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Recycling of spent NiMH batteries: Integration of battery leach solution into primary Ni production using solvent extraction

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ABSTRACT

The utilization of existing metallurgical infrastructure and integration of secondary process streams into primary metals production can provide advantages over separate recycling plants. This paper focuses on the integration of a pregnant leach solution (PLS) into a nickel production plant that contains Ni, Co, Zn, Mn, Fe, Al and Cd ions, derived from a NiMH recycling stream. The solution composition highlights the challenge related to spent battery investigations, as although toxic Cd is not present in NiMH battery chemistries, it ends up into the battery waste collection and prevents direct integration of the battery waste into the primary process. The aim of the study is to remove Zn, Fe, Al, Mn and Cd ions from the PLS, so that the Ni and Co remaining in solution could be integrated into the nickel production process. A two-step solvent extraction process using Di-2-ethylhexyl phosphoric acid (D2EHPA) was developed. In the first step, Zn, Al and Fe were removed at pH 1.5, whereas in the second step Cd and Mn were removed at pH 2.3. Different process parameters (pH, O/A ratio, temperature, extractant concentration, kinetics) were optimized at each step of the solvent extraction. The purified and fully integrable PLS was found to contain Ni ~28 g/L and Co ~3.7 g/L.

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1. Introduction

Primary nickel production is mainly based on sulfide (60%) and laterite (40%) ores, with pentlandite ((Ni,Fe)₉S₈) being the most common of the Ni sulfide minerals. Sulfide ores that are considered suitable for mining, typically contain 1.5–3% Ni and 0.05–0.1% Co [1] and during the primary production process these ores are converted to a metal rich matte after concentration and smelting. The PLS obtained after matte leaching or heap leaching [2], typically contains relatively high amounts of impurities that can be removed by e.g. solvent extraction (SX), precipitation and neutralization. Once the PLS is refined, high purity Ni and Co products are recovered by electrowinning, hydrogen reduction or crystallization as metal salts [3].

Typical impurities found in primary Ni production process solutions include Fe, Al, Zn, and Mn with varying concentrations depending on the mineralogy, process used and stage of process (Table 1). After leaching, Fe is usually the most predominant impurity and can be present at high concentrations (0.3–16 g/L), however its removal by the state-of-art methods is also straight forward [13]. Zn and Mn concentrations highly depend on the mineralogy, e.g. pyrrhotite – pentlandite rich Terrafame ore is rich in Zn (1.5–4.2 g/L) and Mn (2.6–5.6 g/L), whereas sulfide concentrates tend to possess lower amounts of these battery metals. Moreover, Mg, Ca, Si and Cr can be also detected in significant

amounts in primary Ni process streams. In contrast, Cd is not typically found at elevated levels within Ni process solutions as its presence results in a marked decrease Ni electrowinning process efficiency [14,15].

Increased use of batteries in energy storage applications and the associated End-of-life (EoL) waste requires the development of industrially feasible recycling processes. Nickel metal hydride (NiMH) batteries, for example, are increasingly ubiquitous having been used in applications like phones, laptops, power tools and hybrid electric vehicles [16,17,18]. At EoL, NiMH batteries can act as source of main metals present in rare earth elements (REEs) such as lanthanum, cerium, praseodymium and neodymium (anode), zinc, manganese and cobalt [19,20]. Although Cd is not typically present in the NiMH battery chemistry, within NiMH battery waste Cd has been found in significant amounts due to mislabeling of batteries [18,21].

Globally, only 1% of REEs are recovered and recycled from EoL products [22] and therefore, it is important to develop a separate process for REE and Ni/Co recovery. Several studies have been attempted to recover valuable metals from NiMH battery wastes using leaching [23,24], precipitation [25], solvent extraction [26,27] and electrowinning [28].

Table 2 summarizes some the research on solvent extraction that has been undertaken to recover valuable metals from sulfuric acid based NiMH battery leaching PLS. Results from the literature show that extractants like 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC88A) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) have the potential to remove impurities like Fe, Cd, Mn, whereas Di-2-ethylhexyl phosphoric acid (D2EHPA) has been demonstrated to

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Table 1
Concentrations of Ni, Co, Fe, Zn, Al and Mn in some industrial hydrometallurgical primary plant solutions.

Process	Concentration (g/L)						References
	Ni	Co	Fe	Zn	Al	Mn	
CESL process, Canada ^a	30	1	3	0.4	–	–	[4]
Moa Bay, Cuba ^a	4.5	0.45	0.3	0.2	2.5	1.2	[4]
Mondo minerals, Finland ^a	12.6	0.55	32.2	–	–	–	[5]
Terrafame, Finland ^a	0.9	0.02	6.9	2.2	–	2.6	[2]
Terrafame, Finland ^a	2.15	0.044	14.9	5.03	–	6.07	[6]
Anonymous hydrometallurgical plant ^a	141	–	15.9	0.23	0.02	–	[7]
Norrnickel, Finland ^b	120	1	–	–	–	–	[1]
Sherritt, Ambatovy, Madagascar ^b	90	7	–	–	–	–	[1]
CESL process, USA ^b	20.3	1.06	–	0.032	0.021	0.44	[8]
Anglo American Platinum's Rustenburg base metal refinery, South Africa ^b	68	0.14	0.003	0.012	–	–	[9]
Impala Platinum Refineries, South Africa ^b	24.6	–	0.7	–	–	–	[10]
Bulong, Australia ^b	2.8–3.5	0.21–0.28	<0.002	0.03	<0.001	0.75–0.99	[11,12]
Anonymous hydrometallurgical plant ^b	144	–	0.004	0.02	<0.001	–	[7]

^a After leaching.

^b After certain amount of PLS purification steps.

be the best reagent for the removal of Cd, Zn, Al and Mn at low pH values [18,38]. A majority of studies related to NiMH battery waste recycling have so far been performed either with synthetic solutions or using PLS that has not been subjected to a detailed chemical analysis. Consequently, there is a critical information missing related to the extraction behavior of all the impurities or metals present in significant amounts within the real leach solution. When investigating the integration of NiMH recycling stream to primary Ni process solution, the removal of Cd is a crucial aspect to address during solvent extraction as the primary Ni electrowinning process is unable to handle the presence of Cd.

In the previous study of Porvali et al. [39], REEs were recovered using double salt precipitation from sulfuric acid NiMH battery waste leachate. Nevertheless, the PLS produced could not be directly integrated to the state-of-art nickel processes due to the contamination by Cd. The present work continues the process development by focusing on the purification of the PLS after REE recovery, with the primary aim of Cd removal in order to tailor the solution such that it is integrable to the PLS of primary Ni production (Table 1). This is an essential step as Cd is typically found as a contaminant in NiMH battery waste due to the presence of counterfeit batteries that often contain Ni-Cd and is detrimental for Ni electrowinning process. A process flowsheet consisting of two-steps solvent extraction using D2EHPA is proposed (Fig. 1). Zn, Al and Fe are removed at low pH (1.5) in the first step and then Cd and Mn co-extracted from the remaining solution at pH of 2.3. This results in a Ni and Co rich solution that is directly integrable into the state-of-art processes, where typically Ni and Co are further separated by Cyanex 272 SX [40] and recovered by electrowinning, hydrogen reduction or metal salt crystallization [41,42].

Table 2
Solvent extraction studies performed on waste NiMH battery sulfuric acid leach solutions.

Raw material	Extractant	Elements analyzed	Reference
Synthetic solutions	D2EHPA, Cyanex 272	Zn, Mn, Ni	[29]
Synthetic solutions	D2EHPA, PC88A, Cyanex 272	Ni, Co, Cd	[30]
Synthetic solutions	D2EHPA, Cyanex 272	Mn, Co, Ni	[31]
NiMH batteries	D2EHPA, Cyanex 272	REEs, Fe, Zn, Mn, Co, Ni	[32]
NiMH batteries	D2EHPA, Cyanex 272	REEs, Ni, Co, Cd	[18]
NiMH batteries	D2EHPA, Cyanex 272	REEs, Zn, Fe, Al, Mn, Ni, Co	[33]
Mixed batteries	D2EHPA, Cyanex 272	Zn, Fe, Cd, Mn, Co, Ni	[34]
Mixed batteries	Cyanex 272	Zn, Al, Cd, Mn, Ni, Co	[35]
Mixed batteries	Cyanex 272	Zn, Cd, REEs, Ni, Co, Fe, Mn	[36]
Mixed batteries	Acorga M5640, Cyanex 272	REE, Cu, Co, Ni	[37]

2. Materials and methods

2.1. Chemicals

NiMH battery waste was leached with sulfuric acid (Merck, 96%) and anhydrous sodium sulfate (VWR Chemicals, analytical grade) was used as a precipitating agent for REEs. For solvent extraction experiments, D2EHPA (97%) and TBP (97%) were purchased from Sigma Aldrich and were used directly without purification. Kerosene ($\geq 95\%$) was supplied by Alfa Aesar and used as a diluent in all the experiments. The organic phase comprised of D2EHPA as extractant and TBP (as a phase modifier) in kerosene. The modifier used to improve the phase disengagement and selected based on literature [34,43].

2.2. Preparation of the real NiMH battery leach solution for the research

Spent crushed NiMH battery waste was provided by an industrial battery recycling operator and sieved with a mesh size of 1.0 mm. After sieving, the resulting underflow was washed with water and dried in an oven at 65 °C. 330 g of this raw material was leached using 2 M sulfuric acid in a 3 L glass reactor with mechanical stirring for 1 h at 50 °C and at a constant solid to liquid (S/L) ratio of 1:10. After S/L separation (vacuum filtration), the recovery of REEs from the PLS was performed in a glass reactor vessel (2 experiments, each 1.6 L). 250 mL of sodium sulfate solution (1.17 M) was added to the PLS for precipitation of REEs as double salts at ambient temperature for 24 h, as described previously [39]. The initial concentration of total REEs present in PLS was ~15,000 mg/L and the precipitation yield was found to be >95%, which is consistent with value previously reported in literature [44]. The resulting REE depleted and Ni rich PLS was then investigated in more detail in order to determine the suitability for inclusion in primary Ni processes. The PLS was analyzed using inductive coupled plasma emission spectrometer (ICP-OES, Perkin Elmer Optima 7100 DV, USA) for Al(III) and atomic absorption spectrometer (AAS, Varian AA240) for Ni, Co, Zn, Fe and Mn (Table 3) by diluting the sample with 5% nitric acid solution. The solution was found to be rich in Ni (~43.5 g/L) and Co (~5.9 g/L) and had Mn, Zn, Fe, Al as the main impurities, however a notable amount of Cd (76 mg/L) was also detected.

2.3. Solvent extraction

Solvent extraction experiments, including extraction and stripping stages were carried out in a 100 mL separation funnel. Both leach solution (aqueous phase) and organic phases were mechanically shaken at 250 rotations per minute (rpm) for 15 min to attain equilibrium using a KS 3000i control incubated shaker (IKA, Germany). Funnels were allowed to settle for 5 min to allow for phase disengagement. The

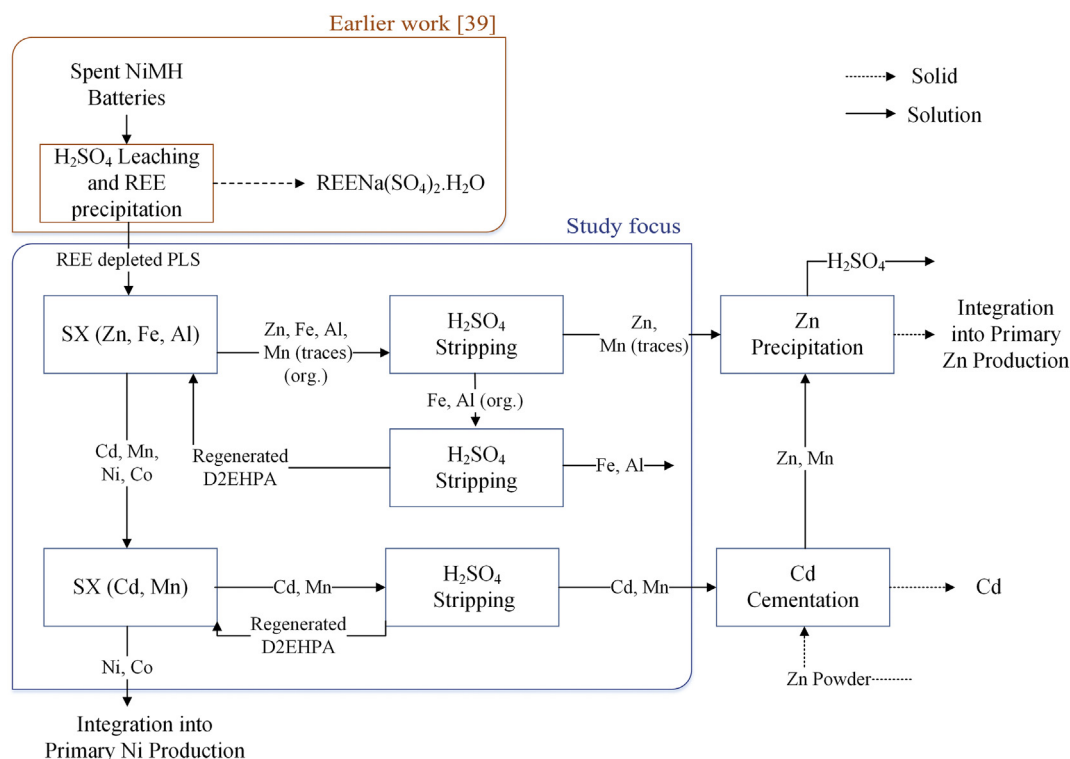


Fig. 1. Schematic flowsheet of the recycling of NiMH battery wastes and the focus of the current study (blue) Earlier sulfuric acid leaching study on waste NiMH batteries marked with red [39].

aqueous phase (~10 mL) was collected and subsequently analyzed by AAS or ICP-OES. The percent extraction of metal ions were calculated by Eq. (1):

$$\text{Extraction}(\%) = \left(\frac{C_{MRn} \cdot V_{org}}{C_{MRn} \cdot V_{org} + C_{M^{n+}} \cdot V_{aq}} \right) \cdot 100 \quad (1)$$

where C_{MR_n} and $C_{M^{n+}}$ are the equilibrium concentration of metal ions in organic and aqueous phases, and V_{org} and V_{aq} are the volume of organic and aqueous phases, respectively.

The pH of the aqueous phase was adjusted using a few drops of 3 M NaOH solution and was recorded by S210 SevenCompact™ pH meter (Mettler Toledo). Five experimental parameters and their different levels were investigated in preliminary solvent extraction experiments (Table 4) to gain insight into extraction behavior of all the metal ions under study to optimize the parameters required for the batch SX experiments.

After this preliminary study, further batch solvent extraction experiments were carried out to remove Zn, Al, Fe (first step) and Cd, Mn (second step) with experimental conditions optimized for both steps. Under optimized conditions, cross current experiments were carried out to purify the solution in 500 mL separatory funnels. At every stage, a fresh organic phase was introduced to contact with the aqueous solution (raffinate) from previous stage and the loaded organic solution originated from each stage were mixed together before performing stripping experiments. Metal ions loaded into the organic phase were stripped out by contact with an aqueous phase that contained H_2SO_4 at room temperature. In addition to the variations of H_2SO_4

concentration (0.01–2 M), used for metal stripping from the organic component, the phase ratio was also varied from 2:1 to 16:1 in the Zn, Fe, and Al stripping experiments. After Zn stripping, Fe and Al was stripped with 4 M sulfuric acid using a 1:16 O/A ratio with 60 min of contact time. The stripping percentage of metal ions from organic phase to aqueous phase were calculated by Eq. (2):

$$\text{Stripping}(\%) = \left(\frac{C_{M^{n+}} \cdot V_{aq}}{C_{MR_T} \cdot V_{org}} \right) \cdot 100 \quad (2)$$

where $C_{MR,T}$ is the initial total concentration of metal ions in the loaded organic phase. In a majority of the industrial SX operations, a counter-current methodology is used and through use of McCabe–Thiele diagrams, the number of theoretical stages required (counter-current mode), were also calculated for the metal removal in both steps.

3. Results and discussion

This experimental study focuses on removal of Cd and other impurities via two solvent extraction steps to integrate the NiMH battery leach solution into primary nickel operation. In all the experiments, real hydrometallurgical leach solution (Table 3) was used as the aqueous phase.

3.1. Preliminary experiments

Different levels of solvent extraction parameters including contact time, pH, TBP% (v/v), D2EHPA% (v/v) and temperature, were

Table 3
Main elements in Ni rich PLS used as starting material in the current study.

[illegible]

Table 4
Experimental parameters and their respective levels.

Experimental parameters	Levels						
Contact time (min)	1	2	5	10	15 ^a	30	–
pH	1	1.5	2 ^a	2.5	3	3.5	4
TBP% (v/v)	5 ^a	10	15	20	–	–	–
Temperature (°C)	25 ^a	35	45	55	–	–	–
D2EHPA% (v/v)	20 ^a	25	30	35	–	–	–

^a Value that was kept constant while other parameters were studied.

investigated in the preliminary experiments to ascertain the general behavior of the PLS during solvent extraction (Table 4). The effect of contact time was investigated between 1 and 30 min and Fig. 2A

shows that the kinetics of Zn(II) extraction with D2EHPA are initially more rapid when compared to Al(III) and Fe(II). Equilibrium for Zn(II) extraction was attained after 2 min, whereas for Fe(II) and Al(III), it took 15 min to reach at equilibrium. In contrast, other metal ions like Mn(II), Cd(II), Co(II) and Ni(II) were not extracted in the organic phase to any significant extent when pH ≤ 2 (Fig. 2B). Nevertheless when the solution pH was increased from 2 to 4, increase in extraction efficiency for a majority of component metals was observed as expected due to the cation exchange reaction between the metal ions and acidic extractant D2EHPA, as shown in Eq. (3) [45]:

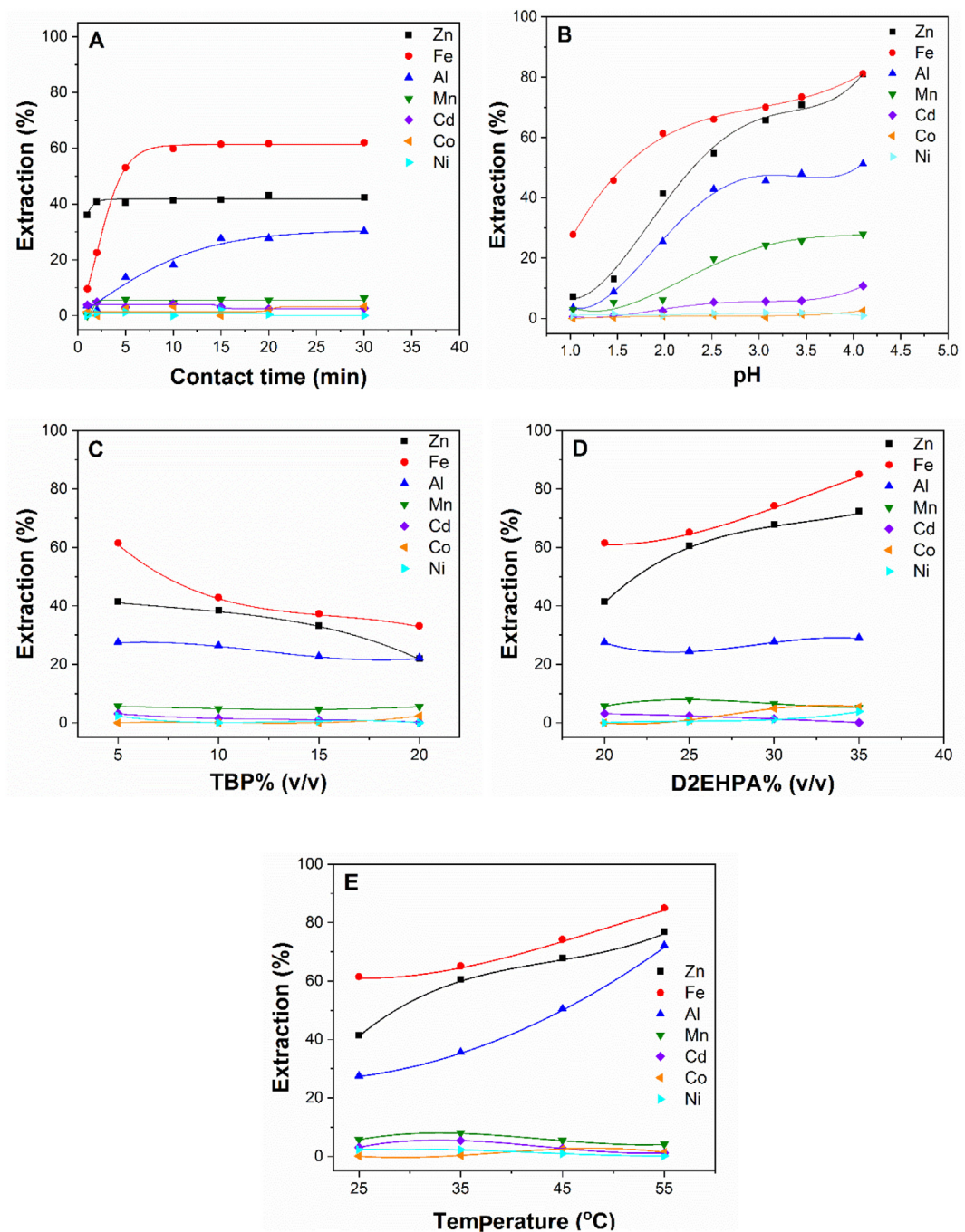


Fig. 2. Effect of (A) contact time, (B) pH, (C) TBP% (v/v), (D) D2EHPA% (v/v) and (E) temperature on extraction of Zn, Fe, Al, Mn, Cd, Co and Ni (pH = 2, *t* = 15 min, [D2EHPA] = 20% (v/v), [TBP] = 5% (v/v), *T* = 50 °C).

where M^{n+} represents the metal ion, $(RH)_2$ represents the dimer form of organophosphorus extractant before dehydrogenation and MR_n $(RH)_{2m-n}$ represents the metal complex formed as a result of extraction reaction. The macron ($\bar{}$) in the equation represents the organic phase. An increase in pH will move the position of equilibrium to right, which will result in higher extraction.

Fig. 2B shows that Zn(II) extraction increased from ~7% to ~80%, Fe(II) from ~27% to ~81%, Al(III) from ~4% to ~51% and Mn(II) from ~3% to ~28% when pH was increased. Under the same conditions, the extraction of Cd(II) increased only slightly from 0% to ~10%, whereas no obvious extraction of Ni(II) and Co(II) was observed. From these results, it can be concluded that the extraction of the metals as a function of pH, has the following order: Fe(II) > Zn(II) > Al(III) > Mn(II) > Cd(II) > Co(II) ~ Ni(II) and this is in agreement with previous studies conducted with synthetic solutions [46]. Results from Fig. 2B also demonstrated that Zn(II), Fe(II) and Al(III) can be effectively co-extracted and separated from the remaining elements at pH ≤ 2 . No significant extraction was observed for Mn(II), Cd(II), Co(II) and Ni(II) up to pH of 2, however when pH ≥ 2.5 , Mn(II) extraction to the organic phase becomes more evident (~25%).

TBP was used as a phase modifier to enhance the phase disengagement after SX and the results in Fig. 2C show that an increase in TBP concentration (5–20%), when D2EHPA concentration is fixed, results in decreased Zn(II) (~42% to ~22%) and Fe(II) (~62% to ~33%) extraction. Al(III) extraction was also seen to decrease from ~27% to ~22%, while extraction of the remaining elements (Mn(II), Cd(II), Ni(II) and Co(II)) were not affected by increasing TBP concentration. The decrease in extraction percentage of metal ions with increasing TBP concentration could be result from an antagonistic effect of the extractants, as has been reported previously in the literature [47,48]. Consequently, a 5% (v/v) TBP concentration was chosen for the subsequent experiments, as below this concentration, the phase disengagement was found to be ineffective. In addition, the effect of D2EHPA concentration was investigated (20–35%) and it was found that the extraction of Zn(II) and Fe(II) increased significantly (from ~41% to ~89% and from ~61% to ~96%, respectively) when D2EHPA concentrate was increased from 20 to 40% (v/v), as shown in Fig. 2D, although the separation of Al from Mn was not affected. The higher extraction at higher D2EHPA concentration could again be explained by Eq. (3), as the D2EHPA concentration increases, the equilibrium will shift to the right. As use of elevated D2EHPA concentrations would increase the overall process cost, a 20% (v/v) D2EHPA concentration was selected to further investigate the Zn, Fe and Al removal from the Ni rich PLS.

Investigations performed at higher temperature led to an increase in the extraction of Zn, Fe, Al, whereas levels of Mn, Cd, Ni and Co ions detected at pH 2 remained low (<10%) over the entire temperature range studied (Fig. 2E). The observed enhancements in Zn, Fe and Al extraction levels at higher temperature probably result from more favorable phase disengagement due to the higher solubility and low viscosity of solutions. Based on the results shown in Fig. 2E, the most significant change was seen for Al(III), where extraction increased from ~28% to ~72% when temperature was raised from 25 °C to 55 °C. Similarly, extraction levels of Zn(II) and Fe(II) were increased from ~42% to ~72% and from ~62% to ~85%, respectively. This promising separation of Zn, Al and Fe from the other metal ions present in Ni rich PLS at 55 °C results from the endothermically driven extraction reaction of D2EHPA with Zn(II), Fe(II) and Al(III), which is favored at elevated temperatures.

3.2. Removal of Zn(II), Fe(II) and Al(III)

Although the target of the initial process stage is the removal of Zn, Fe and Al from the NiMH battery leach PLS in order to prepare the solution into the Cd removal stage, it can also be used to provide a route for Zn recovery. Based on the initial experimental results, it was concluded that the most suitable SX conditions for the first stage was a mixture of D2EHPA (20%) and TBP (5%), temperature of 50 °C and a 15 min contact

Table 5

Concentration of metal ions present in Ni rich PLS solution during each stage of cross-current experiment and in mixed organic solution.

Solution	Zn (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)	Cd (mg/L)	Co (mg/L)	Ni (mg/L)
Leach solution (pH = 1.5)	1038	892	760	2043	54.3	4186	31,100
1 st SX stage	477	416	484	1960	53.9	4110	30,918
2 nd SX stage	81	199	164	1852	52.5	4090	30,225
3 rd SX stage ^a	<1	<1	10	1700	52	4021	29,873
Extraction (%)	100	100	~99	~13	~1	<1	<1
Loaded organic	346	297	253	87	1	<1	<1

^a Feed solution for the 2nd step of SX for Cd, Mn removal.

time. Notably 50 °C was chosen in preference to 55 °C due to the safety reasons as low aromatic kerosene has a flash point close to 70 °C. Additionally, a pH value of 1.5 was chosen, in order to minimize any extraction of Cd(II) during this step.

Laboratory scale, cross-current experiments were employed to investigate Zn(II), Fe(II) and Al(III) removal; three batch experiments carried out and at each of the three stages, the aqueous phase was contacted by a fresh organic phase at unit phase ratio. In addition, at each extraction stage, the pH of the treated PLS solution was readjusted to 1.5 using 3 M NaOH solution prior to the next stage of SX, which induced a slight decrease in the metal ion concentration. Results of the counter current SX are shown in Table 5 and it can be clearly seen that with three cross-current SX stages, 100% of Zn(II), 100% of Fe(II) and ~99% of Al(III) were loaded in the organic phase. In addition, although some Mn(II) (~13%) was also co-extracted in the organic phase, there was no significant extraction of Cd(II), Ni(II) and Co(II) observed.

The loaded organic phase obtained from the three-stage cross-current solvent extraction was subjected to a stripping process, which consisted of the organic phase being equilibrated with different H₂SO₄ solution concentrations and phase ratio (Table 6). Increased acid concentration or increased hydrogen ion concentration within the aqueous solution results in the enhancement of back extraction or stripping of metal ions from the loaded organic solution according to Eq. (3). In general, Zn could be readily separated from Al and Fe with sulfuric acid stripping, for example, at an O/A ratio of 2:1 (0.5 M H₂SO₄), ~100% of zinc could be removed in a single contact stage along with only ~6% of aluminum and no iron. Further tests at an O/A ratio of 4:1 found that ~97.5% of zinc could be stripped in one contact, resulting in an increase in the Zn concentration in the sulfuric acid based strip liquor of ~1350 mg/L, along with traces of Mn (~160 mg/L), Al (30 mg/L) and no iron. This finding demonstrates shows that Zn can be stripped and enriched into the aqueous media even with dilute sulfuric acid solutions. This Zn can then be recovered from the strip liquor by state-of-art methods like sulfide precipitation [2] and integrated into primary production through direct leaching [49] or roasting [50], whilst the acid can be recirculated back into stripping stage.

Table 6

Effect of sulfuric acid concentration and phase ratio on stripping of Zn, Fe and Al ions from mixture of D2EHPA (20%) and TBP (5%) in kerosene.

[H ₂ SO ₄] (M)	O/A ratio	Stripping (%)			Strip solution composition (mg/L)		
		Zn(II)	Fe(II)	Al(III)	Zn(II)	Fe(II)	Al(III)
0.01	2:1	4.3	<0.1	<0.1	30	<0.1	<0.1
0.1	2:1	57.8	<0.1	1.4	400	<0.1	7
0.5	2:1	99.7	<0.1	6.2	690	<0.1	31
1	2:1	99.9	<0.1	11.2	691	<0.1	56
2	2:1	99.9	2.2	17.9	691	13	90
0.5	4:1	97.5	<0.1	3	1349	<0.1	30
0.5	8:1	88.8	<0.1	0.6	2457	<0.1	12
0.5	16:1	61.5	<0.1	0.2	3404	<0.1	9

It was also determined that Fe (~99.5%) and Al (~99%) could be effectively stripped from the D2EHPA and TBP mixture using a 4 M H_2SO_4 solution and three contacts of 60 min duration each, with the regenerated D2EHPA available to be reused extraction. Currently, in hydrometallurgical processes, there is no predominate feasible industrial recovery process for Fe or Al, but they are typically neutralized, then stabilized in products like jarosite, hematite, goethite for Fe and alunite for Al [13,51].

Figs. 3A–C show McCabe-Thiele diagrams generated for Zn(II), Fe(II) and Al(III) by varying O/A ratio from 1:1 to 5:1. From these plots, it was determined that at an operating line (O/A ratio) of 2:1, three theoretical stages were required to extract Zn(II) almost completely from a feed solution containing 1.0 g/L of Zn(II) (Fig. 3A). In contrast, as can be seen from Fig. 3B, only two theoretical stages were required to extract Fe(II) completely from a feed solution containing 0.9 g/L of Fe(II). In the case of Al(III), it was found that four stages were required to completely remove it from PLS containing 0.8 g/L of Al(III), however, the results also highlight that only three theoretical stages are needed to load $\geq 96\%$ of Al(III) in the organic phase with an (O/A) of 2:1 (Fig. 3C). These findings indicate that three counter-current theoretical stages are sufficient to completely remove Zn, Fe and Al ions from PLS at an operating line (O/A) of 2:1 and that the remaining solution should be suitable for the next SX processing step.

It should be noted that three stages of cross-current experiments at unit phase ratio require three times more organic solution compared to aqueous solution to extract Zn, Fe and Al completely while counter-current operation at O/A = 2:1, requires two times more amount of

organic solution than aqueous solution. Overall, counter-current operation was found to be cost effective technique.

3.3. Removal of Cd(II) and Mn(II)

The main challenge in the battery waste integration to the primary production is the presence of Cd in the raw material, therefore a dedicated SX stage designed for Cd(II) and Mn(II) removal is required. Complete removal of Cd(II) from the leach solution is desirable as the levels in primary Ni production processes are much lower than that in the PLS (~51 mg/L) and previous research has shown that even as little as 5 mg/L of Cd can make the electrowinning process unfeasible [14,15]. The PLS after the first stage of metal removal contains 10 mg/L of Al(III), 52 mg/L Cd(II), ~1.7 g/L Mn(II), ~4.1 g/L Co(II) and ~29.8 g/L Ni(II), as shown in Table 5. In addition to the removal of Cd(II) and Mn(II), the other aim of the second SX step was to minimize the extraction of Co(II) and Ni(II) to the organic phase in order to produce a leach liquor is rich in Ni and Co and fully integrable to primary Ni production.

The effect of pH on the extraction of metal ions (Mn, Cd, Co and Ni) from the Zn, Fe and Al depleted liquor was investigated by varying the pH from 2 to 4, in order to determine the optimum pH value for Cd(II) and Mn(II) co-extraction and to maximize the separation from Ni(II) and Co(II). As can be seen from Fig. 4, extraction levels increased from ~29% to ~55% for Mn(II) and ~14% to ~36% for Cd(II), when the solution pH solution was raised from 2 to 4. In addition, at pH ≥ 2.5 , it was found that traces of Co(II) were also extracted in the organic phase, as a

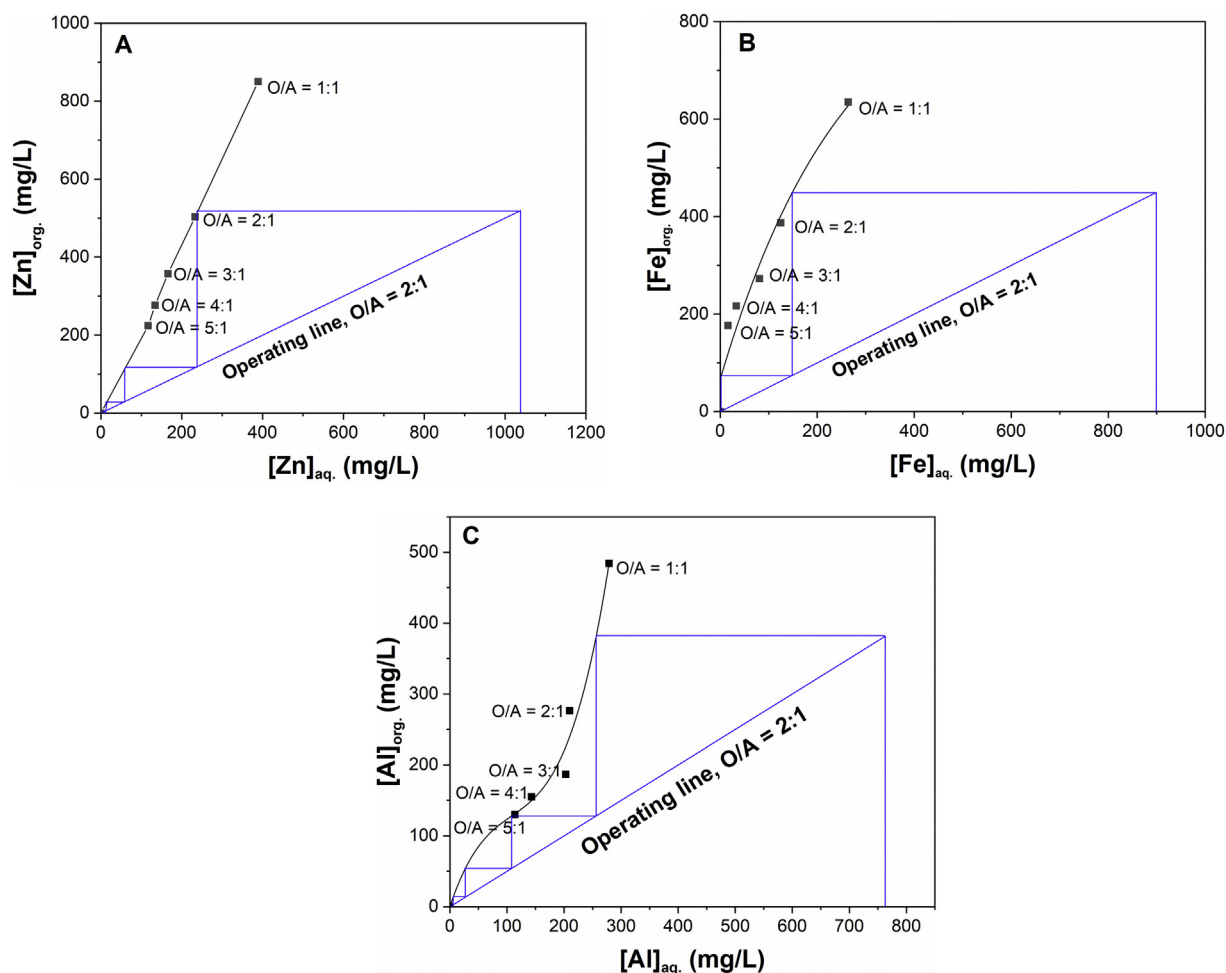


Fig. 3. McCabe-Thiele plots for (A) Zn, (B) Fe and (C) Al extraction from Ni rich PLS using D2EHPA in kerosene ($[\text{Zn}] = 1038$ mg/L, $[\text{Fe}] = 892$ mg/L, $[\text{Al}] = 760$ mg/L, pH = 1.5, $[\text{D2EHPA}] = 20\%$ (v/v), $[\text{TBP}] = 5\%$ (v/v), $T = 50^\circ\text{C}$, $t = 15$ min).

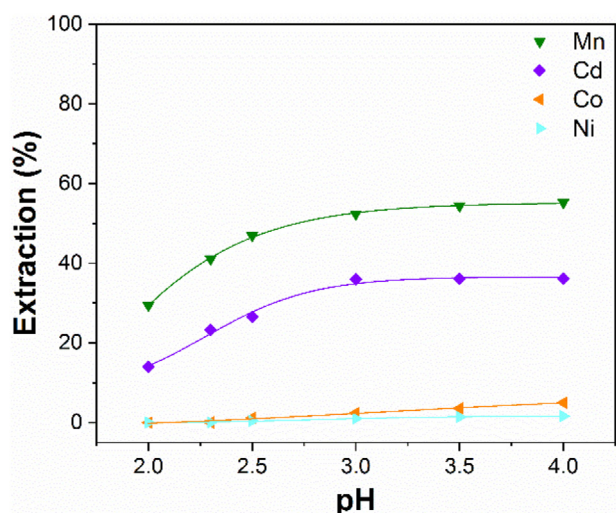


Fig. 4. The effect of pH on extraction of Mn, Cd, Co and Ni using D2EHPA in kerosene ([D2EHPA] = 20% (v/v), [TBP] = 5% (v/v), $T = 50^\circ\text{C}$, $t = 15$ min).

Table 7

Concentration of metal ions present in Zn, Fe and Al depleted leach solution during each stage of cross-current experiment and in loaded organic solution.

Solution	Al (mg/L)	Mn (mg/L)	Cd (mg/L)	Co (mg/L)	Ni (mg/L)
Zn, Fe, Al depleted feed solution (pH = 2.3)	9.5	1608	49	3827	28,360
1 st SX stage raffinate	<1	948	36	3806	29,027
2 nd SX stage raffinate	<1	462	23	3776	28,682
3 rd SX stage raffinate	<1	161	13	3725	28,488
4 th SX stage raffinate	<1	65	6	3720	28,299
5 th SX stage raffinate	<1	15	<1	3650	27,489
Extraction (%)	100	~99	100	~1.6	<1
Loaded organic	1.9	318	9.8	12	<1

consequence, an optimum pH value of 2.3 was chosen to achieve maximum co-extraction of Cd and Mn with concurrent Co and Ni separation.

Cross-current experiments were employed to remove Mn(II) and Cd(II) from the Zn, Fe and Al depleted leach solution. Five batch experiments were carried out at unit phase ratio and at each stage of extraction the raffinate pH was adjusted back to 2.3 using 3 M NaOH solution prior to the next SX stage. As can be seen from the results (shown in Table 7) after five cross-current SX stages ~99% of Mn(II) and 100% of

Cd(II) were loaded in the organic phase, whereas Al(III) was completely extracted in the first SX stage. Under the same conditions, only trace amounts of Co(II) was extracted, whilst no significant extraction of Ni(II) was observed.

After the second SX stage treatment, the remaining metal ions within the leach liquor were found to be 27.5 g/L Ni and 3.7 g/L Co and 0.015 g/L Mn only. These results suggest, that after two stages of SX, the solution is fully integrable to primary Ni production process.

The Mn(II)/Cd(II) loaded organic phase obtained after the five cross-current experiments was stripped using 1 M H_2SO_4 solution. After stripping, it was found that $\geq 99\%$ of Mn(II) and $\geq 95\%$ of Cd(II) was stripped with one contact at 4:1 O/A ratio, resulting in a stripped solution that contained ~1.3 g/L of Mn(II) and ~37 mg/L of Cd(II). Industrially, Cd is typically recovered by an applied cementation process that uses Zn powder [52,53]. After Cd cementation, the resulting solution is rich in both Zn and Mn so it could be potentially integrated to the leach liquor obtained after from first SX step. Alternatively, the Zn containing solution could be stripped with H_2SO_4 before further processing using sulfide precipitation, as applied in the Terrafame process [2]. Currently Mn is not commonly recovered by hydrometallurgical processes, however with increased need for Mn due to growing consumer demand for EV batteries, the recovery of Mn is becoming more important. In the case outlined here, the addition of a promising, cost effective and highly selective step based on the oxidative precipitation of MnO_2 , would allow Mn to be recovered from solutions containing Zn [54].

McCabe-Thiele diagrams were generated for Mn(II) and Cd(II) extraction by varying O/A ratio from 1:1 to 5:1 and these are shown in Fig. 5. It was determined that at an operating line (O/A ratio) of 5:1, four theoretical stages were required to completely extract Mn(II) from a feed solution containing 1.7 g/L of Mn(II) while five theoretical stages were required to extract Cd(II) completely from a feed solution containing 49 mg/L of Cd(II). Clearly, for Mn and Cd co-extraction step, both cross-current and counter-current operations require five times more organic solution compared to leach solution for complete removal of Mn and Cd ions.

4. Conclusions

The proposed flowsheet allows NiMH battery leach solution, obtained after leaching and REEs precipitation, to be integrated into primary nickel plant unit processes. The development of such a new recycling process may accelerate or allow smaller scale operations to be undertaken as only a relatively straightforward hydrometallurgical pre-treatment is required prior to integration into the existing process. Furthermore, the extraction of Cd contamination from NiMH waste

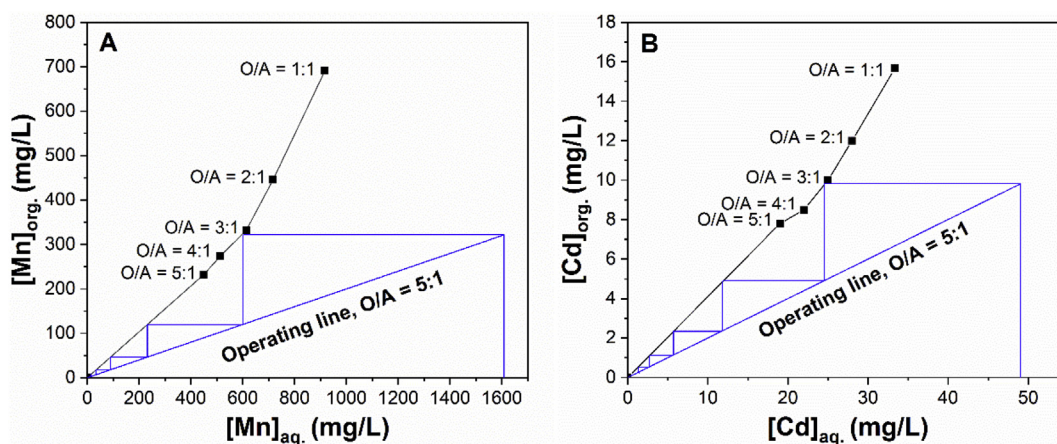


Fig. 5. McCabe-Thiele plots for (A) Mn and (B) Cd extraction from Zn, Fe, Al depleted PLS using D2EHPA in kerosene ([Mn] = 1.6 g/L, [Cd] = 49 mg/L, pH = 2.3, [D2EHPA] = 20% (v/v), [TBP] = 5% (v/v), $T = 50^\circ\text{C}$, $t = 15$ min).

process solution removes a detrimental element that would challenge its use in primary plant operations.

Two solvent extraction purification steps (20% D2EHPA, 5% TBP, 75% kerosene) were applied to tailor the solution for integration into primary Ni production. In the first step, Zn, Fe and Al were removed simultaneously from leach solution ($\text{pH} = 1.5$, $\text{O/A} = 1:1$, $T = 50^\circ\text{C}$, $t = 15$ min, $\text{D2EHPA} = 20\%$, $\text{TBP} = 5\%$) in three cross-current SX stages. Zn was selectively stripped ($\sim 99\%$) from loaded organic solution using $0.5\text{ M H}_2\text{SO}_4$ at O/A ratio of 2:1 to obtain a Zn rich solution, which can be integrated into primary Zn production after sulfide precipitation. In the second purification solvent extraction step, Cd and Mn ions were co-extracted ($\text{pH} = 2.3$, $\text{O/A} = 1:1$, $T = 50^\circ\text{C}$, $t = 15$ min, $\text{D2EHPA} = 20\%$, $\text{TBP} = 5\%$) from the raffinate of the first step, using five cross-current stages. The stripping results demonstrated that $1\text{ M H}_2\text{SO}_4$ solution was enough to strip Cd ($\geq 95\%$) and Mn ($\geq 99\%$) ions at 4:1 O/A ratio from loaded organic solutions. Only traces of Ni and $\sim 1.6\%$ of Co was lost after completion of both solvent extraction steps. The resulting PLS containing $\sim 27.5\text{ g/L Ni}$, 3.7 g/L Co was suitable to be integrated into primary Ni production.

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