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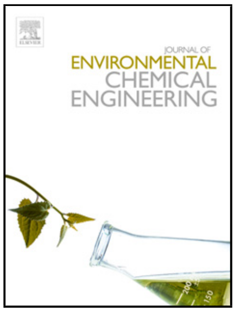

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The optimal use of tris-2-ethylhexylamine to recover hydrochloric acid and metals from leach solutions and comparison with other extractants

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Highlight

- More than 96% HCl may be extracted by single stage extraction with dilute TEHA.
- Mn, Li, Fe, and HCl can be separated at optimal conditions of extraction, stripping and scrubbing
- Recovery of HCl will solve disposal problem of HCl bearing effluents.

Abstract

This paper describes the use of TEHA for HCl recovery from a leach solution generated by a hydrometallurgical plant. Four organic extractants were tested including TEHA, Alamine 336, Cyanex 923 and TBP. TEHA organic system performed best in terms of acid extraction, stripping and scrubbing efficiency. The successive extraction shows that more than 99 % HCl was extracted after three stages of extraction. Scrubbing tests with different A/O ratios at different temperatures were conducted to identify the optimal conditions to separate HCl, Mn and Fe. After scrubbing the loaded organic solution at an A/O ratio of 1:4 and 22°C, 94–100% of entrained metals were removed in a single contact with only 5.2% acid lost in the loaded scrub liquor. It was found that the phase disengagement time was in the range of 2– 4 min for both extraction and stripping, indicating reasonable fast phase separation. Based on these results from batch tests, it can be expected that after optimisation in a counter current circuit consisting of extraction, scrubbing, selective and bulk stripping, nearly all metals and HCl would be recovered and recycled.

Key words: Solvent extraction, HCl Recovery, TEHA

1. Introduction

Acids are extensively used for hydrometallurgical treatment of metals and minerals. Typical treatments include steel pickling, leaching, etching and galvanizing [1-5]. As a result, large amounts of acidic waste solutions are generated, causing environmental problems. These waste streams are problematic because they may contain high concentration of acid, heavy metals and metalloids [1]. The minerals industry is increasingly being forced by regulatory and cost pressures to reduce the amount of liquid acidic waste they produce. This requires a strong focus on waste reduction by recycling, regeneration and reuse. The recovery of acid will not only benefit the environment and the economics of the operation, but it can also provide a secondary source of valuable metals, and extend the life of the acid used [1-2]. Furthermore, recycling of acid would mean elimination of the safety problems associated with its transport to the site. HCl is an acid of interest because it is commonly used in mineral processing and hydrometallurgical extraction. Thus waste can be minimised by linking acid demand to most of the hydrometallurgical processes which generally use HCl.

The current approaches to manage acidic waste solutions include neutralization, flocculation, filtration, evaporation and bioremediation. However, acid recovery using current technologies has not proven to be viable as most of these processes fail to produce sufficient volume and quality of acid whereas others do not provide the selectivity necessary to create the valuable product streams suitable for recycle or re-use [1-4]. In these processes, the by-product sludge can itself become a disposal problem. A closed loop process is the ultimate aim, where acid and metal from hydrometallurgical waste streams are recycled and the only output from the process is a saleable product.

Solvent Extraction (SX) is a well-known treatment method which is used to purify and recover resources (metals) from waste solutions [1-10], while research into acid recovery is a new area of application. SX is the distribution of a solute or solutes between two immiscible liquids or phases. It commonly takes place with aqueous and organic solutions [11]. The organic phase usually consists of extractant dissolved in diluent, but in some cases, a modifier, and a synergistic agent may be required. The modifier is added to improve the physical properties of the system (e.g., to cause phase disengagement after mixing the two phases) while the synergistic agent is used for improvement and enhancement of extractant [11]. SX is an economically viable method when both the solute concentration and waste water flowrates are high, but uneconomical when the concentration of the contaminant to be recovered is very low [1, 2]. Nowadays, a very large number of stable solvents (extractants) are available for use in hydrometallurgy, with potential for excellent selectivity for a particular metal ion, coupled with advances in engineering and increasing demands for higher purity products and more environmentally friendly routes [4-9].

A number of extractants including TEHA (tris-2-ethylhexylamine), Alamine 336 (a mixture of trioctyl/decyl amines), Aliquat-336[$(R_3NCH_3)^+Cl^-$,R = octyl/decyl], TBP (tri-butyl phosphate) and Cyanex 923 (a mixture of alkyl phosphine oxides) have been reported in the literature to be able to recover various acids such as H_2SO_4, HNO_3, HCl and H_3PO_4 [1-8]. Kesieme and Aral [2] have reported the use of TEHA for H_2SO_4 recovery from acidic mining waste solutions, while Agrawal et al. [8] reported on the recovery of H_2SO_4 from zinc electrowinning bleed stream containing 173.5 g/L of H_2SO_4 using 75% TEHA in kerosene. The results show that TEHA had a very good acid extraction capacity even in the presence of a large amount of zinc. In a similar study, Sarangi et al. [5] investigated the recovery of HCl from a synthetic leach liquor using TBP, Cyanex 923, Alamine 336 and Aliquat 336. However, the TEHA organic system was not examined despite its effectiveness in HCl recovery. Eyal and Canari [6] reported that HCl can be extracted using straight chain aliphatic amines diluted in alcoholic diluents due to its ion pair formation. While these studies reported the recovery of various acids using different extractants, the optimal use of TEHA extractants to recover HCl and metals from real leach solutions from hydrometallurgical processes has not been addressed previously. Furthermore, for the development of a process for HCl recovery from hydrometallurgical plants, a systematic study on the extractants is necessary to understand its viability to recover acid and this has been addressed in the present work. Particular attention has been given to the comparison of the performance of different organic systems with possible commercial applications. The extractants of interest are TEHA, Alamine 336, Cyanex 923 and TBP. The reason for the selection of these extractants is based on their high loading metal capacity, good coalescing properties (when mixed with a diluent) and also low solubility in the aqueous phase. Furthermore, they are relatively cost-effective and have been reported in the literature for their effectiveness in acid and metal extraction [1-8]. In addition, the potential to simultaneously recover and separate residual metals like Mn, Li and Fe may be useful from both a financial and environmental point of view and has not been previously reported in the literature. There is no known research to the best of our knowledge, that justifies this optimisation opportunity for TEHA for HCl and residual metal recovery. The recovered acid is expected to be recycled and reused for hydrometallurgical applications. The proposed process flow diagram for HCl and residual metal recovery is shown in Fig 1.

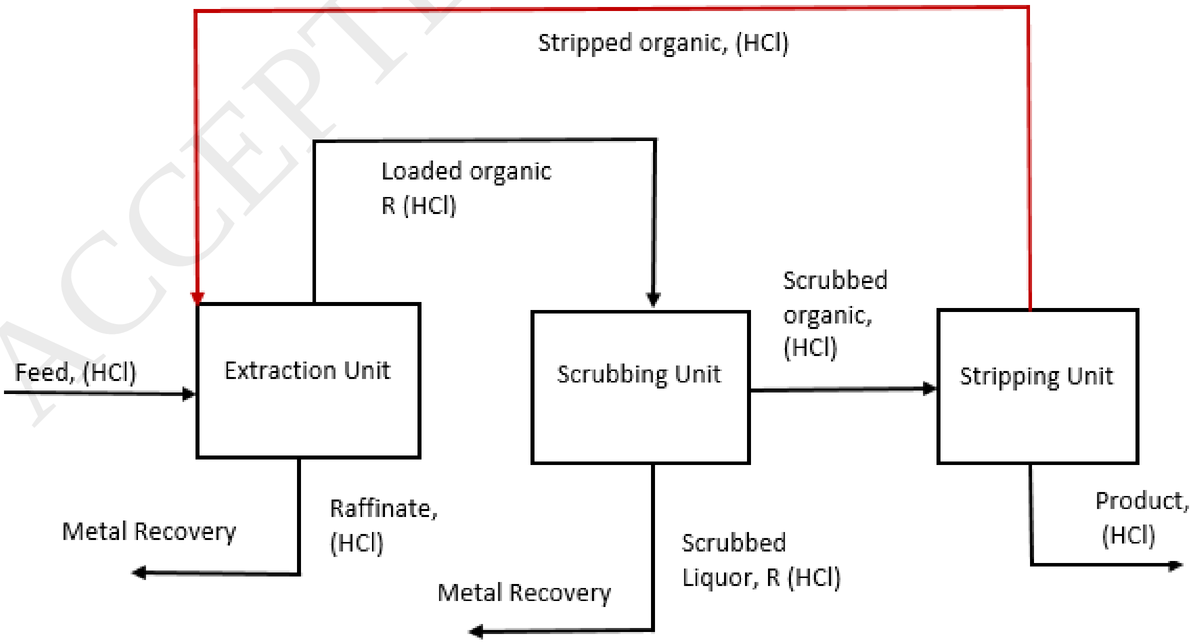

Fig. 1: Proposed flow sheet to recover HCl using SX

2. Materials and methods

2.1. SX Experiment

Four organic extractants (TEHA, Cyanex 923, TBP and Alamine 336) were examined at different concentrations and temperature range of 22– 60 °C at an organic to aqueous (O/A) ratio of 2:1. The organic solvent TEHA was purchased from Sigma-Aldrich. Alamine 336 was supplied by BASF, Cyanex 923 by Cytec and the aromatic diluents Shellsol A150, by Shell Chemicals, Australia. The leach solution was generated from a mining processing plant in Australia and contained 26 g/L Li, 6.41 g/L Fe, 3.77 g/L Mn, 1.38 g/L P and less than 1 g/L of Na, K, Mg and Ca, and 73 g/L HCl. All batch solvent extraction tests were carried out in 100 mL hexagonal glass vessels immersed in a temperature-controlled water bath. Eurostar digital overhead stirrers with 30 mm diameter impellers were used for mixing and the typical mixing time to equilibrum was 10 min. After separation, the organic solution was stripped using water at 60 °C. The loaded strip liquors and the aqueous samples were titrated to determine the acid extraction, stripping and mass balance.

2.1.1. Extraction and stripping kinetics

To determine extraction kinetics, timing started at the point where the selected organic solution was mixed with the leach solution at an O/A ratio of 2:1 at 22 °C. Mixed solution samples were collected at different times for acid titration. For the determination of the kinetics of the stripping process, timing started when the pre-loaded organic solution was mixed with deionised water at 60 °C. Samples were taken at various time intervals for acid titration.

2.1.2. Phase disengagement time test (PDT)

To determine the PDT in extraction, the selected organic system and the leach solution were pre-equilibrated using an O/A ratio of 1:1 at 22 °C. The two phases were separated in a separating funnel. For the stripping PDT tests, the loaded organic solution was stripped using hot water at an O/A ratio of 1:1 at 60 °C. The PDT was measured for both aqueous continuous (A/C) and organic continuous (O/C) modes. For achieving the A/C mode, the pre-heated aqueous solution (100 mL) was placed in the mixing box and stirred for two minutes at 1250 rpm. Then, the pre-heated organic solution (100 mL) was added within 3 - 5 seconds. Mixing was stopped after exactly one minute. The emulsion was rapidly transferred to a 250 mL measuring cylinder and timing was started immediately. The separation of the phases was monitored by recording the time required for every 10 mL increment of clear organic and aqueous phases. Timing was stopped when 90% of the clear organic and aqueous phases were achieved. For achieving the O/C mode, the organic solution was initially stirred. The other procedures were the same as for the A/C mode. Each test was repeated three times to achieve PDT readings within a 10% relative standard deviation (RSD) using the leach solution and organic solutions.

2.1.3. Chemical analysis

The mixed solution samples were allowed to separate to aqueous and organic phases. The aqueous solutions were filtered through 0.45 μm Super membrane filters and the organic solutions through Whatman 1PS papers. Approximately 20 mL of the loaded strip liquor and 20 mL of the aqueous solution (feed) sample were assayed for Li, Fe, Mn and P using inductively coupled plasma with optical emission spectrometry (ICP–OES). Entrainment was removed using scrubbing and acid titration was employed to determine the HCl concentration in the aqueous solution.

3. Results and discussion

3.1. Selection of organic system for HCl recovery

A total of four organic extractants were examined including TEHA, Cyanex 923, TBP and Alamine 336. The selection of the optimal extractant for acid recovery was based on extraction, stripping and scrubbing efficiencies. The extractants were compared by taking into account the maximum workable concentration of each solvent for optimal recovery. The following subsections outline the rationale for the selected organic system for HCl and metal recovery.

3.1.1. Selection of organic system by acid extraction

TEHA, Alamine 336, Cyanex 923 and TBP were examined for their ability to extract HCl from the leach solution at an O/A ratio of 2:1 and 22 °C. Preliminary experiments were performed using the extractants at various concentrations between 20 – 100% (v/v) to identify the best condition for HCl extraction. The effect of the diluent was also examined using Shellsol A150 (100% aromatic), Shellsol 2046 (19% aromatic and 81% aliphatic) and Shellsol D70 (100% aliphatic). It was observed that in terms of diluent type, the acid extractions were in the order of Shellsol A150 > Shellsol 2046 > Shellsol D70. Therefore, further optimisation of the extractant was carried out using Shellsol A150. A similar observation was reported in the literature [3]. For all the organic systems examined, HCl extraction increased as the extractant concentration increased as shown in Fig 2. This observation is in agreement with the results reported in the literature [1-8]. However, for the TEHA and TBP organic systems, the solution mixture became viscous and the phase separation problem was observed when the concentration of the organic system was >50%. Therefore, a concentration of 50% (w/w) of the extractants in an aromatic diluent, Shellsol A150 was used. For Alamine 336, the phase separation problem was observed for the organic solution containing 50% Alamine 336 in Shellsol A150. Therefore, the composition of the Alamine 336 organic system was changed to 35% Alamine 336 and 10% isodecanol which was used as a modifier in Shellsol A150. After the composition change, the phase separation was satisfactory. Agrawal et al. [8] reported the same phase separation problem when the concentration of Alamine was above 35% (v/v) in kerosene. No phase separation problems were observed with the Cyanex 923 system. In fact, the 100% Cyanex 923 system without diluent also performed well in terms of phase separation. After the first stage of extraction using TEHA, Alamine 336 and Cyanex 923, the HCl extraction achieved was 96.74%, 78.35% and 63.12% respectively. Based on the extraction results the TEHA, Alamine 336 and Cyanex 923 systems were selected for further stripping tests. However, HCl extraction with TBP was judged to be too low for further investigation [Fig 2].

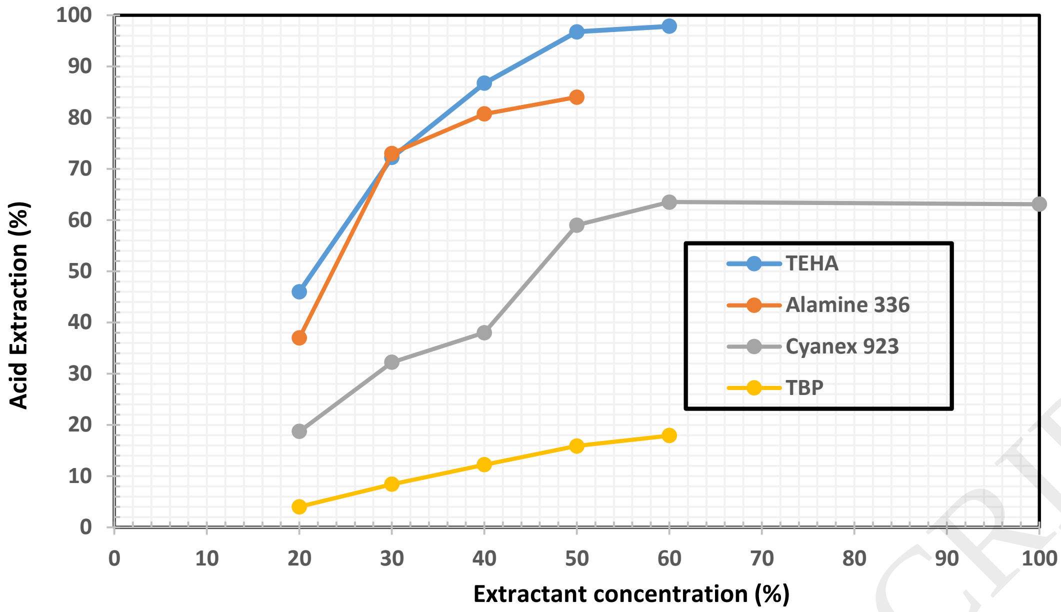

Fig. 2. Effect of extractant concentration on HCl extraction in a single contact at an O/A ratio of 2:1 and 22 °C.

3.1.2. Selection of organic system by stripping

The three organic systems TEHA, Alamine 336 and Cyanex 923 were loaded with the leach solution at an O/A ratio of 2:1 at room temperature for 10 minutes. The loaded organic solutions were stripped at the same O/A at 60 °C for 10 minutes. The acid concentrations in the loaded strip liquors (LSL) were determined by titration. The stripping efficiencies for TEHA and Cyanex 923 are 30.9% and 65.0%, respectively (Table 1). It was observed that only 3.2% HCl was stripped from the loaded Alamine 336 organic solution. Therefore, the Alamine 336 system was not subjected to further investigation.

Table 1: HCl stripping from the selected three loaded organic solutions.

	Organic system	TEHA	Alamine 336	Cyanex 923
Extraction	HCl in feed (g/L)	73.12	73.12	73.12
	HCl in raffinate (g/L)	2.30	15.83	27.00
	Extraction (%)	96.85	78.35	63.07
Stripping	HCl in loaded organic (g/L)	35.41	28.65	23.06
	Stripping (%)	30.9	3.2	65.0

3.1.3. Selection of organic system by successive acid extraction

TEHA and Cyanex 923 extractants were subjected to successive extraction for three times at an O/A ratio of 2:1 at room temperature for 10 minutes. The first extraction was conducted with the fresh organic and leach solution. The second extraction was conducted using fresh organic solution and the raffinate from the first extraction. The third extraction was conducted using fresh organic solution and the raffinate from the second extraction. After three stages of successive extraction, the HCl extraction with the TEHA system reached 99% while for the Cyanex 923 organic system was 98% with only 0.71 g/L and 1.45 g/L HCl in the raffinates, respectively (Table 2). Both organic systems were subjected to further investigation in successive stripping tests.

Table 2: Successive extraction of HCl with the two selected organic systems.

Extraction	Organic system	TEHA	Cyanex 923
Stage 1	HCl in feed (g/L)	73.12	73.12
	HCl in raffinate 1 (g/L)	2.25	26.65
	Extraction (%)	96.92	63.55
Stage 2	HCl in raffinate 2 (g/L)	1.20	4.50
	Extraction (%)	98.36	93.85
Stage 3	HCl in raffinate 3 (g/L)	0.71	1.45
	Extraction (%)	99.03	98.02

3.1.4. Selection of organic system by successive stripping

TEHA and Cyanex 923 were loaded with the leach solution at an O/A ratio of 2:1 and room temperature for 10 minutes. The loaded organic solutions were subjected to two successive stripping stages with the first stage using an A/O ratio of 1:2 and the second stage using at an A/O ratio of 2:1 at 60 °C for 10 minutes. Fresh water was used for the two successive stripping stages. After two stages of successive stripping, the HCl stripping with the TEHA system reached 94.85% while that with the Cyanex 923 system was 100% with only 1.83 g/L and 0 g/L HCl left in the stripped organic solution, respectively (Table 3), suggesting that both organic systems exhibited good performance in terms of acid stripping.

Table 3: Successive stripping of HCl with the two selected organic systems

	Organic system	TEHA	Cyanex 923
Extraction	HCl in feed (g/L)	73.12	73.12
	HCl in loaded organic (g/L)	35.44	23.24
	Extraction (%)	96.92	63.55
Stripping 1	HCl in stripped organic 1 (g/L)	24.29	7.57
	Stripping 1 (%)	31.47	67.46
Stripping 2	HCl in stripped organic 2 (g/L)	1.83	0.00

	Stripping 2 (%)	94.85	100.00

3.1.5. Extraction and stripping kinetics

TEHA and Cyanex 923 were used for the extraction kinetics study at an O/A ratio of 2:1 and 22 °C. Solution mixture samples were taken at 0.5, 1, 2, 3, 5 and 10 minutes. The acid extraction for the TEHA and Cyanex 923 organic systems reached 96.5% and 63% respectively after mixing for 0.5 min and was kept almost constant after that, indicating that the acid extraction kinetics was satisfactory for both extractants (Fig 3). For stripping kinetics, the organic systems TEHA and Cyanex 923 was loaded at an O/A ratio of 2:1 and 22 °C. The pre-loaded organic solution was subjected to stripping with distilled water at an O/A ratio of 1:2 and 60 °C. The acid stripping reached 81% and 90% for TEHA and Cyanex 923 organic systems respectively (Fig 3) in 2.0 minutes of mixing and was kept after that, suggesting that the stripping kinetics for both organic systems was satisfactory.

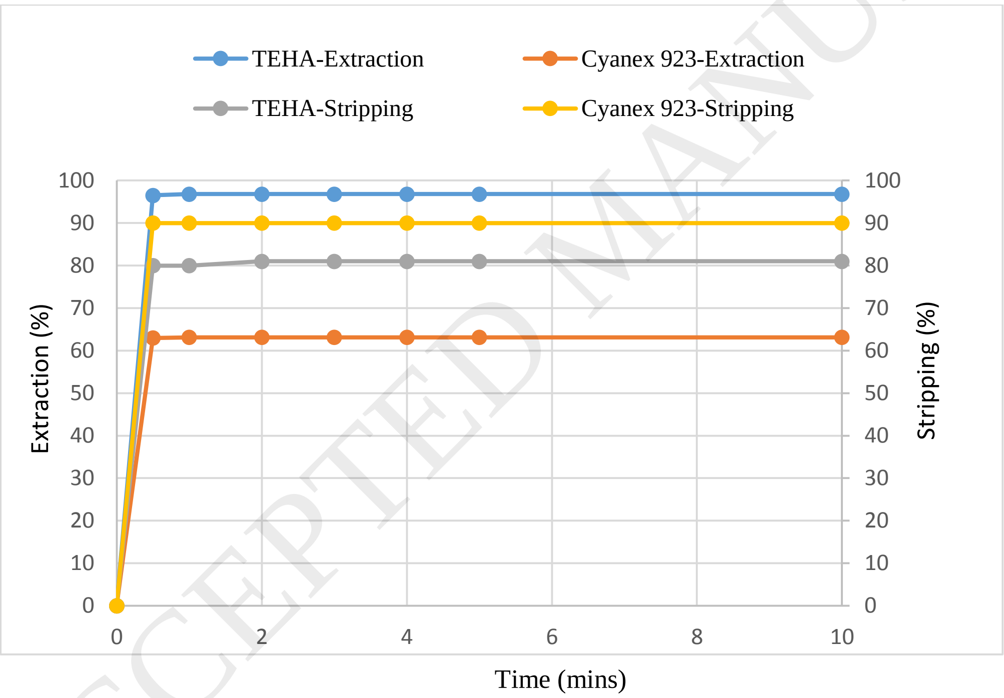

Fig 3: Extraction and stripping kinetics with TEHA and Cyanex 923 organic systems.

3.1.6.

3.1.7. Effect of temperature on acid extraction

TEHA and Cyanex 923 were tested under different temperatures using an O/A ratio of 2:1 at 22 °C. With the increase in temperature from 22 °C to 60 °C, the acid extraction decreased for the TEHA organic system from 96.72% to 85.11% and for Cyanex 923 acid extraction decreased from 63.07% to 56.2% for the initial acid concentration of 73 g/L in the feed solution. This observation is in agreement with the results reported in the literature [1-3]. Based on these results, further extraction studies were performed at 22 °C or room temperature.

The temperature effect was also demonstrated thermodynamically using the Van't Hoff Equation [3]. The enthalpy change (ΔH°) of the extraction process can be obtained from the following equations

$$Log\ D = \frac{-\vartriangle H°}{2.303RT} + C$$

Where R is the gas constant, *D* the distribution ratio, K the absolute temperature and C the integration constant. The above equation can be re-written as

$$Log\ D = \frac{100A}{T} + C$$

$$A = \frac{-\vartriangle H}{2303R}$$

$$\vartriangle H = -2303A\mathrm{R}$$

The plot of log (*D*) against (1000/T) forms a straight line, where A is the slope of the straight line.

Slope values of 0.249 and 0.027 were obtained for the TEHA and Cyanex 923 organic systems respectively as shown in Fig 4 and Fig 5. Based on the results obtained, the values for the enthalpy changes are found to be – 4.8 kJ mol− 1 and – 0.52 kJ mol− 1 for TEHA and Cyanex 923, respectively. Based on the results it may be concluded that HCl extraction by TEHA is more exothermic than that by Cyanex 923. The reaction enthalpies show that acid extraction by Cyanex 923 should be less sensitive to temperature compared to TEHA. The negative value indicates that the extraction is exothermic and hence the increase in temperature decreases acid extraction and increases acid stripping. Haghshenas et al. [10] and Kesieme et al. [3] reported similar results for the TEHA organic system and with enthalpy changes of − 6.34 kJ mol^{-1} and −13.2 kJ mol^{-1} respectively for the recovery of H_2SO_4. The difference in the enthalpy change in the current study is probably due the difference in the acid of interest.

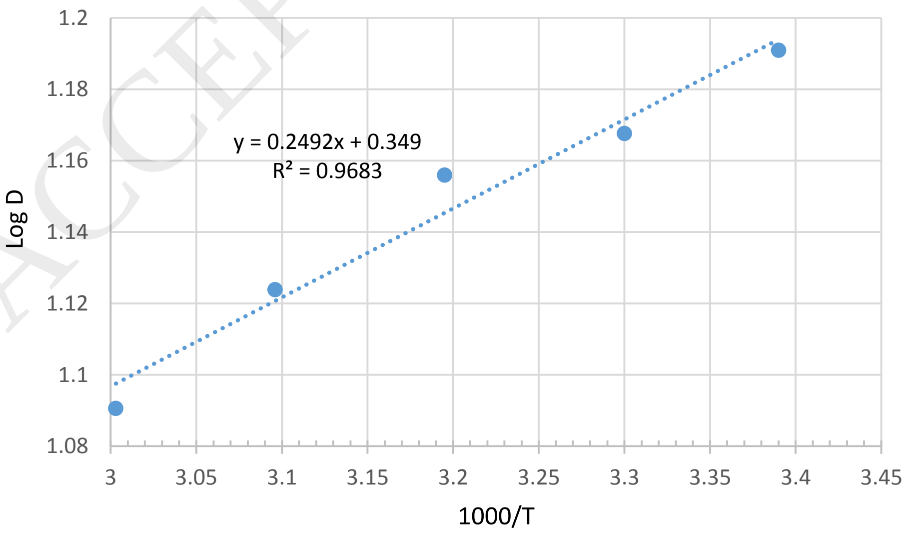

Fig 4. A plot of log *D* (distribution ratio) vs. 1000/T for TEHA organic system.

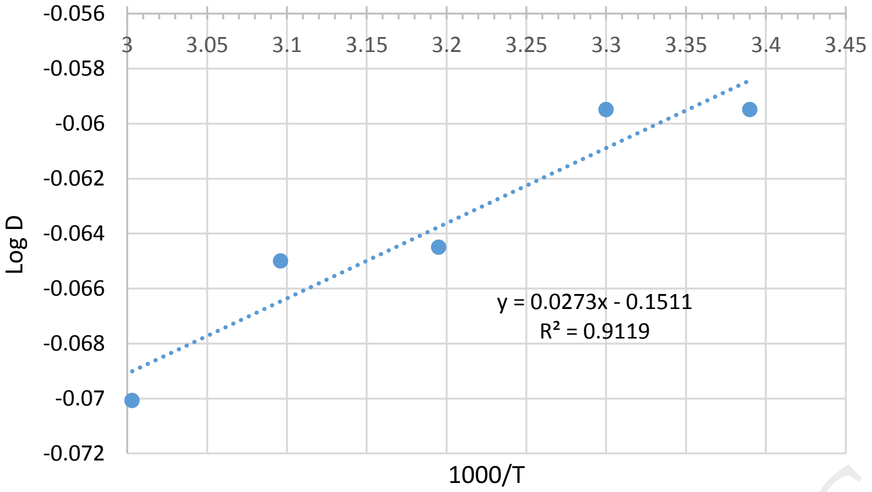

Fig 5. A plot of log *D* (distribution ratio) vs.1000/T for Cyanex 923 organic system.

3.1.8. Phase disengagement times (PDT) in extraction and stripping

The TEHA and Cyanex 923 organic systems were used for the extraction PDT measurement to characterise the phase separation quantitatively. The PDT measurements in extraction at aqueous continuity (A/C) are shown in Fig 6. The primary and secondary PDTs for extraction for the A/C mode are on average of 105 and 138 seconds, respectively, indicating a reasonably fast phase separation for the A/C mode. For the TEHA organic continuity mode, the primary and secondary PDTs for extraction are 144 and 153 seconds, respectively, indicating reasonably fast phase separation for the O/C mode, but slightly higher than the A/C mode. This suggests that extraction can be operated in both modes, but the A/C mode is faster and its use maybe preferred. A similar result was obtained for the Cyanex 923 organic system. The primary and secondary PDTs for the extraction for the A/C mode are 132 and 148 seconds and for the O/C mode it was 145 and 150 seconds respectively. The stripping PDT measurement for TEHA was determined to characterise the phase separation quantitatively. The primary and secondary PDT measurements for extraction for the A/C mode were 104 and 138 seconds, respectively, indicating reasonably fast phase separation for the A/C mode. Similar results were obtained for the Cyanex 923 organic system. This suggests that stripping could be operated in both modes for both the TEHA and Cyanex 923 organic systems.

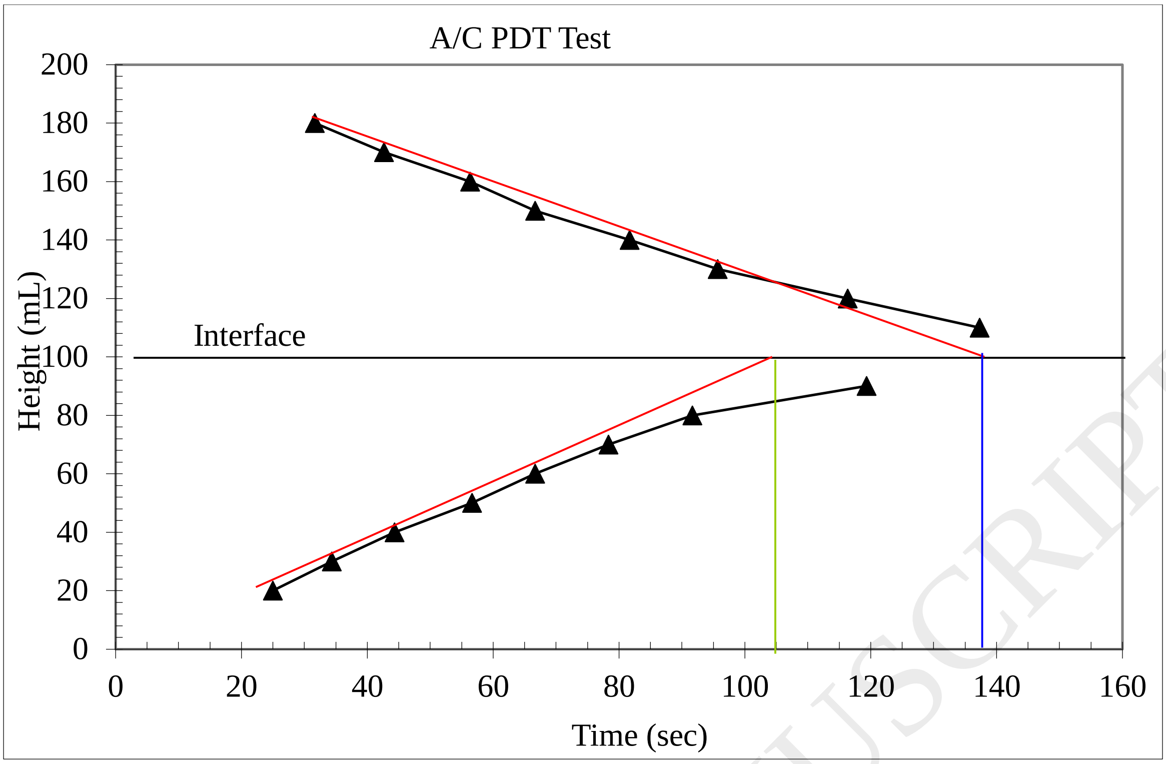

Fig 6: Average PDT at A/C mode in extraction using TEHA organic system.

3.2. Selection of organic system for metal recovery

The successive extraction shows that 98-99% of HCl was extracted using both TEHA and Cyanex 923 and also after two stages of successive stripping, 95-100% HCl was stripped, indicating that the performance of the two systems was satisfactory. Therefore, the two organic systems were further examined for metal and HCl separation in terms of extraction, stripping and scrubbing test.

3.2.1. Metal extraction using TEHA and Cyanex 923

The TEHA and Cyanex 923 organic systems were each mixed with the leach solution at an A/O ratio of 1:2 at 22°C for 10 minutes. The mixed solution samples were allowed to separate to aqueous and organic phases. The aqueous solution samples were assayed for Na, K, Mg, Ca Li, Fe, Mn and P using ICP–OES. The results shows that Li, Na, K, Mg and Ca were not zero using both organic (TEHA and Cyanex 923) systems and deposited in the Raffinate. However, after first single contact, all Fe was extracted by both organic systems (TEHA and Cyanex 923) and over 84% Mn was extracted by the TEHA system and 79% Mn extracted by the Cyanex 923 system (Table 4). This means that Fe will not proceed to the Li recovery stage. However, small amount of HCl and Mn would proceed to the Li recovery stage. After three contacts, over 98% Mn was extracted by the Cyanex 923 system. However, Mn was not extracted further in the second and third contact by the TEHA organic system (Table 4). This may be attributed to the different extraction mechanisms for the two organic systems and to the presence of multiple Mn-Cl species in the feed solution. Phosphorus was not extracted by the TEHA system, while over 89% was extracted by the Cyanex 923 system after three contacts (Table 4).

Table 4: Metal concentrations in feed and raffinates and extractions in successive extraction tests

Sample	A/O Ratio	Concentration (g/L)			Extraction (%)		
		Fe	Mn	P	Fe	Mn	P
Feed		6.407	3.766	1.383	---	---	---
TEHA Successive EX1 Raff.	1:2	0.001	0.581	1.440	99.99	84.56	0.00
TEHA Successive EX3 Raff.	1:2	0.001	0.578	1.387	99.98	84.65	0.00
C923 Successive EX1 Raff.	1:2	0.001	0.766	0.507	99.99	79.67	63.32
C923 Successive EX3 Raff.	1:2	0.0003	0.043	0.143	100.00	98.87	89.68

3.2.2. Metal stripping

The loaded organic solutions were subjected to two successive stripping stages with the first stage using an A/O ratio of 1:2 and the second stage using an A/O ratio of 2:1 at 60 °C for 10 minutes. Fresh deionised water was used for the two successive stripping stages. As shown in section 3.1.4, almost all the HCl was stripped by the two organic systems after two successive stripping stages. Li, Mg, Na, K and Ca were not extracted by the two organic systems as shown in section 3.2.1. Therefore, the resulting concentrations of these metals in the loaded strip liquors (LSL) were virtually zero. For the TEHA organic system, 88% Fe was stripped in the second successive stripping and 100% Mn was stripped in the first successive stripping (Table 5). With the Cyanex 923 system, Fe was not stripped in the first stripping stage, while 98% Mn and 75% P were stripped in the first successive stripping and 53% Fe, 3% Mn and 22.5% P were stripped in the second successive stripping. The total stripping for Fe, Mn and P with the Cyanex 923 organic system was 53%, 100% and 98%, respectively (Table 5). The overall stripping results indicate that (i) the stripping of manganese was much easier than that of iron, and (ii) the iron stripping with the Cyanex 923 system was more difficult than that with the TEHA system. Therefore, the TEHA system is better in terms of Fe stripping. The co-extracted manganese could be scrubbed or selectively stripped from the loaded TEHA organic system so that the two metals are separated.

Table 5: Metal concentrations in feed, raffinate and loaded strip liquor in successive stripping tests

Sample	A/O Ratio	Concentration (g/L)			Extraction (%)		
		Fe	Mn	P	Fe	Mn	P
Feed		6.407	3.766	1.383	---	---	---
TEHA EX Raff.	1:2	0.002	0.566	1.412	99.96	84.98	0.00
		Concentration (g/L)			Stripping (%)		
STRIP 1 TEHA LSL 1	1:2	0.006	3.223	0.063	0.09	100	---
STRIP 2 TEHA LSL 2	2:1	1.408	0.045	0.002	88.02	0.00	---
Total stripping					88.12	100	---
		Concentration (g/L)			Extraction (%)		

C923 EX Raff.	1:2	0.002	0.759	0.508	99.97	79.85	63.26
		Concentration (g/L)			Stripping (%)		
STRIP 1 Cyanex LSL 1	1:2	0.003	2.959	0.663	0.05	98.39	75.78
STRIP 2 Cyanex LSL 2	2:1	0.854	0.058	0.099	53.34	3.87	22.51
Total stripping					53.39	100	98.69

3.3. Acid and metal scrubbing test

A preliminary experiment to identify the best conditions to separate HCl, Mn and Fe was conducted taking into account the different A/O ratio and temperature (22 – 60 ºC). The results show that the optimal removal of Mn and the reduction of HCl loss was achieved at 22 ºC. The loaded organic solution containing 34.94 g/L HCl, 2.94 g/L Fe and 1.48 g/L Mn was subjected to scrubbing at 22 °C using A/O ratios of 1:2, 1:4 and 1:6, respectively (Tables 6-8). The HCl concentrations in the feed, raffinate and loaded scrub liquors (LSCL) were determined by titration and the concentrations of Fe and Mn by ICP-OES. The results from Tables 6-8, show that the scrubbing of HCl and Mn increased with the decrease in the A/O ratio. For instance, at an A/O ratio of 1:2, 23.7% HCl and 93.2% Mn were scrubbed, respectively, while at an A/O ratio of 1:4, 10.4% HCl and 94.8 % Mn were scrubbed, respectively. Therefore, to scrub Mn and minimise acid loss, a lower temperature like 22 °C and A/O ratio of 1:4 or even 1:6 should be used. It was noted that small amount of Fe was scrubbed, indicating very good separation of Mn from Fe.

Table 6: HCl concentrations in feed and raffinate and scrubbing with different temperatures and A/O ratios (LSCL= loaded scrub liquor).

			HCl concentration (g/L)			HCl (%)	
Operation	Temp. (°C)	A/O	In feed	In raff.	In organic	EX	SC
Extraction	22	1:2	72.12	2.25	34.94	96.88	---
				In LSCL	Scrubbed from org.		
Scrubbing	22	1:2		16.57	8.29		23.7
		1:4		14.39	3.62		10.4
		1:6		15.14	2.52		5.22
	60	1:2		17.20	8.6		24.62

		1:4		23.68	5.92		16.95
		1:6		23.98	4.00		11.44

Table 7: Fe concentrations in feed and raffinate and scrubbing with different temperatures and A/O ratios (LSCL= loaded scrub liquor).

			Fe concentration (mg/L)			Fe (%)	
Operation	Temp. (°C)	A/O	In feed	In raff.	In organic	EX	SC
Extraction	22	1:2	5875	<0.1	2937	100.00	
				In LSCL	Scrubbed from org.		
Scrubbing	22	1:2		29.4	15		0.50
		1:4		17.0	4.2		0.14
		1:6		12.2	2.0		0.07
	60	1:2		3.79	1.9		0.06
		1:4		3.53	0.9		0.03
		1:6		2.41	0.0		0.01

Table 8: Mn concentrations in feed and raffinate and scrubbing with different temperatures and A/O ratios (LSCL= loaded scrub liquor).

			Mn concentration (mg/L)			Mn (%)	
	Temp. (°C)	A/O	In feed	In raff.	In organic	EX	SC
Extraction	22	1:2	3475	514	1480	85.20	

				In LSCL	Scrubbed from org.		
Scrubbing	22	1:2		2760	1380		93.22
		1:4		5259	1315		94.82
		1:6		7235	1206		94.45
	60	1:2		1701	850		57.45
		1:4		4922	1230		83.12
		1:6		6088	1015		83.54

3.3.1. Scrubbing, selective and bulk stripping

The scrubbed organic solution was subjected to selective stripping with water at an A/O ratio of 2:1 at 60 °C. The selectively stripped organic solution was subjected to bulk stripping with water, again, at an A/O ratio of 2:1 and 60 °C. The HCl concentrations in the feed, raffinate, loaded scrub liquors (LSCL), loaded selective strip liquor (LSSL) and loaded bulk strip liquors (LBSL) were determined by titration and the concentrations of Fe and Mn by ICP-OES. The scrubbing test results using an A/O ratio of 1:4 at 22 °C, shows that 5.5% HCl, 0.07% Fe and 90% Mn were scrubbed, resulting in an LSCL containing 5.2 g/L HCl, 0.004 g/L Fe and 4.26 g/L Mn, which was basically a very pure manganese solution for its recovery. The selective stripping test using an A/O ratio of 2:1 at 60 °C, shows that 72.1% HCl, 10.5% Fe and 12% Mn were scrubbed, resulting in an LSSL containing 12.5 g/L HCl, 0.295g/L Fe and 0.256 g/L Mn, which was basically a HCl solution for recycling. Based on these results from batch tests, it can be expected that after optimisation in a counter current circuit consisting of extraction, scrubbing, selective and bulk stripping, all Fe and nearly all Mn and HCl would be extracted by the organic system.

4. Conclusions

Four extractants for the recovery and separation of HCl and metals were examined including TEHA, Alamine 336, Cyanex 923 and TBP. The TEHA organic system performed best in terms of acid extraction, stripping and scrubbing. The successive extraction shows that more than 99 % HCl was extracted. It was observed that the phase disengagement time was in the range of 2–3 min for both extraction and stripping, indicating reasonable fast phase separation. The extraction and stripping kinetics were also fast. Within 0.5 min, the extraction had reached equilibrium and 97.8% acid was extracted. The value of the enthalpy is found to be – 4.8 kJ mol^{-1} and – 0.52 kJ mol^{-1} for TEHA and Cyanex 923, respectively.

In conclusion, (i) after extraction using TEHA, an aqueous solution containing no Fe, and small amount of HCl and Mn would be obtained for Li recovery, (ii) after scrubbing, an aqueous solution containing most of the Mn and no or traces of Fe and HCl would be obtained for Mn recovery, (iii) after selective stripping, an aqueous solution containing most of the HCl and a small amount of Fe and Mn would be obtained for HCl recycling, and (iv) after bulk stripping, an aqueous solution containing most of the Fe and a small amount of HCl would be obtained for Fe disposal and the stripped organic solution would be suitable for recycling to extraction.

Based on these results from batch tests, it can be expected that after optimisation in a counter current circuit consisting of extraction, scrubbing, selective and bulk stripping, all of the Fe and nearly all Mn and HCl would be extracted by the organic system and recovered. Most of the extracted Mn would report to LSCL from which pure Mn product such as $MnCO_3$ can be obtained. Most of the extracted HCl would report to LSSL containing a small amount of Fe and Mn. LSSL would be recycled to leaching after concentration if necessary.

This investigation shows that application of SX using the TEHA organic system to recycle HCl and metals such Li, Fe and Mn may help in reducing various environmental problems confronting the hydrometallurgical industry. Acid is increasingly becoming essential for various applications in mining including processes such as leaching. The recovery of acid and precious metals from waste materials can mitigate operational costs associated with waste disposal and could also provide opportunities to reduce the environmental risks and liabilities posed by the disposal of the untreated substances. Furthermore, the ability to separate Mn, Li and Fe may be financially useful. The Mn price has been rising and its demand is primarily driven by the steel industry, which consumes 90% of all manganese ore produced [12]. The manganese market is highly concentrated within a small group of global suppliers and is an essential element to the iron and steel production industry. As an alloying element it decreases the brittleness of steel and imparts strength. Important non-metallurgical uses of Mn include battery cathodes, soft ferrites used in electronics, micronutrients found in fertilizers and animal feed, water treatment chemicals and other chemicals such as those used as a colourant for car undercoat paints, bricks, glass, textiles, and tiles.

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