HCl. The Mn and Cd aqueous solution obtained via stripping was then subjected to a Cyanex 923 extraction to selectively recover the Cd(II) from the Mn(II).

Table 6.4 presents the results obtained from the experiments conducted with 5% and 10% Cyanex 923 to selectively recover Cd(II) from an aqueous solution containing $CdCl_2$ and $MnCl_2$. In this experiment, a synthetic solution was applied and a pH of 0.3 fixed using an HCl solution (Gupta et al., 2001). The concentrations of Cd and Mn in the synthetic solution were a bit higher compared to the effluent from the D2EHPA process (stripping with HCl in Table 6.4).

In the 5% and 10% Cyanex 923 experiments, almost all of the Cd(II) was extracted into the organic phase (99.7% and 97.7%, respectively), leaving the Mn in the aqueous solution (0.34% and 2.96%, respectively). Similar results were obtained by Gupta et al. (2001). According to their results, 99% of Cd(II) was selectively recovered from a solution containing both Cd(II) and Mn(II) in a chloride medium (O/A ratio of 1/1, pH = 0.3).

6.6.3.4 Performance of D2EHPA stripping using H_2SO_4 followed by the electrodeposition of Cd (second method)

6.6.3.4.1 Results of the stripping stage using H_2SO_4

The stripping experiments were conducted by mixing 1.2 M H_2SO_4 into the Cd(II) and Mn(II) organic phase derived from the scrubbing performed on the Cd(II)- and Mn(II)-loaded organic phase (Fig. 6.2). Three experimental D2EHPA organic extraction and scrubbing assays were performed under the optimum conditions identified in the previous sections. The results obtained confirmed our hypotheses and can be found in Table 6.5.

The ability of different concentrations of H_2SO_4 and O/A ratios (0.4 M and ratio 2/1, 1.2 M and ratio 4/1) to remove Cd(II) and Mn(II) from the organic phase were also studied (Table 6.5). These results indicate high levels of purity related to $CdSO_4$ and $MnSO_4$ were obtained when

1.2 M and 0.4 M of H_2SO_4 was used as a stripping solution. Indeed, when using 1.2 M of H_2SO_4, the aqueous phase derived from the stripping stage contained 0.02 g Co L^{-1} and 0.06 g Ni L^{-1} compared to 0.02 mg L^{-1} and 0.04 mg L^{-1} for those experiments carried out with 0.4 M of H_2SO_4. After the solution was stripped for 10 min at 50°C using an H_2SO_4 solution (0.4 M) and an O/A ratio of 2/1, approximately 100% of Cd(II) and Mn(II) were transferred from the organic phase to the aqueous phase. The final Cd(II) and Mn(II) concentrations reached 2.34 g L^{-1} and 13.3 g L^{-1}, respectively. Higher O/A ratio (O/A ratio = 4/1) and acid concentrations (1.2 M) were tested while the other parameters were kept constant to transfer the Cd(II) and Mn(II) into the aqueous phase. When a higher O/A ratio was used, the acid concentration needed to be increased to maintain the stripping efficiency (Table 6.5). Under these operating conditions, up to 93.4% of Cd(II) and 94.1% of Mn(II) was transferred to the aqueous phase. The final Cd(II) and Mn(II) concentrations reached 4.28 g L^{-1} and 24.9 g L^{-1}, respectively. These results are in accordance with the observations of Agrawal et al. (2012), who concluded that stripping efficiency increased with the increase of the concentration of the acidic solution used. Therefore, the following conditions were retained for the remainder of the experiments: O/A ratio of 4/1, H_2SO_4 concentration of 1.2 M. The aqueous solution derived from the stripping stage, which contained Cd and Mn in H_2SO_4, was used in the next step to recover Cd by electrodeposition.

6.6.3.5 The electrodeposition of Cd

The Cd electrodeposition experiments were carried out on the aqueous solution derived from the D2EHPA stripping step. Fig. 6.4 presents the residual concentration of Cd measured in the aqueous solution during the electrodeposition step as performed at different intensities (180 and 360 A m^{-2}). The synthetic aqueous solution initially contained 4.3 g Cd L^{-1} and 27 g Mn L^{-1}.

According to these results, the concentration of Cd(II) decreased from 4.2 to 0.5 g L^{-1} and from 4.2 to 0.01 g L^{-1} after 90 min of electrodeposition. This experiment was conducted with an intensity of 180 and 360 A m^{-2}, respectively. These results indicate that the use of an intensity of 360 A m^{-2} was more favorable for the electrodeposition of Cd on the cathode compared to 180 A m^{-2}. Indeed, a rapid diminution of the concentration of Cd(II) was observed for the experiments performed at 360 A m^{-2}. Oztekin and Yazicigil (2006) observed a similar trend for metal electrodeposition as current density increased. The Mn(II) concentration slightly decreased from 27.3 g L^{-1} to 26.9 g L^{-1} at 360 A m^{-2} after 6 h of electrodeposition while it remained constant at 180 A m^{-2}. These results suggest that high current densities are more favorable to the oxidation of Mn(II) to Mn(IV) and its deposition on the anode. Thus, a current density of 360 A m^{-2} and a retention time of 90 min were chosen for the next experiments.

Additional experiments were performed with a retention time of 90 min (one electrodeposition step of 90 min and two successive electrodeposition steps of 45 min each). Fig. 6.5 illustrates the residual concentration of Cd measured in the aqueous solution during these experiments. It was found that a single 90 min run was more efficient for the electrodeposition of Cd than two successive steps of 45 min each. Indeed, up to 98.4% of Cd(II) was recovered in its metallic form after a single 90 min run, whereas approximately 94.2% was recovered after two 45 min runs.

The Cd deposits obtained at the end of the electrodeposition was easily peeled from the electrode surface. However, washing the Cd powder obtained was necessary to remove undesirable components such as dissolved Mn(II). The Cd powder was rinsed for 10 min using distilled water with an S/L ratio of 1/10 (w v^{-1}). After one washing, approximately 4.3 g of metallic Cd with a purity of 99% was obtained.

6.6.3.6 Precipitation of Mn from the aqueous solution derived from the electrodeposition of Cd

Fig. 6.6 illustrates the hydrometallurgy process utilized to recover Cd, Mn, Ni and Co from the PLS solution.

The precipitation experiments were conducted on the Cd-depleted aqueous solution derived from the electrodeposition assay that yielded 25.5 g L^{-1} of Mn as $MnSO_4$. From the results obtained (not showed), 99% of Mn(II) was precipitated from the sulfate solution at pH = 8-9 after the addition of NaOH and Na_2CO_3. After three washings, 60 g of $MnCO_3$ with a purity of 94% (as $MnCO_3$) was obtained as a final product from 1 L of the Zn-depleted PLS.

6.6.4 Ability of Cyanex 272 to remove the impurities from the Zn-, Mn- and Cd-depleted PLS – recovery of Ni

The Zn-, Mn- and Cd-depleted PLS obtained from the D2EHPA extraction initially contained 0.21 g Mn L^{-1}, 0.16 g Cd L^{-1}, 2.39 g Ni L^{-1} and 0.17 g Co L^{-1}. This aqueous solution was intensively mixed with a Cyanex 272 organic solution at a O/A ratio of 0.5 (Fig. 6.6). The pH of the solution was maintained at 5.0-5.5. From the results presented in Table 6.6, the impurities, including Cd(II), Co(II) and Mn(II), were removed from the Zn-, Mn- and Cd-depleted PLS with efficiencies of 99.4% for the Cd, 97.3% for the Co and 98.0% for the Mn, while only 1.68% of Ni was co-extracted. Similar results were obtained by Tsakiridis and Agatzini-Leonardou (2004). Indeed, according to these authors, Co(II) could nearly be extracted from a solution containing 0.63 g

Co L^{-1} at an equilibrium pH of 5- 6 using 20% Cyanex 272 and 5% TBP in Exxsol. The Zn-, Mn-, Cd- and Co-depleted PLS containing only Ni (as $NiSO_4$) was then subjected to precipitation to recover Ni as $NiCO_3$. At pH = 10, 99% of Ni(II) was precipitated. After two washings, approximately 4 g of $NiCO_3$ with a purity of 95% were obtained as a final product from 1 L of Zn-depleted PLS.

The Co-loaded organic phase was stripped ($[H_2SO_4]$ =0.4 M, O/A ratio = 2/1 (v v^{-1}), t = 10 min and T = 50°C) to recover the Co and allow the recycling of the organic phase within the Cyanex 272 extraction process. Under these operating conditions, 49 - 67% of the Cd(II), Co(II) and Mn(II) extracted in the organic phase were stripped and transferred to an aqueous phase. This solution could then be reused as a stripping solution to remove the impurities from Cyanex 272 organic solvents until the solution became saturated. With accumulation to a certain concentration, Co could be recovered by precipitation.

6.7 Conclusion

Our results indicate that Cd(II) and Mn(II) can be simultaneously extracted using D2EHPA at low equilibrium pH values between 2.6 and 2.9 while leaving Ni(II) and Co(II) in an aqueous solution. Scrubbing conducted on the Cd(II)- and Mn(II)-loaded organic phase did not efficiently remove such impurities as Co (60%) and Ni (23%). However, an increase in the Cd concentration was observed in the organic phase after scrubbing, which could help improve the efficiency of the electrodeposition performed on the aqueous phase obtained via stripping. A comparison of the two methods tested to recover Cd highlighted that the H_2SO_4 stripping step followed by electrodeposition was the most practical method based on economics and its ease of implementation. The stripping of the Cd(II)- and Mn(II)-loaded organic phase in the presence of H_2SO_4 (1.2 M, O/A = 4/1) was highly efficient and allowed the recovery of 100% of the Cd(II) and Mn(II). Cd can be selectively electrodeposited from a $CdSO_4$ and $MnSO_4$ aqueous solution with a purity of 99%. Co(II) was efficiently isolated from the Zn-, Mn- and Cd-depleted PLS using Cyanex 272, with removal yields reaching 99%. Pure Mn and Ni carbonates can be recovered from the aqueous solution derived from the electrodeposition step and from the Cyanex 272 extraction step, respectively.

6.8 Aknowledgments

The authors acknowledge the Natural Sciences and Engineering Research Council of Canada for the financial support to this research (grant RGPIN-2014-04794).

6.9 References

Best, P.S., , Spas D. Kolev, June R.P. Gabriel, Robert W. Cattrall, 2016. Polymerisation effects in the extraction of Co(II) into polymer inclusion membranes containing Cyanex 272. Structural studies of the Cyanex 272–Co(II) complex. Journal of Membrane Science 497, 9.

Biswas, R.K., Karmakar, A.K., Kumar, S.L., Hossain, M.N., 2015. Recovery of manganese and zinc from waste Zn-C cell powder: Characterization and leaching. Waste Manag 46, 529-535.

Buzatu, T., Popescu, G., Birloaga, I., Saceanu, S., 2013. Study concerning the recovery of zinc and manganese from spent batteries by hydrometallurgical processes. Waste Management 33, 699-705.

Charette, S.L., 2014. Essai présenté au Centre universitaire de formation en environnement et développement durable en vue de l'obtention du grade de maître en environnement. Université de Sherbrooke.

Cheng, C.Y., 2000. Purification of synthetic laterite leach solution by solvent extraction using D2EHPA. Hydrometallurgy 56, 369-386.

Cortina J.L., N.M., A.M. Sastre, M. Aguilar, 1995. Solid-liquid extraction studies of Zn (II) , Cu (II) and Cd (II) from chloride media with impregnated resins containing mixtures of organophosphorus compounds immobilized on to Amberlite XAD2. Hydrometallurgy 37.

Cytec, 2008. Cyanex272 Extractant, p. 16.

Gloe, K., Kerstin, G., Wenzel, M., Lindor L.F. and F., Li, 2014. Supramolecular Chemistry in Solvent Extraction: Toward Highly Selective Extractants and a Better Understanding of Phase-Transfer Phenomena. Taylor&Francis Group, Florida, United state.

Gupta, B., A., Deep and M., Poonma 2001. Extraction and recovery of cadmium using Cyanex 923. Hydrometallurgy 61, 6.

Haghshenas Fatmehsari, D., Darvishi, D., Etemadi, S., Eivazi Hollagh, A.R., Keshavarz Alamdari, E., Salardini, A.A., 2009. Interaction between TBP and D2EHPA during Zn, Cd, Mn, Cu, Co and Ni solvent extraction: A thermodynamic and empirical approach. Hydrometallurgy 98, 143-147.

Hubicki, Z., H., Hubicka, 1996. Studies on the extraction process of nickel(II) sulphate purification using Cyanex 272. Hydrometallurgy 40, 11.

Larsson, K., Ekberg, C., Odegaard-Jensen, A., 2012. Using Cyanex 923 for selective extraction in a high concentration chloride medium on nickel metal hydride battery waste. Hydrometallurgy 129, 35-42.

Mahon, M., Alfantazi, A., 2014. Manganese consumption during zinc electrowinning using a dynamic process simulation. Hydrometallurgy 150, 184-191.

Mellah, A., Benachour, D., 2006. The solvent extraction of zinc and cadmium from phosphoric acid solution by di-2-ethyl hexyl phosphoric acid in kerosene diluent. Chemical Engineering and Processing: Process Intensification 45, 684-690.

Meshram, P., Pandey, B.D., Mankhand, T.R., 2016. Process optimization and kinetics for leaching of rare earth metals from the spent Ni-metal hydride batteries. Waste Manag 51, 196-203.

Moradkhani, D., Rasouli, M., Behnian, D., Arjmandfar, H., Ashtari, P., 2012. Selective zinc alkaline leaching optimization and cadmium sponge recovery by electrowinning from cold filter cake (CFC) residue. Hydrometallurgy 115-116, 84-92.

Nogueira, C.A., F., Delmas, 1999. New flowsheet for the recovery of cadmium, cobalt and nickel from spent Ni–Cd batteries by solvent extraction. Hydrometallurgy 52, 20.

Oztekin, Y., Yazicigil, Z., 2006. Recovery of metals from complexed solutions by electrodeposition. Desalination 190, 79-88.

Padhan, E., Sarangi, K., Subbaiah, T., 2014. Recovery of manganese and nickel from polymetallic manganese nodule using commercial extractants. International Journal of Mineral Processing 126, 55-61.

Pereira, D.D., Rocha, S.D.F., Mansur, M.B., 2007. Recovery of zinc sulphate from industrial effluents by liquid-liquid extraction using D2EHPA (di-2-ethylhexyl phosphoric acid). Separation and Purification Technology 53, 89-96.

Reddy, B.R., Priya, D.N., 2006. Chloride leaching and solvent extraction of cadmium, cobalt and nickel from spent nickel-cadmium, batteries using Cyanex 923 and 272. Journal of Power Sources 161, 1428-1434.

RISInternational, 2007. Canadian Consumer Battery baseline Study.

Roberge, J., 2010. Les piles domestiques. Recyc-Quebec, Quebec, Canada.

Rodrigues, L.E.O.C., Mansur, M.B., 2010. Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel–metal–hydride batteries. Journal of Power Sources 195, 3735-3741.

Rudnik, E., Nikiel, M., 2007. Hydrometallurgical recovery of cadmium and nickel from spent Ni-Cd batteries. Hydrometallurgy 89, 61-71.

Salgado, A., 2003. Recovery of zinc and manganese from spent alkaline batteries by liquid–liquid extraction with Cyanex 272. Journal of Power Sources 115, 367-373.

Tanong, K., Coudert L., Mercier G. and Blais J.F., 2016a. Modeling and optimization of metals leaching from unsorted spent batteries using response surface methodology. L'Institut national de la recherche scientifique, Quebec, Submitted, p. 33.

Tanong, K., Tran L.H., Coudert L., Mercier G. and Blais J.F., 2016b. Recovery of Zn from unsorted spent batteries using solvent extraction and electrodeposition. L'Institut national de la recherche scientifique, Quebec, Submitted, p. 38.

Tsakiridis, P.E., Agatzini-Leonardou, S., 2004. Process for the recovery of cobalt and nickel in the presence of magnesium from sulphate solutions by Cyanex 272 and Cyanex 302. Minerals Engineering 17, 913-923.

Yong, C.C., 2000. Purification of synthetic laterite leach solution by solvent extraction using D2EHPA. Hydrometallurgy 56, 17.

6.10 NOTATION

A m^{-2}: Current density (ampere per meter square).
HA: Extractant;
K_{ex}: Equilibrium constant for the extraction;
O/A ratio: Organic/aqueous phase ratio;

6.11 List of figures

6.12 List of tables

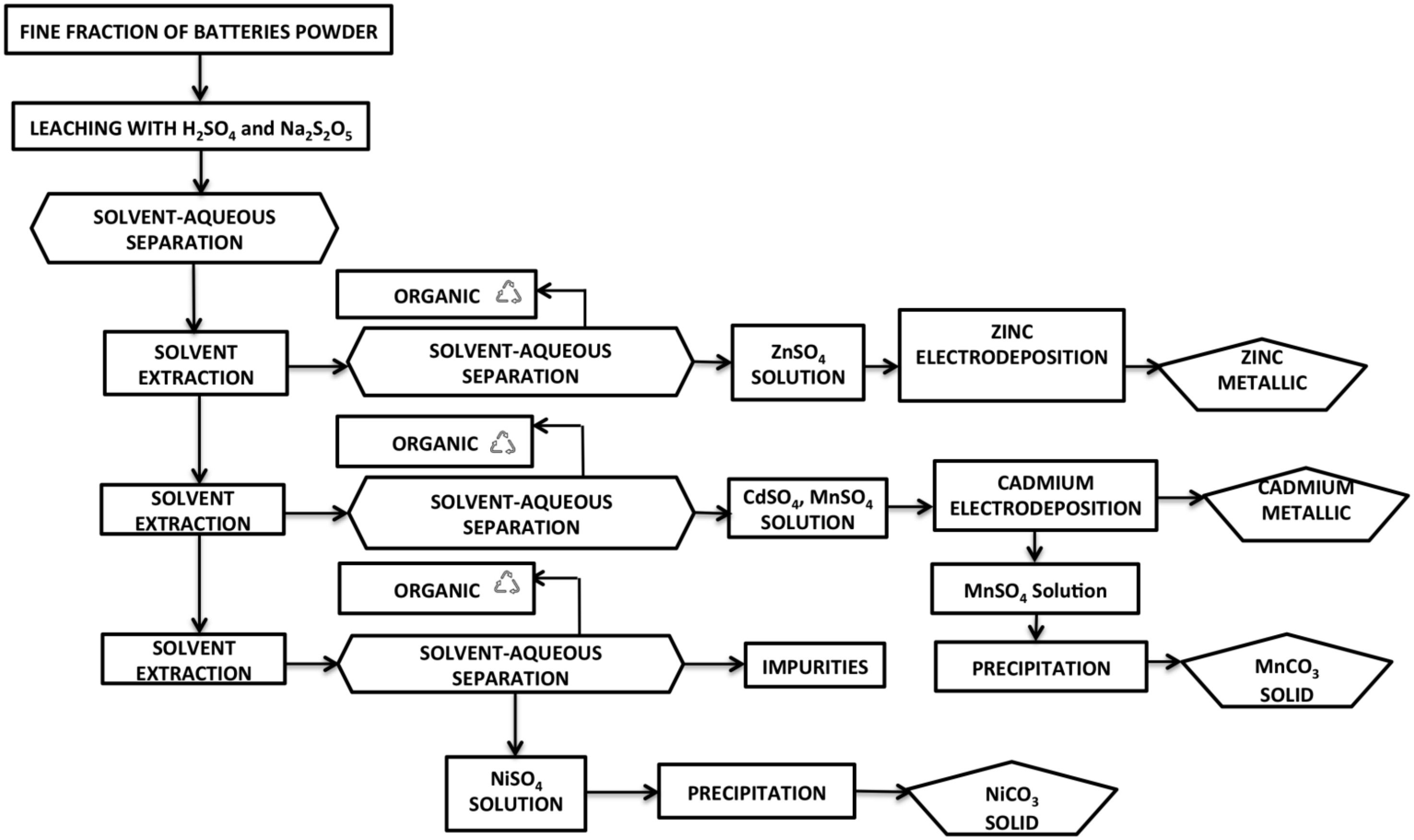


Figure 6.1 Schema of the hydrometallurgical processes developed to selectively recover valuables metals from unsorted spent batteries

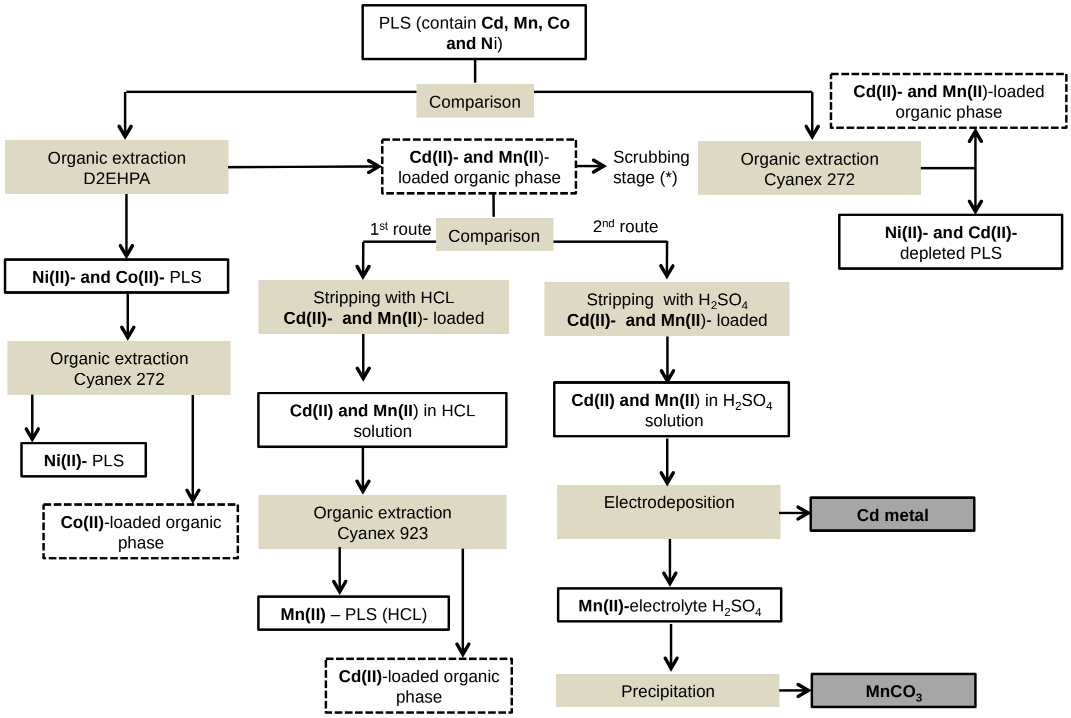


Figure 6.2 Investigated methods for the selective recovery of Cd, Mn, Ni and Co in the experimental study

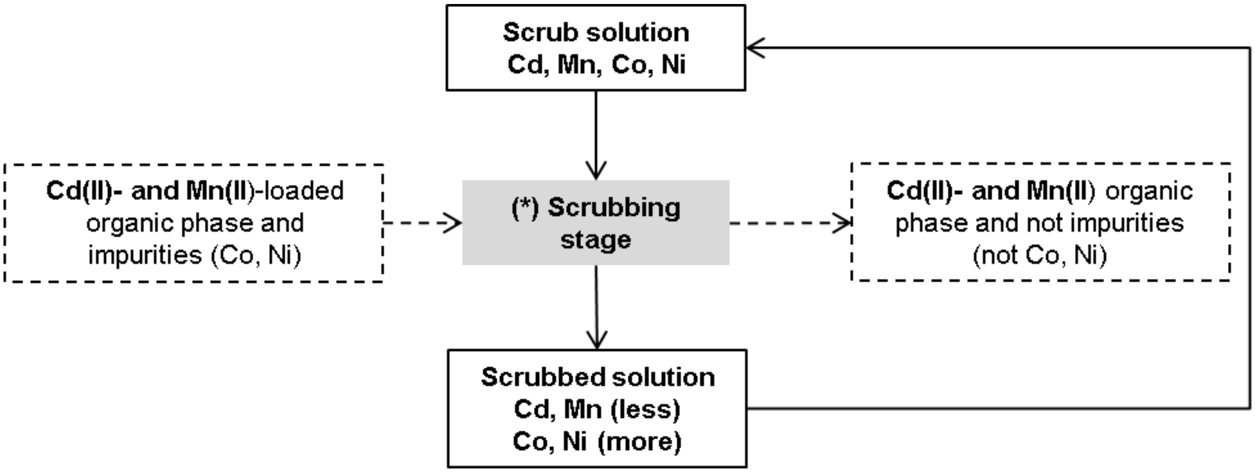


Figure 6.3 **Scrubbing performed to eliminate impurities (Co, Ni) in the Mn-, Cd-enriched organic phase**

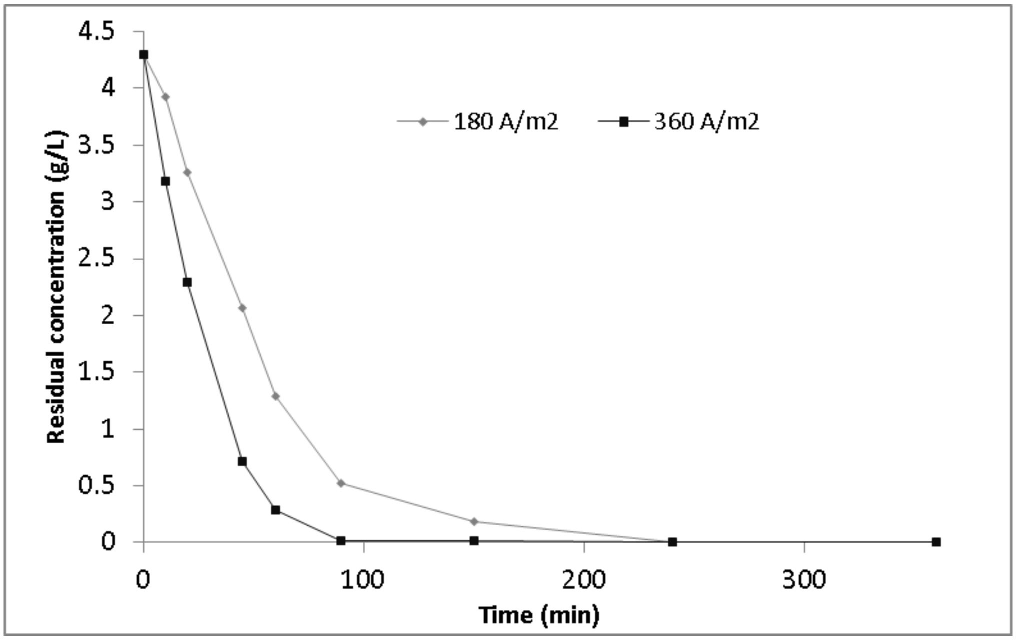


Figure 6.4 Cd electrodeposition at different current densities (pH = 2, reaction time = 360 min)

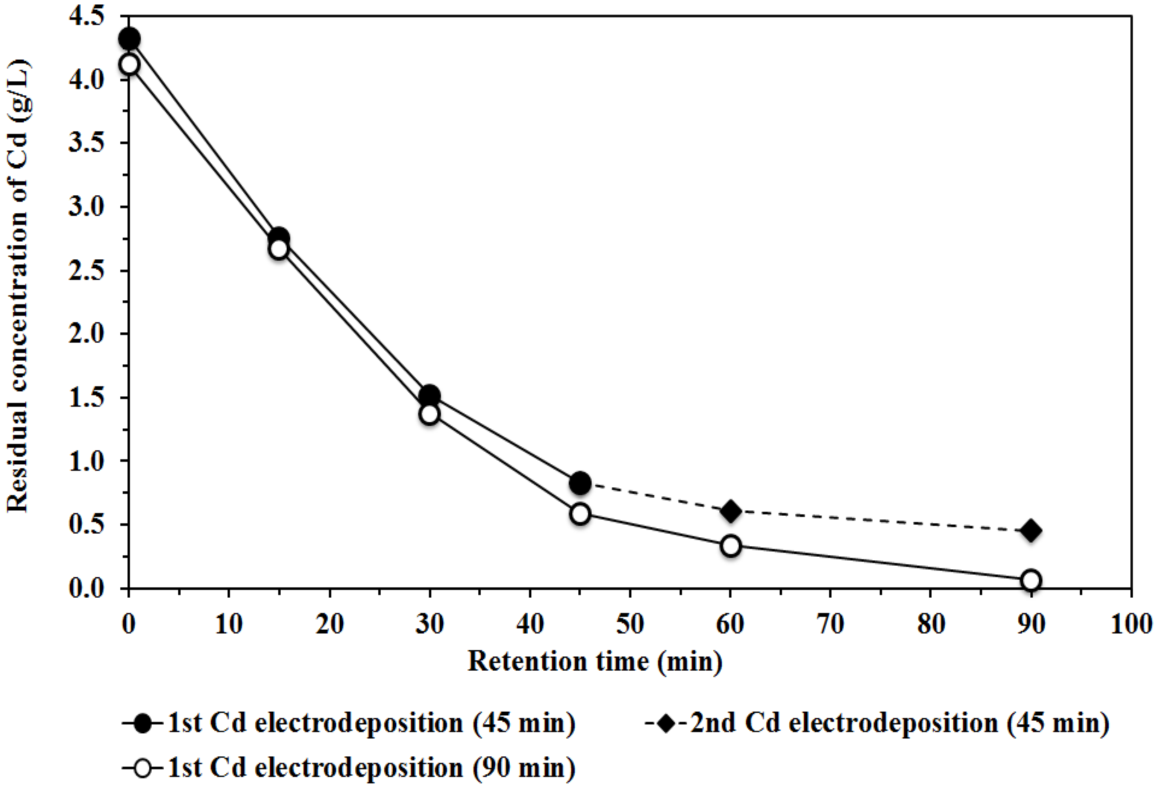


Figure 6.5 Cd electrodeposition at different electrodeposition times (360 A m^{-2}, pH = 2)

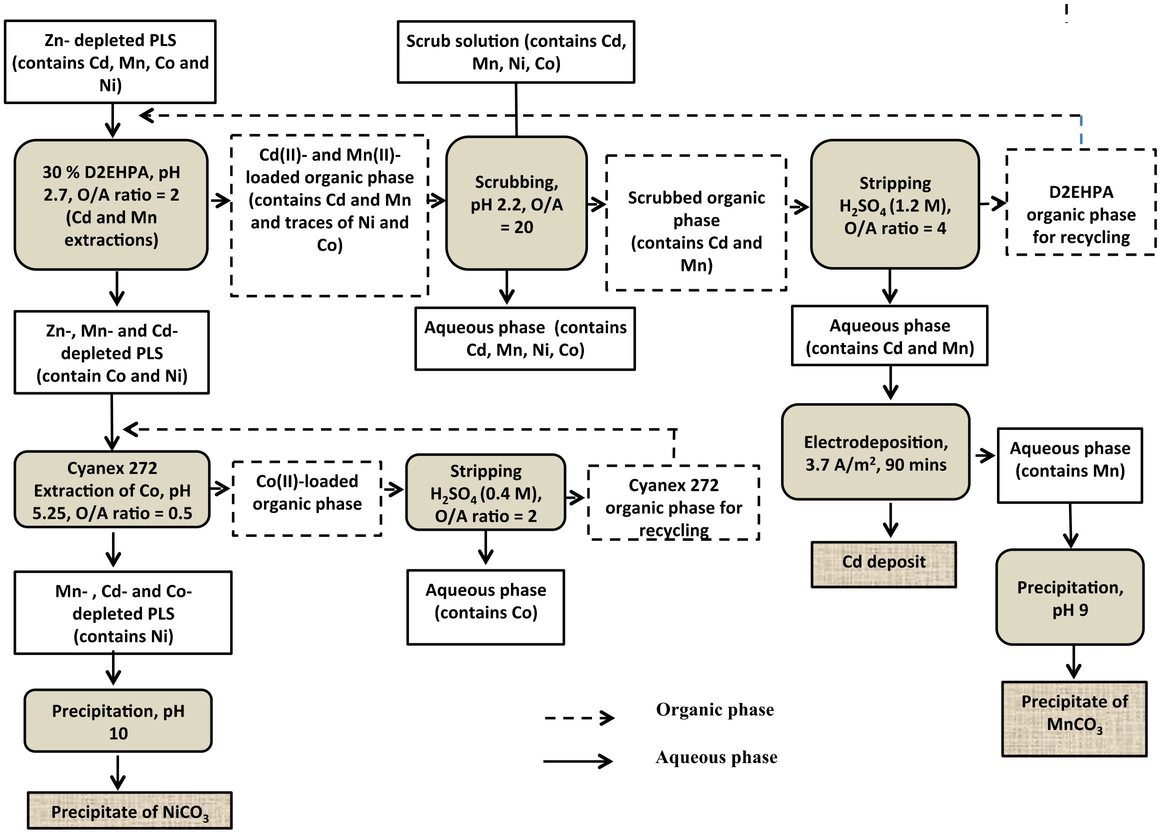


Figure 6.6 Hydrometallurgical process retained for the recovery of Cd, Mn, Ni and Co from a PLS solution

Table 6.1 **Comparison of Cyanex 272 (30% ($v\ v^{-1}$) Cyanex 272 + 2% ($v\ v^{-1}$) TBP in kerosene) and D2EHPA (30% ($v\ v^{-1}$) D2EHPA + 5% ($v\ v^{-1}$) TBP in kerosene) solvent extraction experiments on the recovery of Cd, Co, Mn and Ni from a PLS (single extraction; O/A ratio = 2/1)**

Metals	**Residual concentration measured in the aqueous phase (g L^{-1})**						
	Cyanex 272 extractant				**D2EHPA extractant**		
		pH				**pH**	
	Initial (Zn-depleted PLS)	**3.0**	**3.5**	**4.0**	**Initial (Zn-depleted PLS)**	**2.0**	**2.5**
Cd	2.99 ± 0.19	2.8 ± 0.0	2.6 ± 0.0	2.4 ± 0.1	3.8 ± 0.5	2.2 ± 0.0	2.1 ± 0.0
Co	0.23 ± 0.02	0.21 ± 0.00	0.19 ± 0.00	0.17 ± 0.00	0.30 ± 0.01	0.26 ± 0.0	0.25 ± 0.00
Mn	21.7 ± 3.0	17 ± 0	14 ± 0	12 ± 0	27 ± 0	11 ± 0	9.6 ± 0.5
Ni	2.82 ± 0.07	2.7 ± 0.1	2.7 ± 0.1	2.6 ± 0.1	3.2 ± 0.0	2.9 ± 0.0	2.9 ± 0.0
Zn	0.75 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.24 ± 0.00	n.a.[*]	n.a.

[*] n.a. = not applicable (metal concentration was not investigated).

Table 6.2 Extraction of Cd and Mn from a PLS using D2EHPA after two extraction runs (30% ($v\ v^{-1}$) D2EHPA and 5% ($v\ v^{-1}$) TBP, O/A of 2/1) at different pHs

Metals	**Initial amount (g)**	**Amount of metal in organic phase (g)**						
		1st extraction (O/A = 2)			**2nd extraction (O/A =2)**			**2nd extraction (O/A = 1)**
		pH 2.0	pH 2.5	pH 2.7	pH 2.0	pH 2.5	pH 2.7	pH 2.5
Cd	3.8 ± 0.5	1.6 ± 0.1	1.7 ± 0.0	2.1 ± 0.1	2.4 ± 0.1	3.1 ± 0.0	3.6 ± 0.0	2.4 ± 0.3
Co	0.30 ± 0.01	0.04 ± 0.00	0.04 ± 0.04	0.06 ± 0.01	0.05 ± 0.00	0.05 ± 0.00	0.12 ± 0.66	0.05 ± 0.01
Mn	27 ± 0	16 ± 0	17 ± 1	20 ± 0	22 ± 0	25 ± 0	26 ± 0	21 ± 0
Ni	3.2 ± 0.0	0.38 ± 0.02	0.38 ± 0.04	0.55 ± 0.00	0.44 ± 0.00	0.46 ± 0.00	0.58 ± 0.01	0.6 ± 0.1
Zn	0.24 ± 0.00	n.a.*	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. = not applicable (metal concentration was not investigated).

Table 6.3 Quantity of metals present in the organic phase after scrubbing conducted with different O/A ratios of the Cd(II)- and Mn(II)-loaded D2EHPA organic solution (pH = 2.2, V_{org-i} = 4 L)

Metals		Cd	Co	Mn	Ni
Initial in the organic phase (mg)		2,451	46	22,570	432
		in	out	out	out
Output and input of metals in organic phase (mg)	O/A = 10	1,394 ± 39	14.2 ± 0.3	527 ± 38	153 ± 1
		in	out	out	out
	O/A = 20	892 ± 1	21.1 ± 1.1	499 ± 0	105 ± 0

Table 6.4 **Stripping of Cd and Mn from the Cd(II)- and Mn(II)-loaded D2EHPA solution using HCl and the selective extraction of Cd from the aqueous solution obtained using Cyanex 923**

Metals	**Amounts of metals present in the organic phase for the stripping stage and in the aqueous phase for the extraction stage (g)**					
	Stripping stage using HCl			**Extraction stage using Cyanex 923**		
	Initial (organic phase)	**Final 1 M HCl**	**Final 2 M HCl**	**Initial (aqueous phase)**	**5% Cyanex 923**	**10% Cyanex 923**
Cd	2.6 ± 0.	0.31 ± 0.07	0.29 ± 0.07	3.5 ± 0.1	3.5 ± 0.1	3.4 ± 0.0
Co	0.04 ± 0.00	0.02 ±0.00	0.02 ± 0.00	0.05 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Mn	24 ± 0	0.89 ± 0.09	0.23 ± 0.03	35 ± 0	1.0 ± 0.2	0.12 ± 0.02
Ni	0.49 ± 0.04	0.29 ± 0.09	0.38 ± 0.01	0.15 ± 0.01	0.05 ± 0.00	0.01 ± 0.00

Table 6.5 Confirmation of 30% D2EHPA extraction (pH = 2.8, O/A ratio = 2, two extractions), scrubbing (pH = 2, O/A ratio = 20, single extraction) and stripping of Cd and Mn from the Cd(II)- and Mn(II)-loaded D2EHPA solution using H_2SO_4 at different concentrations and O/A ratios

Metals	**Initial (g) (V = 1 L)**	**Metals extracted in organic (g) (V = 4 L)**	**Metal in organic phase (g) after scrubbing (V = 4 L)**	**Stripping concentration (g L^{-1})**	
				$[H_2SO_4]$ = 0.4 M and O/A ratio = 2/1 (V = 2 L)	$[H_2SO_4]$ = 1.2 M and O/A ratio = 4/1 (V = 1 L)
Cd	3.7 ± 0.1	3.6 ± 0.1	4.6 ± 0.1	2.3 ± 0.1	4.3 ± 0.1
Co	0.29 ± 0.01	0.12 ± 0.01	0.04 ± 0.01	0.02 ± 0.00	0.02 ± 0.01
Mn	26 ± 0	26 ± 0	26 ± 0	13 ± 0	25 ± 1
Ni	3.2 ± 0.1	0.79 ± 0.14	0.54 ± 0.13	0.04 ± 0.01	0.06 ± 0.02

Table 6.6 **Selective extraction of Co using Cyanex 272 from the Zn-, Mn- and Cd-depleted PLS**

Metals	Concentration in aqueous phase (g)		
	Initial	After extraction	After stripping
Cd	0.16 ± 0.00	0.00 ± 0.00	0.08 ± 0.00
Co	0.17 ± 0.02	0.00 ± 0.00	0.11 ± 0.00
Mn	0.28 ± 0.01	0.00 ± 0.00	0.14 ± 0.02
Ni	2.4 ± 0.0	2.4 ± 0.0	0.00 ± 0.00

7 CHAPITRE 7

RECOVERY OF ZN(II), MN(II), CD(II) AND NI(II) FROM THE UNSORTED SPENT BATTERIES USING SOLVENT EXTRACTION, ELECTRODEPOSITION AND PRECIPITATION METHODS

Revue : Journal of Cleaner Production

Auteurs : Kulchaya Tanong[a], Lan Huong Tran[b], Guy Mercier[c], Jean-Francois Blais[d*]

[a] Ph.D. Student, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-4677 ext. 4473, Fax: (418) 654-2600, email: kulchaya.tanong@ete.inrs.ca

[b] Research Associate, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-2550, Fax: (418) 654-2600, email: lan.huong.tran@ete.inrs.ca

[c] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-2633, Fax: (418) 654-2600, email: guy.mercier@ete.inrs.ca

[d] Professor, Institut national de la recherche scientifique (Centre Eau, Terre et Environnement), Université du Québec, 490 rue de la Couronne, Québec, QC, Canada, G1K 9A9, Phone: (418) 654-2575, Fax: (418) 654-2600, email: jean-francois.blais@ete.inrs.ca

*Corresponding author:
Tel: (418) 654-2575, Fax: (418) 654-2600,
email: jean-francois.blais@ete.inrs.ca

Note

L’étudiante est le premier auteur de cet article. Toutes les manipulations, le traitement des données ainsi que la rédaction ont été effectués par l’étudiante sous la supervision des autres co-auteurs.

Modifications exigées par le comité de lecture de la revue

Les commentaires des réviseurs n’ont pas été reçus.

7.1 Résumé

Cette étude porte sur la récupération des métaux à partir d'une solution de lixiviation (PLS) obtenue par traitement de déchets de piles et de batteries usagées avec de l’acide sulfurique. Le PLS contient principalement du Zn, du Mn, du Cd, du Ni et du Co. Des méthodes d'extraction par solvant et d’électrodéposition ont été utilisées pour récupérer sélectivement 73% du Zn à partir de la solution. Après la récupération du Zn par le Cyanex 272 [acide Di(2,4,4-triméthylpentyl) phosphonique], le Cd et le Mn ont été co-extraits par le D2EHPA [acide 2-éthylhexylphosphonique], un solvant organique; puis 78% du Cd a été sélectivement récupéré par voie électrolytique à partir d'une solution de sulfate de métaux (Cd et Mn). Par conséquent, 83% du Mn a été récupéré sous forme de carbonates. Dans l'étape suivante où le Zn, le Cd et le Mn ont déjà été enlevés, le Cyanex 272 a été utilisé pour éliminer le Co (96%) et quelques impuretés de la solution appauvrie en Zn-Cd-Mn tandis que le Ni n'a pas été extrait. Enfin, 53% du Ni a été précipité sous forme de $NiCO_3$ avec Na_2CO_3. Le revenu des métaux/le coût des produits chimiques est supérieur à 50%, ce qui indique que le processus pourrait être rentable. La valeur des métaux récupérés est égale à 2 313 $/t. Cependant, l'analyse de l'ensemble du modèle économique doit être approfondie pour justifier la rentabilité du procédé.

Mots clés: Cyanex 272, D2EHPA, Électrodéposition, Lixiviat, Batteries usagées

7.2 Abstract

The present paper presents the development of a waste batteries recycling technology, that could lead to the minimization of the amounts of waste discharged, contamination problems and the depleting of natural resources. This study mainly focused on the recovery of metals from a pregnant leach solution (PLS) obtained from a sulphuric leaching process applied to unsorted spent batteries. The PLS mainly contains Zn, Mn, Cd, Ni and Co. Cyanex 272 (di-2,4,4-trimethylpentyl phosphinic acid) was used to selectively recover Zn from the mixed solution. The Zn-Cyanex 272 was stripped and electrodeposited in metallic form and approximately 134 kg of Zn were recovered per ton of waste battery powder. Cd and Mn were co-extracted in the organic solvent D2EHPA (2-ethylhexylphosphonic acid) from the Zn-depleted solution and they were stripped using H_2SO_4. Consequently, Cd was selectively electrodeposited from a sulphate-stripped solution where the amount of Cd recovered was equal to 21.6 kg Cd per ton of waste battery powder. Residual Mn was recovered in the carbonate form by the addition of Na_2CO_3 (238 kg of Mn per ton of waste battery powder). In the following step, Cyanex 272 was used to remove Co and other impurities from the Zn-Cd-Mn depleted solution, while Ni was not extracted. Finally, Ni was precipitated from the pure $NiSO_4$ solution with Na_2CO_3 and 23.8 kg of Ni were recovered per ton of waste battery powder. The costs of the process develop to recover metals (including only chemical costs and energy consumption) are estimated at $814 per ton of battery powder, while the metal revenues obtained are estimated at $2,132 per ton of battery powder. The chemical cost /metal revenue ratio is lower than 50%, which indicates that the process is feasible.

Keywords: Cyanex 272; D2EHPA; Electrodeposition; Chemical precipitation; Leachate; Spent batteries

7.3 Introduction

The number of waste batteries produced is increasing each year in several countries due to the high consumption in various electronic devices, such as mobile phones, laptops, lamps, remote controls and cameras (Barrett et al., 2016). In the province of Quebec, approximately 173 M units of primary cells and 5.2 M units of secondary cells were predicted to be sold in 2015 (Roberge, 2010). There is a possibility that these huge quantities of waste could be discharged into landfill sites due to the ease and low cost of this disposal method. Most of alkaline waste batteries were discharged into landfill sites in Canada (Bonhomme et al., 2013) as well as some other types of waste batteries that could be possibly discharged with municipal wastes (Al-Thyabat et al., 2013). Landfilling could pose a serious threat to the environment through the natural infiltration of metals which could be leaked into the groundwater (Granata et al., 2012). Indeed some metals present in waste batteries could be harmful to aquatic and human life. To avoid this problem, the metals from these wastes should be recycled. In addition to the protection of the environment, the recycling strategy could be an alternative way to alleviate the scarcity of metal resources. Metal recycling not only benefits to the investor but also increases public income through recycling projects (Granata et al., 2012). In addition, the labour cost for battery sorting in the province of Quebec was estimated at 730$ per ton of waste batteries, which could prevent the economic feasibility of battery recycling process (personal contact with Call2Recycle). Therefore, it is of great interest to develop a new process to treat unsorted waste batteries to decrease the operating costs

7.4 Current processes for battery recycling

Among numerous methods, hydrometallurgical and pyrometallurgical processes have been widely applied to recover valuable metals contained in wastes. Pyrometallurgical method usually requires high-energy consumption, expensive investment costs and produces a lot of dust. Therefore, hydrometallurgical processes represent a better option compared to pyrometallurgical ones. Hydrometallurgical processes have several advantages over pyrometallurgical processes, such as higher selectivity toward the individual metal, lower gaseous emission and lower energy consumption (Freitas et al., 2007). However in this method, the need of effective leaching is necessary to separate the individual fraction while pyrometallurgical processes do not (Sobianowska-Turek et al., 2016). There are several efforts made to treat spent batteries at laboratory scale by applying hydrometallurgical processes (Coll et al., 2012; Frohlich and Sewing, 1995; Ku et al., 2016; Rudnik and Nikiel, 2007). Some commercialized processes such as modified Zincex MZP allows the recycling of alkaline and zinc-carbon waste batteries. For example, the company Recytec combines hydrometallurgical, pyrometallurgical and physical treatments to treat all the types of waste batteries. The company Snam-Savam applies an pyrometallurgical process to treat Ni-Cd batteries (Espinosa et al., 2004). Inmetco and Raw Material Company were the main recycling companies in the North of America able to recycle alkaline batteries and to divert most of alkaline waste batteries from landfill sites (Bonhomme et al., 2013). Inmetco applies a pyrometallurgical process to treat alkaline batteries while Raw Material Company uses mechanical method. In Canada, the "polluter pays principle" policy was applied to manage waste batteries. Some waste batteries were recycled and managed by the non-profit organization Call2recycle. The alkaline battery directive in Canada reinforces battery collection points with 45% recovery goal varying in different province (Bonhomme et al., 2013).

7.4.1 Chemical organic solvent for metals recycles

In the present study, solvent extraction method was the main process use to recover the metals from a pregnant leach solution (PLS). Cyanex 272 and D2EHPA were classified in the group of phosphorus extractants that are normally effective in acidic solutions. They were widely used in the field of hydrometallurgy to recover metals at both laboratory and commercial scales. Cyanex 272 was used to separate Co from Ni in laterite ore at Bulong Nickel, Western Australia, due to the high Co/Ni separation factor obtained with this solvent (Hutton-Ashkenny et al., 2015). This organic solvent was also applied by the Sumitomo Metal Mining Company to obtain pure cobalt in a mini-plant (Tsakiridis and Agatzini-Leonardou, 2004). Provazi et al. (2011) recovered individual metals from a leaching solution obtained from unsorted batteries and applied Cyanex 272 to extract the metals at different pH values. Over 99% of Ti^{4+} could be extracted at pH = 1.0; 99% of Zn^{2+} were extracted at pH = 2.5; 85% of Ni^{2+} were extracted at pH = 3.0; and 80% of $Cd^{2+}$and La^{3+} were co-extracted at pH = 3.5. Mishra et al. (2015) applied TOPS-99 (Talcher Organo phosphorus solvent) and Cyanex 272 to selectively recover Zn, Mn, Co and Ni from nickel laterite leach liquor. The results showed that 96% of Mn and 98% of Zn were selectively extracted by TOPS-99 at pH 2.5 and 6.7, respectively. In this study, Co was also removed by Cyanex 272 at pH 3.4 and 99.8 % of Ni were recovered by TOPS-99 at pH 2.5.

7.4.2 Benefits and environmental impacts of an organic solvent extraction, electrodeposition and precipitation methods.

In this study, three methods include solvent extraction, electrodeposition and precipitation were applied. The limitations and advantages of each process were presented as follows.

Solvent extraction has been proven to be an efficient method due to the specific group function, which is highly selective for metal recovery. The high purity of the metal could be achieved by this method, thus fulfilling the need for high-grade metals in industrial processes (Avilaa et al., 2011). Laki et al. (2016) state that, solvent extraction method was considered simplicity, flexibility, economical benefits, rapidity, higher enrichment factors, lower costs and being environmentally friendly, etc. for metals recoveries. However some type of organic solvent are considered as highly flammable, toxic and detrimental to the environment (Li et al., 2016). From the previous reasons, the disposal and handling cost for the waste organic solvent could be expensive (Li et al., 2016) and it could prevent their application in metals recoveries at the commercial scale. Normally the solvent extraction was carried out in close system to prevent the volatilization of the organic compounds so it could mitigate their leakage to the atmosphere. Cyanex272 and D2EHPA could be reused so it could offer the advantage in the term of disposal cost comparing to the metals revenues obtained. Green solvent was one of alternative technology that could be used to replace the conventional solvents. However, they were not yet commercialised. In the future study, the green solvent could be used to replace the current solvent so it could mitigate the environmental impact and improve the social acceptance.

The electrodeposition method has many advantages in the terms of having a low environmental impact, low energy consumption and high metals recovery rate (Diaz et al., 2016). However it was considered as non-viable process for the diluted solution, as high electrical resistances and the development of the concentration polarization phenomena could limit the economic feasibility (Lu et al., 2015).

The precipitation method was widely used in the industrial scale because its simplicity and inexpensive process. However there are some limitations including high sludge volume production, dewatering and disposal sludge problem (Lu et al., 2015) and low metal selectivity (Sobianowska-Turek at al., 2016). These three methods were chosen in this study because there are more advantages comparing to their limitations. However the further study at pilot scale and industrial scale should be conducted to evaluate the feasibility of the process in the term of economic and environment.

7.4.3 Objective of the present study

Generally, existing processes for metal recycling from waste batteries have been only applied to a specific type of waste battery at laboratory scale (Bertuol et al., 2009; De Michelis et al., 2007; Sayilgan et al., 2009) and at commercial scale (Espinosa et al., 2004) as mentioned previously. The main objective of this study is to treat all batteries together without a sorting step, which is considered as the main drawback step in the battery recycling process. Manual sorting as well as automatic sorting has a high labour cost in developed countries, such as those in Europe or North America (Granata et al., 2012).

The present process differs from methods in other studies by combining the solvent extraction and electrodeposition methods for the recovery of metals. A PLS was used instead of a synthetic solution, demonstrating that the process can be applied in reality. This study aims to do the following:

- Apply the experimental conditions (Tanong, 2016) for solvent extraction, electrodeposition and precipitation, obtained from previous studies, to selectively recover metals (Zn, Mn, Cd and Ni) from the PLS obtained from unsorted battery wastes.
- Reuse the organic solvents and acid solutions emerging from the electrodeposition process to observe the potential loss of efficiency of the process when recycling used organic solvents and therefore to limit the production of waste and to reduce the costs related to the consumption of chemical products.
- Investigate the feasibility of the whole process and use PLS on a larger scale (400 mL) compared with the volumes applied in previous studies (50 mL) (Tanong, 2016).
- Evaluate the chemical cost and energy consumption relative to metal revenues".

7.5 Materials and methods

The conditions for metal recovery by solvent extraction, electrodeposition and precipitation methods were previously determined with synthetic solutions (Tanong, 2016). In the present study, the experiment conditions determined in the previous studies were applied to the leach liquor obtained from the mixture of spent batteries. Fig. 7.1 presents the metal recovery process developed in this study. The PLS was obtained from the leaching process developed in previous studies and applied to the mixture of waste batteries. This mixture was mixed in the presence of a solution containing H_2SO_4 and a reducing agent under optimum conditions. Firstly, Zn was selectively extracted from the leach liquor by Cyanex 272 solvent extraction and electrodeposited as Zn metal. Secondly, Cd and Mn were extracted from Zn-depleted leach liquor by D2EHPA solvent extraction and Cd was selectively separated from Mn by electrodeposition. Then, Mn was recovered as carbonate by precipitation. In the final extraction step, the impurities were removed from the Zn-Cd-Mn depleted solution by Cyanex 272 solvent extraction and Ni was finally recovered as $NiCO_3$ by precipitation. All the experiments, including solvent extraction, precipitation and electrodeposition were conducted in triplicate to ensure the reliability of the process.

7.5.1 Preparation of spent batteries powder

The amounts of alkaline, nickel-metal hydride (Ni-MH), nickel-cadmium (Ni-Cd), lithium ion (Li-ion), lithium metallic (Li-M) were estimated according to the information from Recyc-Quebec in 2007. All batteries were crushed to obtain metal powders. These metal particles were leached in sulphuric acid in the presence of a reducing agent, in the optimal conditions found in previous studies (Tanong, 2016). Alkaline, Zn-C, Ni-Cd, Ni-MH, Li-ion and Li-M batteries were mechanically pre-treated by dismantling, crushing and grinding. Li-M and Ni-MH batteries were frozen in liquid nitrogen before dismantling, as they could react violently when exposed to air. The procedure for preparing the battery powder was slightly different for each type of battery. However, in reality, all batteries could be crushed together under a free-oxygen atmosphere. A fine power was obtained from alkaline, Ni-MH and Ni-Cd batteries by manual crushing and grinding with a mortar. Li-ion, Li-M and Ni-Cd cathode materials were uncurled and cut into small pieces, followed by manual grinding to obtain a fine powder. The undesirable coarse particles, including paper and plastic particles, were eliminated through the apertures of 1-mm and 2-mm sieves. The proportions of each type of spent battery in the mixture were fixed according to the battery consumption in the Canadian market (66.5% Zn-MnO_2, 15.4% Zn-C, 15.4% Ni-Cd, 1.7% Ni-MH, 0.3% Li-ion and 0.7% Li-primary batteries) (Roberge, 2010). The mixture of battery powders was dried at 25°C over 24 h and ground by a pulverizer (Fritsh pulverisette, Serial no. 06 2000/01908, Germany) to obtain an average particle size of 333 μm.

7.5.2 Preparation of the pregnant leach solution

In a previous study (Tanong, 2016), the following optimal leaching conditions were defined: 10.9% solid/liquid (S/L) ratio, 1.34 M H_2SO_4 combined with $Na_2S_2O_5$ (0.45 g $Na_2S_2O_5$ g^{-1} of waste battery powder) at ambient temperature (T = 25°C) and a leaching period of 45 min. The chemical products in this step were purchased from Sigma Aldrich, Canada. The leaching solution was obtained after solid/liquid separation on a G6 filter (Fisher Science) and it mainly consisted of 3.58 g Cd L^{-1}, 0.289 g Co L^{-1}, 0.691 g Fe L^{-1}, 28.6 g Mn L^{-1}, 4.41 g Ni L^{-1} and 20.8 g Zn L^{-1} (0.1 g/L Li). It also contained Na (12.8 g L^{-1}), S (54.7 g L^{-1}) and K (5.3 g L^{-1}).

7.5.3 Preparation of the scrub solution

Scrubbing is the additional step in the solvent extraction method to remove the unwanted metals from an organic phase. The concentrated metal solution (preference metal) was used as a scrubbed solution. This solution was mixed intensively with the organic solvent containing the preferred metals and the impurities. The preferred metals in the scrubbing solution can replace the unwanted metals in the organic phase according to the Le Chatelier principle. To prepare the scrubbing solution, chemical grade $MnSO_4$ and $CdSO_4$ (Labouratoire MAT, Canada) were dissolved in distilled water and the pH of the solution was adjusted to 2.0 by a concentrated H_2SO_4 solution.

7.5.4 Laboratory scale method for solvent extraction assays

The solvent extraction assays, including extraction, scrubbing and stripping, were carried out in a 2,000 mL capacity beaker installed on a hot plate (with the temperature set at 50°C). A laboratory overhead paddle stirrer with a velocity of 400 rotations per minute (rpm) was used during the extraction. The volumes of the leaching solution and organic solvent were fixed at 400 mL and 800 mL, respectively. The duration of extraction was set at 20 min.

After extraction, a separator funnel was used to separate the organic phase from the aqueous phase. The metals were stripped from the organic phase by mixing with H_2SO_4 over 20 min at 50°C. A 10 M NaOH solution was used to control the pH in all solvent extraction experiments.

The organic and aqueous phases were separated after the stripping step by a separator funnel. The samples were taken from the aqueous phase and preserved in 5% HNO_3 before analysis.

7.5.5 Cyanex 272-Zn extraction

Cyanex 272 was used to selectively recover Zn from the PLS obtained from the leaching process. To prepare the organic solvent, 20% of Cyanex 272 (Cytec Canada Inc.) and 2% of TBP tributylphosphate (TBP) (97%, Sigma Aldrich, Canada) were dissolved in kerosene (Recochem. Inc., Canada). The percentage of Cyanex 272 was obtained from the stoichiometric calculation. The extraction assays were carried out at pH of 2.2 - 2.5, O/A ratio of 2 and in two extraction stages. Zn was transferred from the organic phase to the aqueous phase by vigorously mixing the organic solvent with 0.4 M H_2SO_4 (O/A = 2). Finally, Zn was recovered from $ZnSO_4$ solution by an electrodeposition method.

7.5.6 D2EHPA-Cd, D2EHPA-Mn extraction

D2EHPA was applied to simultaneously recover Cd and Mn in the organic phase. To prepare the organic solution, 30% D2EHPA (Sigma Aldrich Company) and 5% TBP were diluted in kerosene to decrease its viscosity. The amounts of D2EHPA as well as Cyanex 272 were obtained by stoichiometric calculations. The equilibrium pH was fixed as approximately 2.5-2.9, with an O/A ratio of 2. Two extraction stages were required to recover the maximum quantities of the metals.

The impurities in the organic phase were scrubbed out with concentrated Mn and Cd solutions under an O/A ratio of 20 and mixing at 400 rpm. The scrubbed solution (concentrated in Mn and Cd) was mixed intensively with the D2EHPA organic solvent (containing Cd, Mn, Ni and Co) over 20 min, then the separator funnel was used to separate the aqueous phase from the organic phase. The organic solvent was regenerated by 1.2 M H_2SO_4 with an O/A ratio of 4. After stripping with the acid, a high-purity stripped solution containing mainly $CdSO_4$ and $MnSO_4$ was obtained.

7.5.7 Electrochemical experiment

A reactor made of acrylic with dimensions of 3.5 cm (width), 13.5 cm (length) and 17 cm (depth) was used in the electrodeposition experiments. The rectangular sheets of the cathode and anode were made of stainless steel and Ti/IrO_2, respectively. The geometric area was calculated and estimated to be 110 cm^2. The distance between the two electrodes was equal to 1 cm and the electrodeposition volume was fixed to 500 mL for all electrodeposition experiments. The experiments were carried out at ambient temperature. $ZnSO_4$ (pH = 2) from section 7.4.5 was used in the electrodeposition experiment, in which Zn was deposited on the cathode surface with a current density of 370 A m^{-2} and electrodeposition time of 180 min. The samples were taken at 5, 10, 20, 30, 60, 120 and 180 min. At the end of the electrodeposition experiment, the cathode was rinsed with 5% HNO_3 to determine the impurities present in the deposited Zn.

The stripped solution from section 7.4.6 mainly consisted of Cd and Mn. Cd was separated from Mn by the electrodeposition method, where the initial pH of the solution was fixed to 2.0. A current density of 370 A m^{-2} was also applied for the Zn-electrodeposition assays. The electrodeposition was extended to 240 min, which was different from the previous study (Tanong, 2016). In this experiment, the samples were taken at 10, 30, 60, 120, 180, 240, 300 and 360 min and preserved in 5% HNO_3 before analysis. The purity of the Cd deposited in the electrodeposition experiment was determined by the digestion method (3050B) (APHA, 1999).

7.5.8 Cyanex 272-Ni

Co and the other impurities were removed from a Zn-Cd-Mn free solution at a pH approximately between 5.7-5.9 by Cyanex 272 with an O/A of 0.5. The organic solvent was prepared by dissolving 10% Cyanex 272 and 2% TBP in kerosene. The stoichiometry value of Cyanex 272 was lower than 10%. This concentration was chosen due to the loss of organic solvent during processing, which was not feasible if the percentage of organic solvent was too low (<5%). The unwanted metals were transferred to the organic phase, which was later regenerated by 0.4 M H_2SO_4 with an O/A ratio of 2. Pure $NiSO_4$ solution was obtained in this experimental step.

7.5.9 Precipitation

Sodium carbonate was used to precipitate Ni and Mn from the solutions obtained in section 2.7 and section 2.8, respectively. Distilled water was used to eliminate dissolved sulfur and sodium from the metallic powder after precipitation. The metal sludge was mixed vigorously (200 rpm) with distilled water by applying a S/L ratio of 10% for 10 min. All precipitation experiments were carried out at ambient temperature.

7.5.10 Analytical techniques

Inductively coupled plasma - atomic emission spectroscopy (ICP – AES) (Varian 725 – ES) was used to determine the metals composition in the samples obtained from 3050B (APHA, 1999) digestion method, leaching, solvent extraction, electrodeposition and precipitation assays. Quality control standard (900-3Q-100, Plasmacal, Canada) was used to calibrate the metals concentration in the samples. The samples from digestion, leaching and precipitation assays were filtered with G6 glass fiber paper (G6, Fisher brand, Fisher Scientific, Canada, pore size = 1.5 μm) to remove solid particles before analysis. All samples were preserved in 5% HNO_3 before analysis.

7.5.11 Economic aspect

The economic evaluation including chemical and energy consumption was roughly studied in this process. Table 7.1 shows the unit prices of the different chemical products expressed in USD per ton of chemicals or USD per liter of chemicals for the inputs and the unit price of the products obtained (Zn metallic, Cd metallic, etc.) expressed in USD per ton of product used for the determination of the operating costs of the process. The costs related to the energy consumed, which was not presented in Table 1, were estimated based on the amount of energy required in the process and the unit price of electricity in the Province of Quebec (0.05 USD kWh^{-1}), Canada, 2015. The total costs and the revenues were then evaluated in terms of U.S. dollars per ton of battery powder (USD t^{-1}) based on the amounts of chemicals used and of products obtained and the unit price defined in Table 7.1.

7.6 Results and discussion

7.6.1 Cyanex 272-Zn extraction and stripping

Cyanex 272 has been proven to be an effective agent to selectively recover Zn from PLS consisting mainly of Zn, Mn, Cd, Co and Ni. This PLS solution was obtained from a leaching process using the optimal conditions established in a previous study. The best conditions obtained in the previous study for Zn-Cyanex272 extraction include the following: O/A = 2, 30% Cyanex 272 + 2% TBP in kerosene, pH~2.5, reaction time of 20 min at 50°C and two direct extraction stages (Tanong, 2016). TBP was used as a phase modifier and aided the phase separation (Fatmehsari et al., 2009; Owusu, 1998). After the extraction stage, the raffinate (aqueous phase) was transferred to the next stage. The Zn-Cyanex 272 organic solution was stripped by sulphuric acid to recover Zn and to recycle the Cyanex 272. The results are shown in Table 7.2. A decrease in Zn content from 20.8 g L^{-1} to 0.07 g L^{-1} was observed, with a removal yield of 99.7% at an equilibrium pH ~ 2.2, while the other metals, including Mn, Cd, Co and Ni remained in the solution. The high Zn extraction efficiencies were similar to our previous results for synthetic solutions (Tanong, 2016). Similar results were also observed in the study of Salgado *et al.* (2013), where Zn was easily separated from Mn at pH~2 by 20% Cyanex 272, O/A ratio = 1 and T = 50°C (Salgado et al., 2013). However, the initial metal concentrations in their study, i.e., [Zn] = 5.24 g L^{-1} and [Mn] = 6.69 g L^{-1}, were different from this study. Consequently, a higher concentration of Cyanex 272 was necessary in the present study because of the higher Zn concentration in the PLS.

The co-extraction of Fe is inevitable, as it is extracted at a lower pH value (<2.0) compared with the equilibrium pH for Zn extraction (Cytec, 2008). The mixture of both organic phases was transferred to the stripping stage. From Table 7.2, at the first stripping, the average concentration of iron was decreased from 0.69 g L^{-1} to 0.01 g L^{-1}. This quantity of Fe was co-extracted with Zn and was not washed out with Zn when 0.4 M H_2SO_4 was applied as the strip solution. H_2SO_4 solution is widely used as a strip solution because it is cheap and less corrosive compared to other inorganic acids, such as HCl or HNO_3 (Kul and Oskay, 2015; Quinn et al., 2013). 97% Zn was removed from the Cyanex 272 organic phase, with an O/A ratio of 2 and 0.4 M H_2SO_4 (at the first stripping stage). The average stripping efficiency was estimated at 97%, which was higher compared with the result obtained in a previous study (Tanong, 2016). The high stripping efficiency might be due to the longer reaction time and high agitation rate applied in the present experiments.

To regenerate the solvent, 1 M H_2SO_4 was used to remove Fe from the organic solvent. From Table 7.2, the average efficiency of iron removal was not as high as in the previous result (Tanong, 2016). Fe was removed from the organic phase with an efficiency of 58% in the second stripping stage. This solution was suitable to use for another stripping of Fe in the organic phase.

7.6.2 D2EHPA-Cd, Mn extraction and stripping of Cd and Mn from D2EHPA

The raffinate (Zn-depleted solution) obtained from section 7.5.1 was used in the experimental assays for the recovery of Cd and Mn. The Zn-depleted PLS used for this series of experiments contained 0.30 g Co L^{-1}, 4.36 g Ni L^{-1}, 3.53 g Cd L^{-1} and 27.7 g Mn L^{-1} (the raffinate concentration after the second extraction stage using Cyanex 272). After separation of the organic and aqueous phases, the raffinate (aqueous phase) was transferred to the next stage. The organic phase was transferred to the scrubbing stage to remove impurities, followed by the stripping stage to recover Cd and Mn and to recycle the D2EHPA. The results are shown in Table 7.3.

Using the best conditions obtained in the previous study (Tanong, 2016), approximately 95% Cd and 99% Mn were extracted into the organic phase, while only 77.4% Cd (from 3.53 g L^{-1} to 0.80 g L^{-1}) and 93.1% Mn (from 27.7 g L^{-1} to 1.9 g L^{-1}) were extracted in the present study. The low extraction efficiencies (77.4% Cd and 93% Mn) in this experiment were due to the difference in the equilibrium pH obtained in the assays. In the present study, the average equilibrium pH after extraction was 2.2, while in the previous study, it was 2.7 with the addition of the same amount of NaOH. The low equilibrium pH (pH 2.2) obtained in the present study could not be controlled. This might be due to the presence of other basic consumer substances in the PLS solution, which were not present in the synthetic solution. With a single extraction (Table 7.3), efficiencies of 69.4% for Mn and 46.1% for Cd were recorded at pH = 2.2, which is more efficient compared with the study of Hosseini et al. (2010), in which approximately 30% of Mn was extracted at pH = 2.2 using 20% D2EHPA and an O/A ratio of 1 (Hosseini et al., 2010). In the study by Parhi et al. (2009), only 22% of Cd was extracted by 0.2 M D2EHPA at pH = 2.2 (O/A = 1 for 5 min) (Parhi et al., 2009). The lower efficiency (22% Cd) in their results compared with the present study might be due to the shorter reaction times applied in their study.

At these conditions (pH~2.2), approximately 30.9% Co and 20.8% Ni were co-extracted with Cd and Mn (77.4% and 93.1% for Cd and Mn, respectively). This is consistent with the observation by Babakhani *et al.* (2014), where 36% Ni was co-extracted with 88% Cd at pH = 3.0 (Babakhania et al., 2014). To obtain the high Cd/Ni separation factor in their study, a mixture of Cyanex 302 and the organic solvent D2EHPA was used (for a synergistic effect). At pH = 3 and with this organic mixture, only 3% Ni was extracted with Cd and approximately 100% Cd was recovered (0.15 M D2EHPA + 0.45 M Cyanex 302, O/A = 1) (Babakhania et al., 2014). Cyanex 302 also resulted in improved Cd/Ni separation, but it was not used in this study due to its high cost. Instead of adding Cyanex 302 to the organic solvent D2EHPA, a scrubbing stage was applied to remove impurities from the organic solvent. Pagnanelli et al. (2016) obtained the similar results where 20 % of Ni was co-extracted with 90 % of Mn when D2EHPA was applied. In their study, D2EHPA was used to remove the impurities from leach liquor solution obtaining from li-ion battery leaching. In their experiment results, the high purity of Ni and Co solution was obtained after the impurities removal by precipitation and D2EHPA solvent extraction methods. Cobalt was finally recovered selectively by Cyanex 272 and precipitated as the carbonate form.

Contradictory results were obtained in the study of Rodrigues *et al.* (2010), in which Cd was almost completely separated from Co at pH = 3.0, with the sole application of 0.5 M D2EHPA (O/A = 1 at 25°C) (Rodrigues and Mansur, 2010). From our experimental results, the sequence of metal extraction using D2EHPA and when increasing the pH of the solution was: $Cd^{2+} > Co^{2+} > Ni^{2+}$, which is in agreement with the studies of Fatmehsari *et al.* (2009) and Noguerira and Delmas (1999).

The scrubbing method has been used to achieve elimination of impurities from the organic phase in various studies (Haghighi et al., 2015; Owusu, 1998). The organic solvents from both extraction stages were mixed before scrubbing. In Table 7.3, a total quantity of 123 mg Ni (from 906 mg to 783 mg) and 25 mg Co (from 93 mg to 68 mg) were eliminated from the organic phase by the scrubbing method. The removal yields were similar to previous results (Tanong, 2016). The contaminated scrubbed solution was supposed to be recycled in the extraction process, according to Owusu (1998).

To recover Cd and Mn from the organic solvent, the scrubbed organic solvent was intensively mixed with 1.2 M H_2SO_4 at O/A = 4. The average stripping efficacies were equal to 70% for Cd (2.32 g stripped, compared to 3.31 g extracted in the organic phase) and 84% for Mn (23.8 g stripped, compared to 28.4 g extracted in the organic phase), which are also less than those obtained in the previous study (Tanong, 2016).

It is noteworthy that a small decrease in the extraction and stripping performances was observed when the real solution was applied. Globally, the results for the Cd and Mn extractions were satisfactory but could be improved.

7.6.3 Cyanex 272-Co, Cd and Mn removal (purification of nickel sulphate solution)

The raffinate from section 7.5.2 was used in the experimental assays. The solution contained mainly Ni (3.45 g L^{-1}), and the impurities included Co (0.21 g L^{-1}), Cd (0.79 g L^{-1}) and Mn (1.89 g L^{-1}). A single extraction stage with Cyanex 272 (10% Cyanex 272 and O/A = 1/2) was applied. Cyanex 272 was used in this experiment due to its high success in Co/Ni separation, as per previous reports (Cholico-Gonzalez et al., 2015; Tsakiridis and Agatzini-Leonardou, 2004). After purification using solvent extraction, the aqueous phase was transferred for the precipitation of Ni. The organic phase was submitted to the stripping stage using 0.4 M H_2SO_4 and O/A = 0.5. From these experimental results (Table 7.4), the removal efficiencies of Cd (99.6%), Co (98.7%)

and Mn (98.6%) were similar to the results obtained in the experiment with the synthetic solution. An equilibrium pH of 5.9 was necessary in this experiment, which is higher compared to the assays with the synthetic solution (pH = 5.5). Similar results were also found in the study of Guimaraes *et al.* (2014), where approximately 90% Co and Mn were removed from $NiSO_4$ solution at pH~5.9 (10% Cyanex 272, O/A = 1, T = 50°C and 10 min stirring rate) (Guimaraes et al., 2014). A temperature of 50°C was directly applied for easier separation of the two metals because the extraction of Co is more endothermic than that of Ni (Darvishi et al., 2005). It is noted that solvent extraction could be used to concentrate the metals from the PLS. In this case, after the metal extraction step (O/A = 1/2) followed by the stripping step (O/A = 2), the metal concentrations were four times higher compared with the metal concentrations in the aqueous feed. In this study, the stripped solution contained 2.83 g Cd L^{-1}, 7.28 g Mn L^{-1}, 0.803 g Co L^{-1} and 3.67 g Ni L^{-1}, and it was suitable for use in other stripping experiments, to accumulate metals before Ni recovery and/or to return to the first PLS.

7.6.4 Electrochemical experiments

7.6.4.1 Zn electrowinning

The Zn electrodeposition experiments were carried out in the aqueous solution resulting from the Cyanex 272 stripping step (section 3.1). Fig. 7.2 presents the residual Zn concentration measured in the aqueous solution during the electrodeposition step performed at a current density of 370 A m^{-2}, pH = 2 and two successive electrodeposition stages. The energy consumption (kWh L^{-1}) was also observed as a function of time.

Fig. 7.2 shows the decrease of the Zn concentration during the electrodeposition process. The Zn-rich stripped solution from section 3.1 was used. The chemical reactions of Zn electrodeposition in the solution could be revealed in two cases.

The reactions at the cathode (Majuste et al., 2015) are shown in Equations 7.1 and 7.2:

Equation 7-1 $\mathbf{Zn^{2+} + 2e^- \Leftrightarrow Zn_{(s)},\ E_0 = -\ 0.76\ V}$

Equation 7-2 $\mathbf{2H^+ + 2e^- \Leftrightarrow H_{2(g)},\ E_0 = 0.00\ V}$

The reaction at the anode (Majuste et al., 2015) is shown in Equation 7.3:

Equation 7-3 $\mathbf{4\ H^+ + 4\ e^- + O_2 \Leftrightarrow 2\ H_2O,\ E_0 = -1.229\ V}$

The cathode current efficiency (CE) is defined as Equation 7.4 (Majuste et al., 2015):

Equation 7-4 **CE(%) =** $(\mathrm{nFm/Itm})$ **X100CE (%) = (n.F.m/I.t).100**

where F = 96485 C mol^{-1} *is the Faraday constant, "m" corresponds to the mass deposited (g), "I" represents the total current (C sec*$^{-1}$*) and "t" is the deposition time (s).*

The cathode current efficiency of Zn from the above equation was estimated to be 58% in the present result, which is similar to our previous study (Tanong , 2016).

A high concentration of Cd (55 mg L^{-1}) was present in the stripped Cyanex 272 solution (contained mainly of 9,550 mg Zn L^{-1}), while in our previous study, only 5 mg Cd L^{-1} was present. To attain a potential in Zn electrowinning, the Cd concentration should not be greater than 1 mg L^{-1} (Haghighi et al., 2015). From this previous statement, a scrubbing step is recommended to remove Cd impurities from the Zn–loaded Cyanex 272. Addition of the scrubbing stage should be considered in further work, to improve the purity of metallic Zn.

Selectively recovery of Cd from the aqueous phase containing Cd (II) and Mn (II)

Cd was selectively recovered from the stripped solution from section 7.5.2, which mainly contained Cd and Mn. Cd could be deposited on the cathode surface according to the following equations:

Cathodic reaction (Equation 7.5) (Moradkhani et al., 2012)

Equation 7-5 $Cd^{2+} + 2e^- \Leftrightarrow Cd_{(s)}, E = -0.40\ V$

At the anode, in addition to the reaction of H^+ (Equation 2), the reaction of Mn occurred as follows (Equation 7.6) (Mahon and Alfantazi, 2014):

Equation 7-6 $Mn^{2+} + 2\ H_2O \Leftrightarrow MnO_2 + 4\ H^+ + 2\ e^-, E = +1.23\ V$

The synthetic aqueous solution initially contained 4.29 g Cd L^{-1} and 27.3 g Mn L^{-1}.

According to Equation 7.5, Mn^{2+} is oxidized to MnO_2 at the anode, while only Cd^{2+} is reduced to metallic Cd and deposited on the cathode. From our experimental results, shown in Fig. 7.3, the Cd concentration was decreased from 2,207 mg L^{-1} to 900 mg L^{-1}, 5.6 mg L^{-1} and 4.6 mg L^{-1} after 90, 300 and 360 min, respectively. In the previous study, the Cd concentration was decreased from 4,200 mg L^{-1} to 10 and 8 mg L^{-1} after 90 and 360 min, respectively, under the same experimental conditions. The CE in the present study was only 10 % while in the previous study, it was estimated as 32 %. The decrease in the CE was due to the low initial concentration of Cd (2.2 g/L), which deteriorated the deposition efficiency (Safarzadeh and Moradkhani, 2010). The use of additives in the solution could likely improve the CE (Biswal et al., 2012), or Cd could be concentrated by a solvent extraction method. The Cd concentration could be increased by changing O/A ratio in the extraction or stripping steps. After 360 min, the concentration of Cd was found to be 4.6 mg L^{-1}, while Mn remained almost constant (19.97 g L^{-1} to 19.2 g L^{-1}) (results not shown). The Cd powder was easily peeled off and washed with distilled water to remove the dissolved Mn (Moradkhani et al., 2012). 2.36 g of Cd was obtained and washed with distilled water, to obtain ~98% purity.

7.6.5 Precipitation

Ni and Mn were completely precipitated at pH = 9 by adding Na_2CO_3. 1 L of $MnSO_4$ and 1 L of $NiSO_4$ (effluent from section 7.5.4) needed 65 g and 13 g of Na_2CO_3, respectively, to form the precipitated solids.

However, the $MnCO_3$ and $NiCO_3$ had a low purity due to the co-precipitation of sodium and sulfur. To eliminate Na, K and S, distilled water was intensively mixed with the precipitated solids, and two successive washing steps were necessary. From the experimental results, the average removal efficiencies were determined to be 91 ± 5% for Na, 99 ± 10% for K and 96 ± 2% for S, and $MnCO_3$ of average purity 97 ± 0.4% was obtained. For solid $NiCO_3$, the average removal efficiencies of Na and S were 97± 1% and 90 ± 1%, respectively, after two successive washing steps. The average purity of $NiCO_3$ was 97 ± 1%, which is acceptable.

7.6.6 Mass balance

Fig. 7.4 presents the chemical products for the input and the metal recovery for the outputs. From this figure, it can be noticed that 109 g of black mass were mixed with 1 L of leaching solution containing sulphuric acid and a reducing agent as mentioned in the previous section. The leach liquor contains 20.8 g of Zn, 28.6 g of Mn, 4.49 g of Ni, 3.57 g of Cd, 0.69 g of Fe and 3.57 g of Co. Firstly, Zn was extracted using Cyanex 272 and stripped using sulphuric acid. Consequently, 16.4 g of Zn were recovered in metallic form by electrodeposition. It could be seen that, the electrodeposition efficiency was not high (85.9%) and needed to be optimized to maximize Zn-electrodeposition rate. Secondly, Cd and Mn were extracted using D2EHPA and stripped using sulphuric acid. Then, 2.36 g of Cd were selectively electrodeposited and 23.8 g of Mn were recovered as carbonate. The impurities (Co, Mn and Cd) were eliminated from the Zn-Cd-Mn-depleted solution using Cyanex 272 (extraction at pH = 5.9) to obtain a pure $NiSO_4$ solution. Approximately 2.38 g of Ni were then recovered as carbonates. The cobalt was not recovered and remained in the scrubbed solution emerging from the D2EHPA extraction step and in the stripped solutions emerging from the Cyanex 272 extraction process (extraction at pH = 5.9). From these results, around 70% of the metals including Zn, Mn, Cd and Ni were recovered from the solution leach liquor. Further improvements in the performances of metals recoveries should be done. Table 7.5 shows the volume of water recycled in the process. Ideally, the input and output should be equal. In this present study, the balance errors of water varied between 0.8 and 1.0, which was similar to the study carried out by Janin et al. (2012). A deviation of 20% was found for the $NiCO_3$ precipitation step, which could be due to a water loss during the filtration of the precipitate of $NiCO_3$.

Table 7.6 reveals the metal mass balance for the whole process defined for the treatment of 1 ton of waste battery powder. The sum of outputs (recovered metals) including the leaching residue and the accumulation of metals in the process are equal to the inputs (initial metals in battery powder). In Table 7.6, from the 193.5 kg of Zn initially present in one ton of battery powder, approximately 33.9 kg of Zn remained in the solution after the electrodeposition process, 5.8 kg in the Zn-loaded Cyanex 272 and 2.8 kg in the final residue (residue of battery powder). The high accumulation of Zn in the aqueous phase was found due to the high Zn residual in the effluent from electrodeposition process in the study. A high amount of Mn was found in the aqueous phase (67.0 kg) as well as in the organic phase (44.5 kg) due to the non-effective leaching efficiencies and its accumulation during solvent extraction.

After D2EHPA extraction step, the residual amounts of Mn and Cd present in the aqueous phase were transferred to the Cyanex 272 (10%) organic solvent at pH = 5.7 (See figure 7.4). Considering the stripping stage, the Cd and Mn stripping efficiencies were not as high as expected.

Non-effective dissolution of Ni (78%) led to the high quantity of Ni in the final residues (11.5 kg) (Tanong, 2016). A high amount of Ni (14.5 kg) was co-extracted with Cd and Co during the D2EHPA and Cyanex 272 extractions. The Co was not recovered and remained in the stripped solution from Cyanex 272 extraction at pH = 5.7

7.6.7 Chemical agents costs and metal revenues

Table 7.7 reveals the quantity of each chemical product and their total cost for each assay. The highest quantity of chemical products was used in the leaching experiment, while the lowest chemical quantity was used in the electrodeposition assay. In this study, the organic solvent lost during the process was considered as the quantity of chemical used. In the case of Cyanex 272, D2EHPA, TBP and kerosene, the percentages of organic solvent lost were determined as approximately 50 ppm for each operation. These data were obtained from personal contact with the company. A very high quantity of NaOH was required for neutralization during the organic extraction, and this was the main drawback of the solvent extraction at an industrial scale.

In the present study, Zn, Mn, Ni and Cd were recovered in different forms. The final products can be used in many industrial applications. Metallic Zn is widely used in the field of corrosion-resistant coatings and energy storage (Samir et al., 2016). Metallic Cd can be used in many applications, including photovoltaic applications (Rudnik and Nikiel, 2007), coatings for corrosion protection, control rods in nuclear power plants, etc. (Safarzadeh and Moradkhani, 2010). $MnCO_3$ can be used to fabricate anodes in Li-ion products (Aragon et al., 2011). Nickel can be used to produce catalysis, coins, jewellery, batteries, industrial plumbing, nickel alloys, spark plugs, electroplating, machinery parts, stainless-steel, nickel-chrome and resistance wires (Salcedo et al., 2016).

From Table 7.7, the metal revenue in this study was equal to \$2,132 t^{-1} of battery power treated. The total chemical cost was evaluated to be \$814 t^{-1} of battery powder treated. It can be seen that the chemical cost is approximately 50% of the metal revenue. Thus, it can be concluded that the process is economically feasible.

In summary, solvent extraction, electrodeposition and precipitation were used to selectively recover metals from a PLS to obtain high-purity products (more than 90%). The effluent from the process (recycled water) should be treated with care so as to limit the metals discharged into sewers (Cd = 0.5 mg L^{-1}, Co = 5 mg L^{-1}, Mn = 5 mg L^{-1}, Ni = 2 mg L^{-1}, Zn = 2 mg L^{-1}) (MDDELCC, 2015).

7.6 CONCLUSIONS

Green alternative solvent could be tested to replace the solvent used in this study when they will be available on the market. Green solvent could mitigate the environmental and disposal problems due to the expensive costs related to the management of waste emerging from the current solvent extraction process. The pre-treatment method should be further conducted at pilot scale by applying the cryogenics system. The leaching performance should be further improved at pilot scale to obtain the maximum metals yields in leach liquor. In the recovery steps, some metals lost should be mitigated and the improvement in recovering efficiencies needs to be achieved. Consequently, if more metals could be recovered from process optimization, it means that better financial results could be obtained. In conclusion, the experiments were conducted only in laboratory scale, so further researches are necessary at pilot scale to validate the process performances. Metals of high purity were obtained in this study owing to the solvent extraction process developed. Cyanex 272 and D2EHPA were proved as effective agents for the selective recovery of individual metals. However, there is still needs to improve some processing steps, especially in the electrodeposition stage due to its low current efficiency and the presence of impurities in the deposited metals. When the PLS was used, similar process efficiencies were found for the solvent extraction step as those obtained for the assays carried out with the synthetic solution, where the metals recovering efficiencies were superior to 80% (from PLS synthetic and PLS obtained from the leaching process). However, lower electrodeposition efficiencies for the cadmium (CE = 10%) were found when the PLS was used instead of the synthetic solution because of the lower initial concentrations of metals (4.3 g/L Cd in the previous study, 2.2 g/L Cd in the present study). In the present study, only 77% of Zn were recovered by electrodeposition while almost 100% of Zn were electrodeposited from the synthetic solution (same electrodeposition times). For Cd, it was necessary to remove the maximum of Cd from Mn. In the present study, the electrodeposition time required to remove Cd from Mn (approximately of 99.5% of Cd electrodeposition efficiency) was longer in PLS solution compared to the synthetic solution. In conclusion, 73% of Mn (218.3 kg), 78% of Zn (134 kg), 41% of Ni (23.8 kg) and 59% of Cd (21.6 kg) were recovered per ton of mixture of battery powder.

7.7 Acknowledgments

The authors acknowledge the Natural Sciences and Engineering Research Council of Canada for the financial support to this research (grant RGPIN-2014-04794).

7.8 REFERENCES

- Al-Thyabat, S., Nakamura, T., Shibata, E., Lizuka, A., 2013. Adaptation of minerals processing operations for lithium-ion (LiBs) and nickel metal hydride (NiMH) batteries recycling. Miner. Eng. 45, 4-17.
- Alibaba, 2015. Available at: http://www.alibaba.com, Consulted on May 2016.
- APHA, 1999. Standards methods for examination of water and wastewaters. American Public Health Association, US.
- Aragon, M.J., Leon, B., Vicente, C.P., Tirado, J.L., 2011. A new form of manganese carbonate for the negative electrode of lithium-ion batteries. J Power Sources 196, 2863-2866.
- Avilaa, M., Grinbaumb, B., Carranzac, F., Mazuelosc, A., Romeroc, R., Iglesiasc, N., Lozanod, J.L., Pereza, G., Valiente, M., 2011. Zinc recovery from an effluent using Ionquest 290: From laboratory scale to pilot plant. Hydrometallurgy 107, 63-67.
- Barnard and Shiers. Available at: https://publications.csiro.au/rpr/download?pid=csiro:EP105301&dsid=DS4, Consulted on May 2016.
- Bunnings, 2016. Available at: http://www.bunnings.com.au/our-range/paint-decorating/paint-accessories/chemicals-solvents/kerosene, Consulted on May 2016.
- Babakhania, A., Rashchia, F., Zakerib, A., Vahidic, E., 2014. Selective separation of nickel and cadmium from sulfate solutions of spent nickel–cadmium batteries using mixtures of D2EHPA and Cyanex 302. J Power Sources 247, 6.

- Barret, H.A, Borkiewicz, O., Krekeler, M.P.S., 2011. An investigation of zincite from spent anodic portions of alkaline batteries: An industrial mineral approach for evaluating stock material for recycling potential. J Power Sources 196, 508-513.
- Bertuol, D.A., Bernardes, A.M., Tenorio, J.A.S., 2009. Spent NiMH batteries-The role of selective precipitation in the recovery of valuable metals. J Power Sources 193, 914-923.
- Biswal, A., Padhy, K., Sarangi, C.K., Tripathy, B.C., Bhattacharya, I.N., Subbaiah, T., 2012. The effects of magnafloc and zinc on electrowinning of cadmium in sulfate solutions. Hydrometallurgy 117, 13-17.
- Bonhomme, R., Gasper, P., Hines, J., Miralda, J.P., 2013. Enonomic Feasibility of a Novel Alkaline Battery recycling process, Faculty of Worcester Polytechnic Insititute, Massachusetts, USA.
- Cholico-Gonzalez, D., Chagnes, A., Cote, G., Avila-Rodriguez, M., 2015. Separation of Co(II) and Ni(II) from aqueous solutions by bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) using trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) as solvent. J Mol Liq 209, 203-208.
- Coll, M.T., Fortuny, A., Kedari, C.S., Sastre, A.M., 2012. Studies on the extraction of Co(II) and Ni(II) from aqueous chloride solutions using Primene JMT-Cyanex272 ionic liquid extractant. Hydrometallurgy 125, 24-28.
- Cytec, 2008. Cyanex 272 extractant. Cytec, Canada, p. 16.
- Darvishi, D., Haghshenas, D.F., Alamdari, E.K., Sadrnezhaad, S.K., Halali, M., 2005. Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA. Hydrometallurgy 77, 227-238.
- Deep, A., Sharma, A.L., Mohanta, G.C., Kumar, P., Kim, K.H., 2016. A facile chemical route for recovery of high quality zinc oxide nanoparticles from spent alkaline batteries. Waste Manage 51, 190–195.

- De Michelis, I., Ferella, F., Karakaya, E., Beolchini, F., Veglio, F., 2007. Recovery of zinc and manganese from alkaline and zinc-carbon spent batteries. J Power Sources 172, 975-983.
- Diaz, L.A., Lister, T.E., Parkman, J.A., Clark, G.G., 2016. Comprehensive process for the recovery of value and critical material from electronic waste. J Clean Prod 125 236-244.
- Espinosa, D.C.R., Bernardes, A.M., Tenório, J.A.S., 2004. An overview on the current processes for the recycling of batteries. J Power Sources 135, 311-319.
- Fatmehsari, D.H., Darvishi, D., Etemadi, S., Hollagh, A.R.E., Alamdari, E.K., Salardini, A.A., 2009. Interaction between TBP and D2EHPA during Zn, Cd, Mn, Cu, Co and Ni solvent extraction: A thermodynamic and empirical approach. Hydrometallurgy 98, 143-147.
- Freitas, M.B.J.G., Pegoretti, V.C., Pietre, M.K., 2007. Recycling manganese from spent Zn-MnO2 primary batteries. J Power Sources 164, 947-952.
- Frohlich, S., Sewing, D., 1995. The BATENUS process for recycling mixed battery waste. J Power Sources 57, 27-30.
- Granata, G., Pagnanelli, F., Moscardini, E., Takacova, Z., Havlik, T., Toro, L., 2012. Simultaneous recycling of nickel metal hydride, lithium ion and primary lithium batteries: Accomplishment of European Guidelines by optimizing mechanical pre-treatment and solvent extraction operations. J Power Sources 212, 205-211.
- Guimaraes, A.S., da Silva, P.S., Mansur, M.B., 2014. Purification of nickel from multicomponent aqueous sulphuric solutions by synergistic solvent extraction using Cyanex 272 and Versatic 10. Hydrometallurgy 150, 173-177.
- Haghighi, H.K., Moradkhani, D., Salarirad, M.M., 2015. Separation of zinc from manganese, magnesium, calcium and cadmium using batch countercurrent extraction simulation followed by scrubbing and stripping. Hydrometallurgy 154, 9-16.

- Hosseini, T., Rashchi, F., Vahidi, E., Mostoufi, N., 2010. Investigating the Synergistic Effect of D2EHPA and Cyanex 302 on Zinc and Manganese Separation. Sep Sci Technol 45, 1158-1164.
- Hutton-Ashkenny, M., Ibana, D., Barnard, K.R., 2015. Reagent selection for recovery of nickel and cobalt from nitric acid nickel laterite leach solutions by solvent extraction. Minerals Engineering 77, 42-51.
- ICIS, 2015. Available at: http://www.icis.com/about/price-reports/?cmpid=PSC%7CCHEM%7C2012-GLOBAL-adwd-generalprices&sfid=70120000000Hu8n&utm_term=icis%20price&matchtype=b-25780357814&gclid=CKPN7a-1-dACFU-1wAodfi4Dlw&gclsrc=aw.ds, Consulted on May 2016.
- Janin, A., Coudert, L., Blais, J.B., Mercier, G., Cooper, P., Gastonguay, L., Morris, P., Design and performance of a pilot-scale equipment for CCA-treated wood remediation. Separ Sci Technol 85, 90-95.
- Kul, M., Oskay, K.O., 2015. Separation and recovery of valuable metals from real mix electroplating wastewater by solvent extraction. Hydrometallurgy 155, 7.
- Ku, H., Jung, Y., Jo, M., Park, S., Kim, S., Yang, D., Rhee, K., EM, An., Sohn, J., Kwon, K., 2016. Recycling of spent lithium-ion battery cathode materials byammoniacal leaching. J Hazard Mater 313, 138-146.
- Laki, S., Shamsabadi, A.A., Kargari, A., 2016. Comparative solvent extraction study of silver (I) by MEHPA and Cyanex 302 as acidic extractants in a new industrial diluent (MIPS). Hydrometallurgy 160, 38-46.
- Li, Z., Smith, K.H., Stevens, G.W., 2016. The use of environmentally sustainable bio-derived solvents in solvent extraction application- A review. Chin J Chem Eng 24, 215-220.
- Lu, H., Wang, Y., Wang, J., 2015. Recovery of Ni2+ and pure water from electroplating rinse wastewater by intergrated two-stage electrodeionization process. J Clean Prod 92, 257-266

- Mahon, M., Alfantazi, A., 2014. Manganese consumption during zinc electrowinning using a dynamic process simulation. Hydrometallurgy 150, 184-191.
- Majuste, D., Martins, E.L.C., Souza, A.D., Nicol, M.J., Ciminelli, V.S.T., 2015. Role of organic reagents and impurity in zinc electrowinning. Hydrometallurgy 152, 190-198.
- MDDELCC (Ministère du Développement durable de l'Environnement et de la Lutte contre les changements climatiques), 2015. Modèle de règlement relatif aux rejets dans les réseaux d'égout des municipalités du Québec.
- Mishra, R.K., Rout, P.C., Sarangi, K., Nathsarma, K.C., 2016. Solvent extraction of zinc, manganese, cobalt and nickel from nickel laterite bacterial leach liquor using sodium salts of TOPS-99 and Cyanex 272. T Nonferr Metal Soc 26, 301-309.
- Moradkhani, D., Rasouli, M., Behnian, D., Arjmandfar, H., Ashtari, P., 2012. Selective zinc alkaline leaching optimization and cadmium sponge recovery by electrowinning from cold filter cake (CFC) residue. Hydrometallurgy 115, 84-92.
- Nogueira, C.A., Delmas, F., 1999. New flowsheet for the recovery of cadmium, cobalt and nickel from spent Ni-Cd batteries by solvent extraction. Hydrometallurgy 52, 267-287.
- Owusu, G., 1998. Selective extractions of Zn and Cd from Zn-Cd-Co-Ni sulphate solution using di-2-ethylhexyl phosphoric acid extractant. Hydrometallurgy 47, 205-215.
- Pagnanelli, F., Moscardini, E., Altimari, P., Atia, T.A., Toro, L., 2016. Cobalt products from real waste fractions of end of life lithium ion batteries. Waste Manage 51, 214-221.
- Parhi, P.K., Das, N.N., Sarangi, K., 2009. Extraction of cadmium from dilute solution using supported liquid membrane. J Hazard Mater 172, 773-779.
- Provazi, K., Campos, B.A., Espinosa, D.C.R., Tenorio, J.A.S., 2011. Metal separation from mixed types of batteries using selective precipitation and liquid-liquid extraction techniques. Waste Management 31, 59-64.

- Quinn, J.E., Wilkins, D., Soldenhoff, K.H., 2013. Solvent extraction of uranium from saline leach liquors using DEHPA/Alamine 336 mixed reagent. Hydrometallurgy 134-135, 5.
- Roberge, J., 2010. Les piles domestiques Fiches informatives. Recyc-Québec.
- Rodrigues, L.E.O.C., Mansur, M.B., 2010. Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel-metal–hydride batteries. J Power Sources 195, 6.
- Rudnik, E., Nikiel, M., 2007. Hydrometallurgical recovery of cadmium and nickel from spent Ni-Cd batteries. Hydrometallurgy 89, 61-71.
- Safarzadeh, M.S., Moradkhani, D., 2010. The electrowinning of cadmium in the presence of zinc. Hydrometallurgy 105, 168-171.
- Salcedo, A.F.M., Ballesteros, F.C., Vilando, A.C., Lu, M.C., 2016. Nickel recovery from synthetic Watts bath electroplating wastewater by homogeneous fluidized bed granulation process. Separation and Purification Technology, 8.
- Salgado, A.L., Veloso, A.M.O., Pereira, D.D., Gontijo, G.S., Salum, A., Mansur, M.B., 2003. Recovery of zinc and manganese from spent alkaline batteries by liquid-liquid extraction with Cyanex 272. J Power Sources 115, 367-373.
- Samir, I., Bakkara, A., Ahmeda, E., Selim, A., 2016. Effect of additives and current mode on zinc electrodeposition from deep eutectic ionic liquids. Electrochimica Acta 191, 8.
- Sayilgan, E., Kukrer, T., Ferella, F., Akcil, A., Veglio, F., Kitis, M., 2009. Reductive leaching of manganese and zinc from spent alkaline and zinc-carbon batteries in acidic media. Hydrometallurgy 97, 73-79.
- Sigmaaldrich, 2015. Available at: http://www.sigmaaldrich.com/catalog/product/aldrich/237825?lang=fr&region=CA, Consulted on May 2016.

- Sobianowska-Turek, A., Szczepaniak, W., Maciejewski, P., Gawlik-Kobylińska, M., 2016. Recovery of zinc and manganese and other metals (Fe, Cu, Ni, Co, Cd, Cr, Na, K) from Zn-MnO2 and Zn-C waste batteries : hydroxyl and carbonate co-precipitation from solution after reducinh acidic leaching with use of oxalic acid. J Power Sources 325, 220-228.
- Tanong, K., 2016. Hydrometallurgical recovery of metals from the mixture of waste batteries, thesis for PhD in Water Sciences, National Institute of Scientific Research Centre Eau Terre Environnement, Canada.
- Tsakiridis, P.E., Agatzini-Leonardou, S., 2004. Process for the recovery of cobalt and nickel in the presence of magnesium from sulphate solutions by Cyanex 272 and Cyanex 302. Minerals Engineering 17, 913-923.

7.9 FIGURE CAPTION LIST

7.10 TABLE CAPTION LIST

Table 7.1 Unit price of the chemicals used in the process and products obtained at the end of the process

Table 7.2 Selective extraction performances of Zn from PLS using Cyanex 272 after two stages of extraction (30% (v v^{-1}) Cyanex 272 and 2% (v v^{-1}) TBP in kerosene, O/A = 2/1) at pH = 2.5.

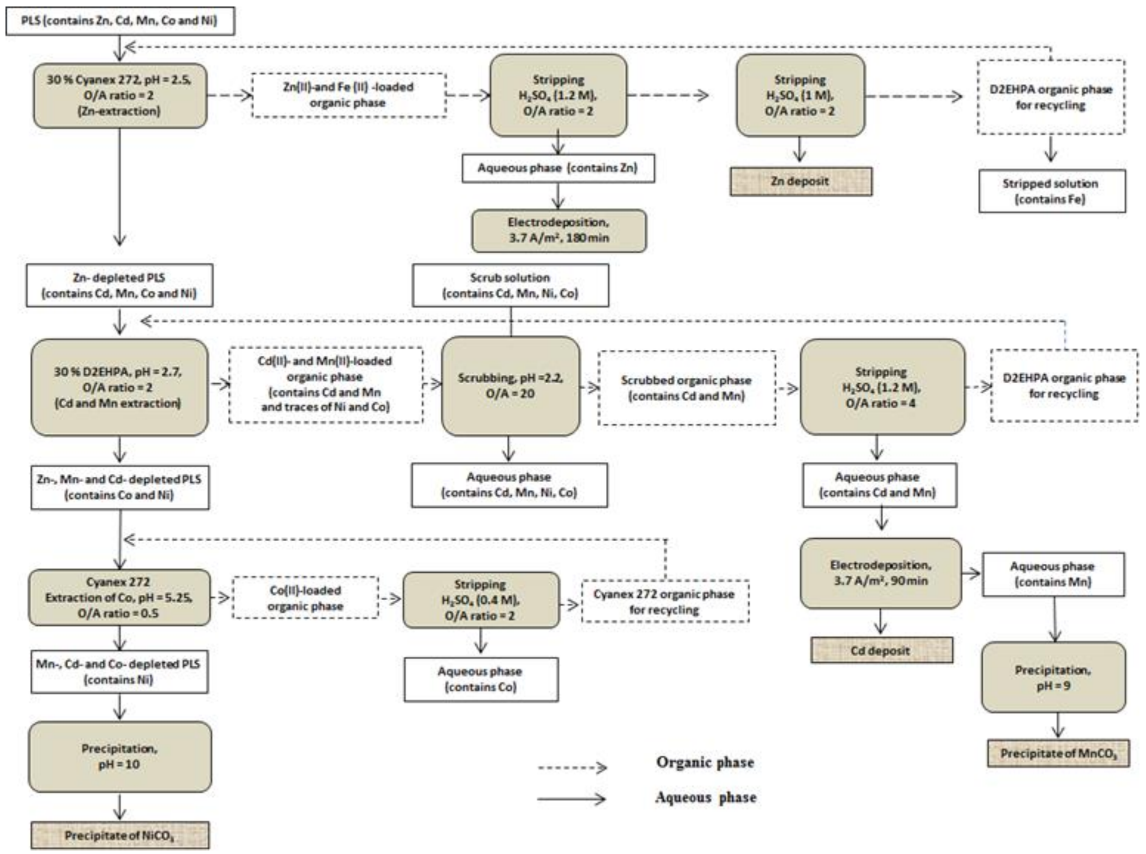
Table 7.3 Simultaneously extraction performances of Cd and Mn from Zn-depleted PLS using D2EHPA after two stages of extraction (30% (v v^{-1}) D2EHPA and 5% (v v^{-1}) TBP in kerosene, O/A = 2/1) at pH = 2.2 following the scrubbing stage (O/A = 20) and stripping stage (O/A = 4, 1.2 M H_2SO_4).

Table 7.4 Removal of the impurities from Cd-, Mn- depleted PLS using Cyanex 272 after one stage of extraction (10% (v v^{-1}) Cyanex 272 and 5% (v v^{-1}) TBP in kerosene, O/A = 1/2) at pH = 5.9 to recover Ni.

Table 7.5 Water balance of the metal recycling process from spent batteries.

Table 7.6 Mass balance of metals defined for the treatment of one ton of battery powder (unity = kg).

Table 7.7 The summary chemical cost in each step of metal extraction and the metal revenue.



Stripping: Process where acid solution was applied to remove the metals from the organic phase
Stripped solution: Acid solution rich in metals obtained after the stripping process
PLS: Pregnant leach solution rich in metals emerging from the leaching process
Metal-depleted PLS: Aqueous solution obtained after metal removal by solvent extraction (ex. Zn-depleted PLS: pregnant leach solution obtained after Zn removal by extraction)
Metal-loaded organic phase: Organic solvent rich in target metal obtained by solvent extraction (ex. Zn-loaded organic phase: organic solvent rich in Zn)
Scrubbing: Process in solvent extraction which was applied to remove the impurities from the organic solvent
Scrub solution: Solution rich in target metal which was introduced in the scrubbing process
Scrubbed solution: Effluent emerging from the scrubbing process rich in impurities.

Figure 7.1 Detailled flowsheet of the hydrometallurgical route to treat the mixture of waste batteries.

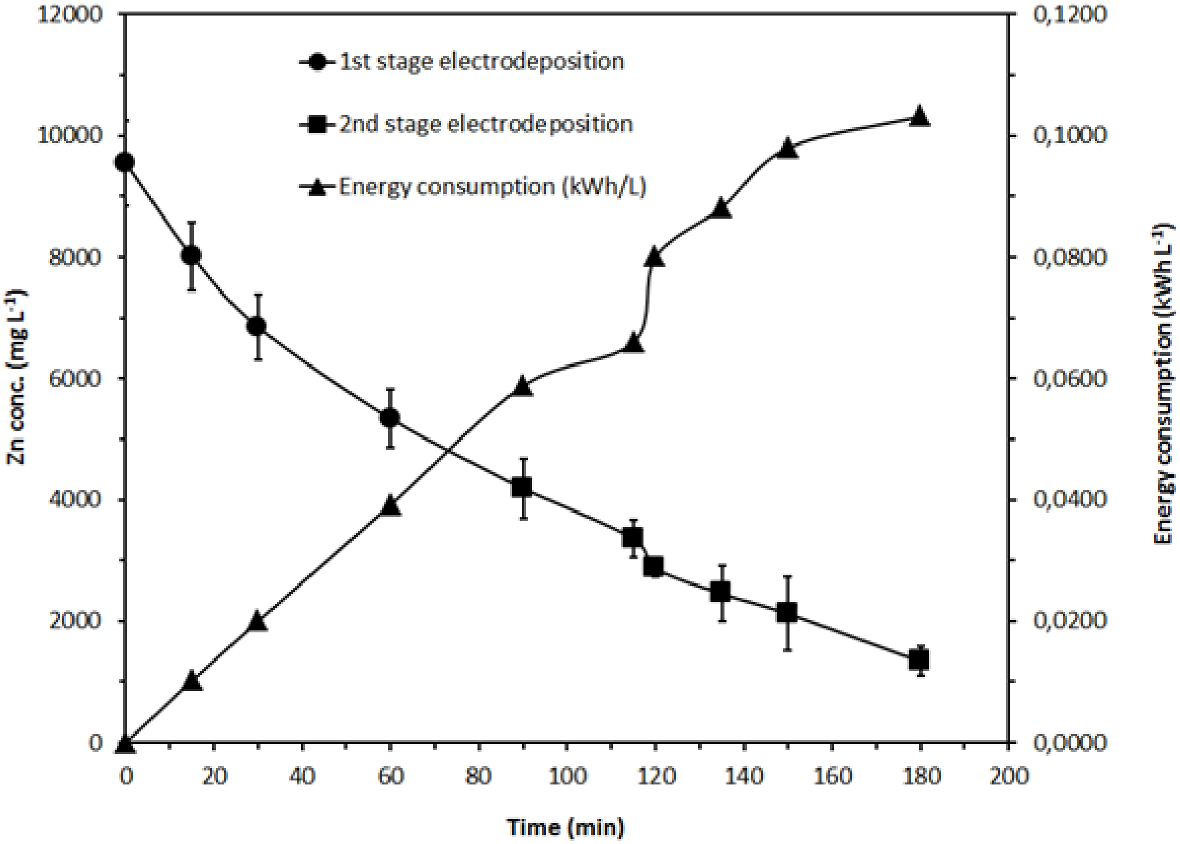


Figure 7.2 Variation of residual Zn concentration and energy consumption in two stages of Zn electrodeposition in function of the deposition time applying a current density of 370 A m^{-2}.

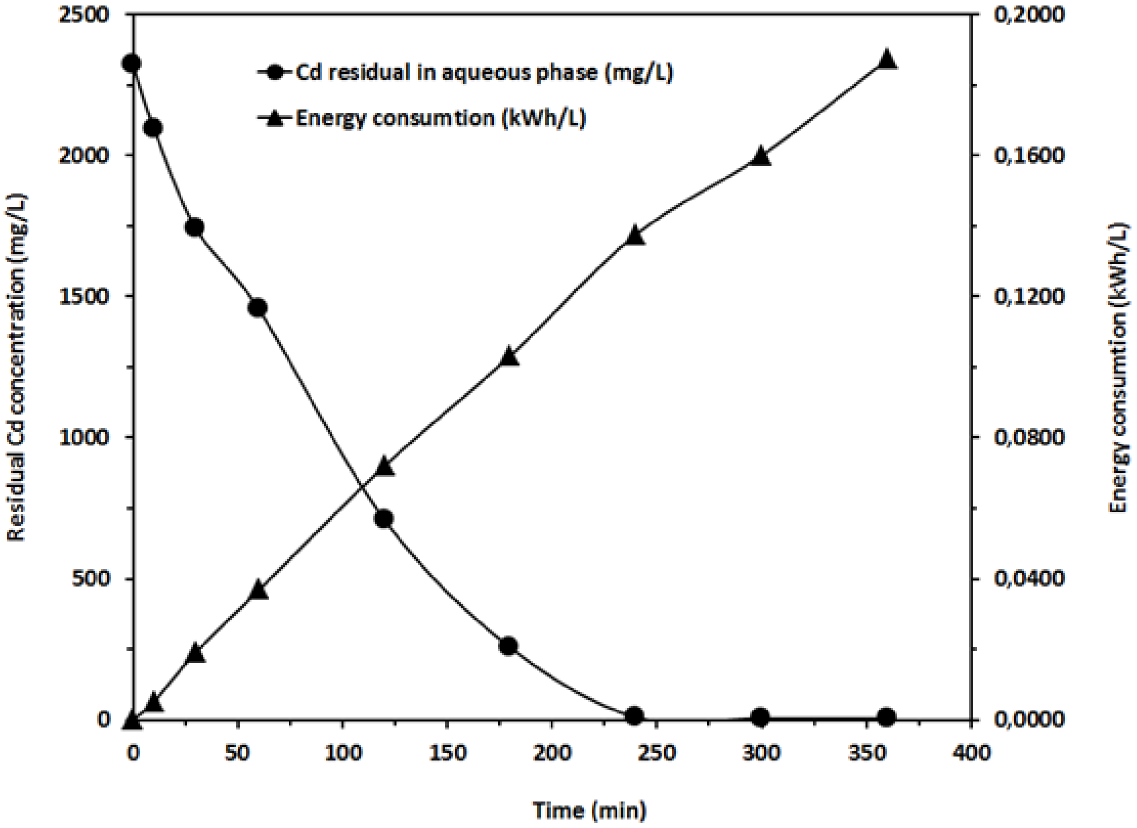


Figure 7.3 Variation of residual Cd concentration and energy consumption during electrodeposition in function of the deposition time applying a current density of 370 A m^{-2}.

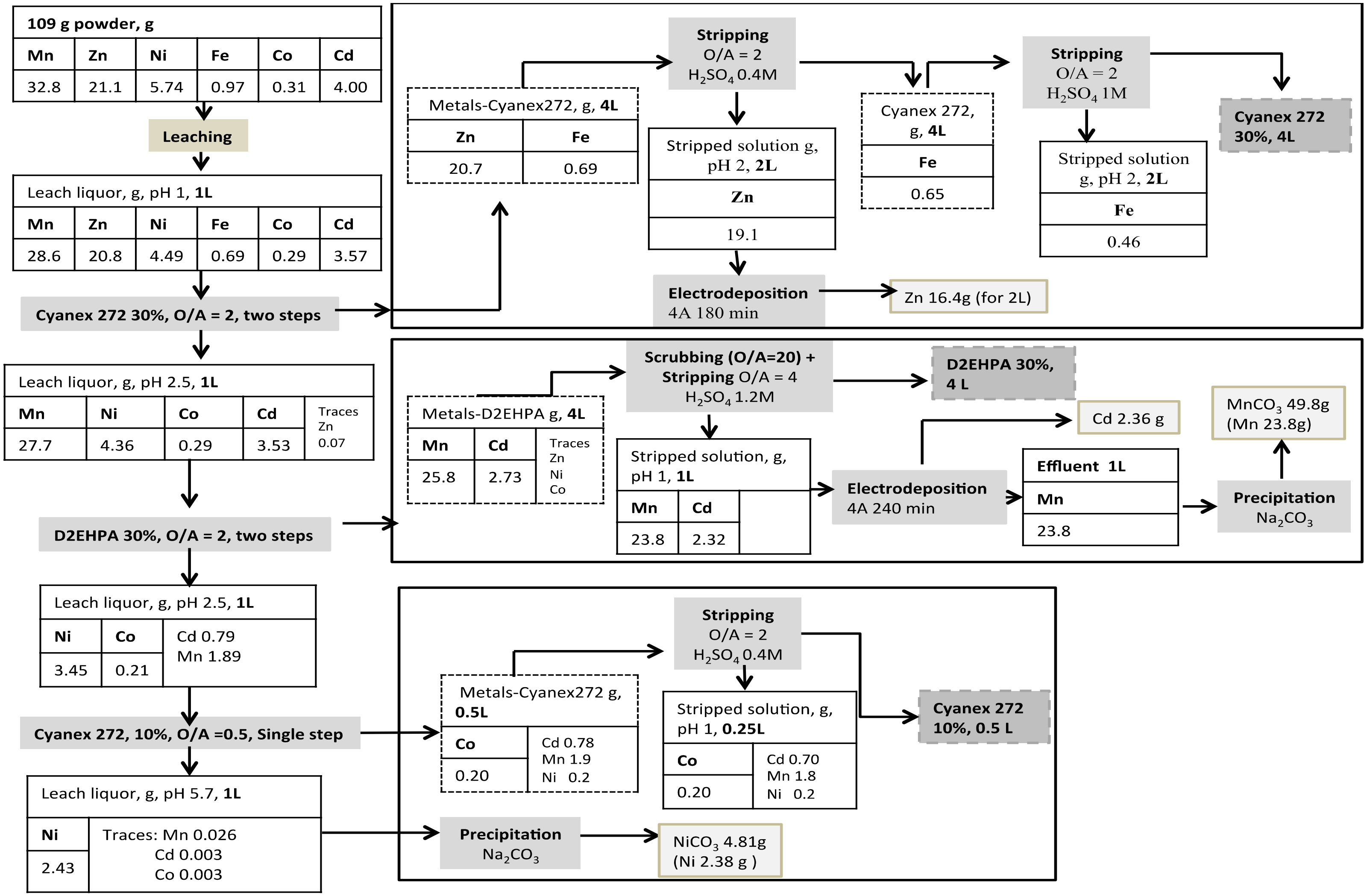


Figure 7.4 Metal compounds and chemical products at the different steps of the hydrometallurgical process for the treatment of spent batteries.

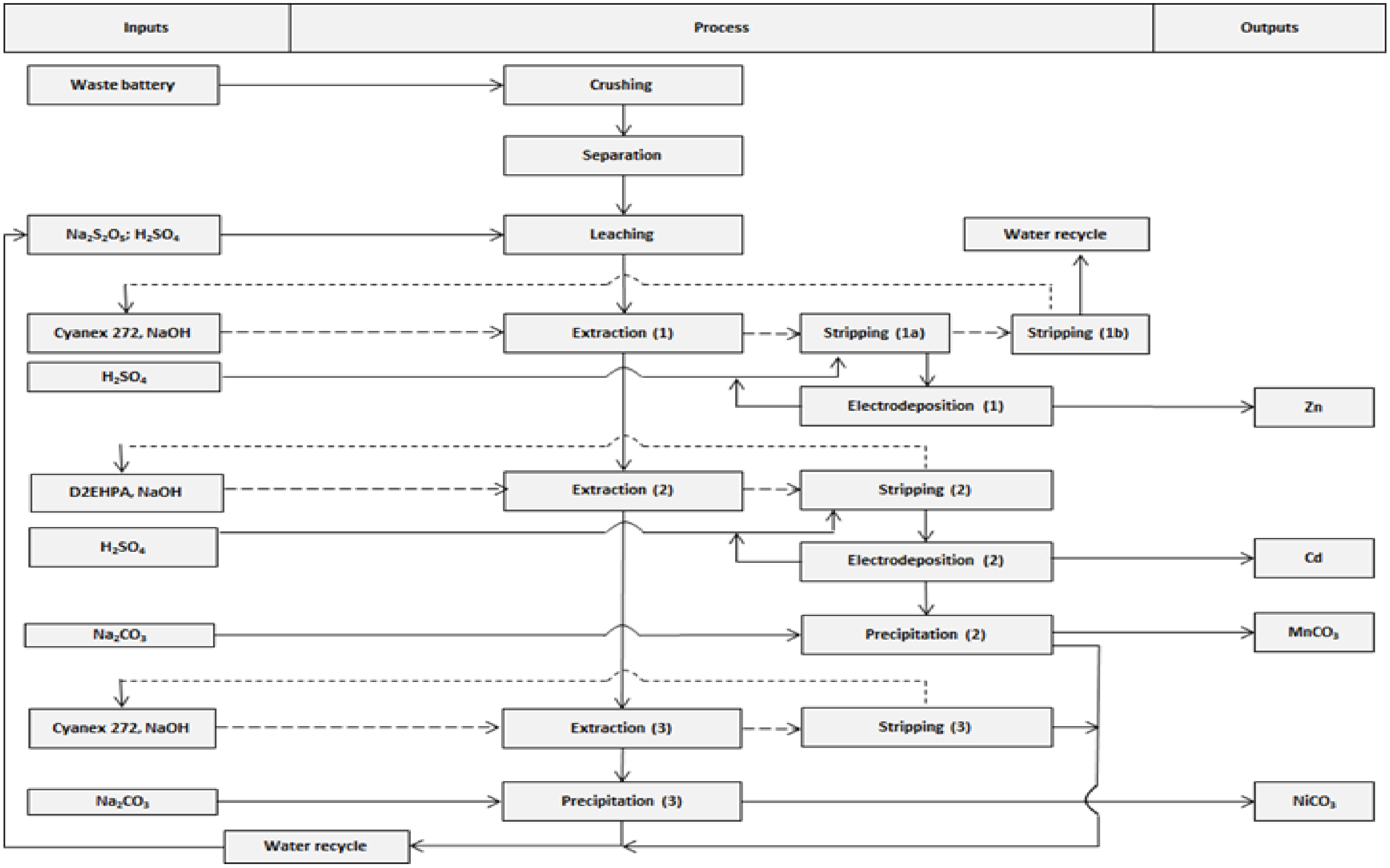


Figure 7.5 Illustrative of the selective Cd electrodeposition in the solution containing $MnSO_4$ and $CdSO_4$.

Table 7.1 Chemical products cost

Chemical products	Price ($ USD per ton)	References
Inorganic products		
• H_2SO_4	100	ICIS, 2015
• $Na_2S_2O_5$	250	Alibaba, 2015
• NaOH	250	Personal contact with Cytec company, 2014
• Na_2CO_3	159	Alibaba, 2015
Metals		
• Zn metal	6,500	Alibaba, 2015
• Cd metal	1,000	Alibaba, 2015
• $MnCO_3$	1,300	Alibaba, 2015
• $NiCO_3$	13,500	Alibaba, 2015
Organic products	$/L	
• Cyanex 272	71.2	Barnard and Shiers
• D2EHPA	37.8	Sigmaaldrich, 2015
• TBP	2.15	Barnard and Shiers
• Kerosene	1.00	Bunnings, 2015

Table 7.2 Selective extraction performances of Zn from PLS using Cyanex 272 after two stages of extraction (30% (v v^{-1}) Cyanex 272 and 2% (v v^{-1}) TBP in kerosene, O/A = 2/1) at pH = 2.5.

	Residual concentration measured in the aqueous phase (g L^{-1})					
	Cd	**Co**	**Fe**	**Mn**	**Ni**	**Zn**
PLS solution (1L)	3.6 ± 0.1	0.29 ± 0.02	0.69 ± 0.18	28 ± 2	4.5 ± 0.7	21 ± 0.
EXTRACTION STAGE						
1st extraction	3.6 ± 0.1	0.29 ± 0.01	0.01 ± 0.00	29 ± 1	4.5 ± 0.1	6.3 ± 0.2
2nd extraction	3.5 ± 0.3	0.30 ± 0.02	0.00 ± 0.00	28 ± 2	4.4 ± 0.3	0.07 ± 0.04
STRIPPING STAGE						
1st stripping (2L)	0.05 ± 0.01	0.01 ± 0.00	0.03 ± 0.01	0.82 ± 0.02	0.05 ± 0.02	9.6 ± 0.4
2nd stripping (2L)	0.00 ± 0.00	0.00 ± 0.00	0.20 ± 0.01	0.03 ± 0.01	0.00 ± 0.00	0.47 ± 0.04

Table 7.3 Simultaneously extraction performances of Cd and Mn from Zn-depleted PLS using D2EHPA after two stages of extraction (30% (v v^{-1}) D2EHPA and 5% (v v^{-1}) TBP in kerosene, O/A = 2/1) at pH = 2.2 following the scrubbing stage (O/A = 20) and stripping stage (O/A = 4, 1.2 M H_2SO_4).

	Concentration measured in the aqueous phase (g L^{-1})				
	Cd	**Co**	**Mn**	**Ni**	**Zn**
EXTRACTION STAGE					
Zn-depleted PLS (1L) (raffinate of extraction using Cyanex 272)	3.5 ± 0.3	0.29 ± 0.02	28 ± 2	4.4 ± 0.3	0.07 ± 0.04
1st extraction	1.9 ± 0.1	0.22 ± 0.01	8.5 ± 0.8	3.5 ± 0.2	n.d
2nd extraction	0.80 ± 0.11	0.21 ± 0.00	1.9 ± 0.5	3.5 ± 0.0	n.d
Amount in organic phase after extraction (g) (before scrubbing)	*2.73*	*0.09*	*26*	*0.91*	*0.07*
SCRUBBING STAGE (O/A=20)					
Scrub solution - before scrubbing	7.40	0	32.0	0	0
Direction of metal to organic phase	in	out	in	out	
Scrubbed solution - after scrubbing	4.50 ± 0.46	0.13 ± 0.04	19.1 ± 2.60	0.62 ± 0.25	
Amount in organic phase after scrubbing (g)	*3.3*	*0.07*	*28*	*0.78*	
STRIPPING STAGE (O/A=4)					
Stripped solution (1L)	2.3 ± 0.0	0.01 ± 0.00	24 ± 0	0.02 ± 0.01	0.13 ± 0.01

n.d = non detection.

Table 7.4 Removal of the impurities from Cd-, Mn- depleted PLS using Cyanex 272 after one stage of extraction (10% (v v^{-1}) Cyanex 272 and 5% (v v^{-1}) TBP in kerosene, O/A = 1/2) at pH = 5.9 to recover Ni.

	Concentration measured in the aqueous phase (g L^{-1})			
	Cd	**Co**	**Mn**	**Ni**
Cd-, Mn-depleted PLS (raffinate of extraction using D2EHPA)-1L	0.79 ± 0.11	0.21 ± 0.00	1.9 ± 0.5	3.5 ± 0.0
After EXTRACTION (O/A = 2)				
Raffinate – 1 L	0.003 ± 0.001	0.003 ± 0.001	0.026 ± 0.002	2.4 ± 0.1
Extraction efficiency (%)	99.6	98.7	98.6	29.6
After STRIPPING (O/A=2)				
Stripped solution – 0.25 L	2.8 ± 0.1	0.80 ± 0.04	7.3 ± 0.1	3.7 ± 0.1
Stripping efficiency (%)	88.9	98.2	97.4	89.6

n.d = non detection.

Table 7.5 Liquid balance of the metal recycling process from spent batteries.

Inputs		**Outputs (Recycle)**		**Output/Input ratio**
Process	**Volume (L)**	**Process effluent**	**Volume (L)**	
Leaching	10	Precipitation (3) ($NiCO_3$)	0.9	0.90
Stripping (1a) - (Zn^{2+} solution)	20	Electrodeposition (1) (Zn)	20	1.00
Stripping (1b) - (Fe^{2+} solution)	20	Water recycling	20	1.00
Stripping (2) - (Cd^{2+} Mn^{2+}solution)	10	Precipitation (2) ($MnCO_3$)	9.5	0.95
Stripping (3)	2.5	Water recycling	2.5	1.00
Washing electrodeposition (1) Zn	5.0	Water recycling	5.0	1.00
Washing electrodeposition (2) Cd	0.3	Water recycling	0.3	1.00
Washing precipitation (2) $MnCO_3$	4.8	Water recycling	4.5	0.94
Washing precipitation (3) $NiCO_3$	1.0	Water recycling	0.8	0.80
Total	68.6	Total	66.6	0.97

Table 7.6 Mass balance of metals (unity = kg t^{-1} of battery powder).

Metals	**A**	**B**		**C**		**Metal recovery (%)**	**Output/Input (B+C)/A**
		Aqueous phase	Organic phase	Solid residual	Recovered metal		
Zn	194 ± 7	34 ± 4	5.8 ± 0.7	2.8 ± 0.3	150 ± 2	64	0.99
Cd	50 ± 2	10 ± 1	10 ± 1	3.9 ± 0.2	21 ± 0	59	0.90
Mn	360 ± 9	67 ± 5	45 ±3	39 ± 3	218 ± 3	73	1.02
Co	2.8 ± 0.2	2.1 ± 0.2	0.5 ± 0.0	0.2 ± 0.0	0.0	-	0.96
Ni	53 ± 2	3.1 ± 0.4	15 ± 1	12 ± 1	22 ± 1	41	0.97
Fe	8.9 ± 1.4	3.9 ± 0.7	2.6 ± 0.3	2.6 ± 0.3	0.0	-	1.02

A = *Input (metals in powder and in scrub solution)*

B = *Residual of metals in the process*

C = *Output (metals in residual after leaching and recovered metal)*

Table 7.7 The summary chemical cost in each step of metal extraction and the metal revenues.

Inputs		**Outputs**	
Experiment step	**Cost (\$US t^{-1})**	**Metals**	**Revenue (\$US t^{-1})**
Chemical leaching	219	Zinc	799
Solvent extraction	335	$MnCO_3$	716
Electrodeposition	205	Cd	21.2
Precipitation ($MnCO_3$)	45.9	$NiCO_3$	596
Precipitation ($NiCO_3$)	9.18		
Total	814	Total	2132

8 DEMANDE DE BREVET INFORMELLE AU CANADA

DEMANDE DE BREVET - CONFIDENTIELLE

Type de demande	Informelle	
Pays	CA	
Titre	**METHOD FOR RECYCLING VALUABLE METALS FROM SPENT BATTERIES**	
Priorité	aucune	
Notre réf.	5199-66	
Votre réf.	n/d	
Déjà publié ?	**Non**	
Version No.	FINALE	
Date	09 décembre 2015	
Figure Repr.	**Fig. 8**	
Titulaire	INRS	490, rue de la Couronne, Québec, QC G1K 9A9, CANADA
Petite entité	**Oui**	
Inventeurs	BLAIS, Jean-François Cit: CA	187, rue Baudrier, Beauport, QC G1B 3M5, CANADA
	MERCIER, Guy Cit: CA	3640, rue Lacoste, Québec, QC G2E 4P8, CANADA
	TANONG, Kulchaya Cit: TH	16, Krapiat, Chawang, Nakhonsrithammarat, 80260,THAILAND
	TRAN, Lan Huong Cit: CA	1025 Blvd des Chutes, Québec, QC G1E 2E6, CANADA
	COUDERT, Lucie Cit: FR	1 Résidence Le Clos des Bois 16 340 L'Isle d'Espagnac, France
Agente de brevet	Louise G. BERNIER, Ph.D.	Tel. (418) 780-1977 lbernier@robic.com

AVOCATS, AGENTS DE BREVETS ET DE MARQUES DE COMMERCE
2828, boulevard Laurier, Tour 1, bureau 925, Québec,
Québec, Canada G1V 0B9
www.robic.ca