Direct solvent extraction of indium from a zinc residue reductive leach solution by D2EHPA

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ABSTRACT

A direct solvent-extraction process was developed to selectively recover indium from solutions generated by reductive leaching of zinc residues. This approach avoids the traditional steps of intermediate precipitation, solid–liquid separation, and re-leaching. Copper in the leach solution is easily removed by cementation with iron powder and the remaining Fe(III) is reduced to the ferrous state, which avoids the possibility of its co-extraction with indium. Indium is effectively extracted from the zinc sulfate solution by 20% (v/v) di(2-ethylhexyl)phosphoric acid (D2EHPA) dissolved in kerosene at an initial pH of 0.5 and aqueous-to-organic phase ratio (A:O) of 6:1 using three countercurrent stages. Indium extraction is 96.1%, zinc and iron are barely extracted, and the separation factors of indium with respect to zinc and iron are 3640 and 4809, respectively. The complete stripping of indium from the loaded organic phase is achieved using 4 mol/L HCl at an A:O of 1:6. A scheme for direct solvent extraction of indium in zinc hydrometallurgical processing is suggested, by which indium can be concentrated into a small volume of strip solution containing 11 g/L of indium, which is 85 times its concentration in the feed solution.

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1. Introduction

Indium consumption is growing at an increasing rate, mainly owing to applications in indium tin oxide, semiconductor materials, and low melting point alloys (Lupi and Pilone, 2014). Indium is most commonly found in association with zinc-bearing materials, such as in solid solution in sphalerite and marmatite (C.X. Li et al., 2010; Cook et al., 2011), so it is an important byproduct of zinc metal processing operations (Alfantazi and Moskalyk, 2003; Jiang et al., 2011; Zhang et al., 2010).

In the hydrometallurgical treatment of zinc concentrates, more than 98% of the indium reports to the neutral leach residue, usually in isomorphic form in zinc ferrite ($ZnO \cdot Fe_2O_3$). The indium content is low—often only tens to a few hundred parts per million (ppm). The traditional process for recovering indium from zinc residues is by leaching in hot acid, enriching the indium by precipitation, following which indium is further separated and purified by re-leaching, purification, and solvent extraction (Li et al., 2006; Deng and Xie, 2007; Javad Koleini et al., 2010). One of the traditional processes for extraction of indium from zinc residue leach solutions includes the following steps: ferric is removed by jarosite precipitation, during which indium reports to the jarosite; zinc and indium are then recovered from the jarosite by reduction roasting with carbon powder via Waelz kilns and indium reports to the roaster dust; the roaster dust is then dissolved by neutral then acidic

leaching; and, finally, indium is extracted from the acidic leach solution by solvent extraction (H.B. Li et al., 2010; Ning and Chen, 1997; Yuan et al., 2008). This process is complicated and uneconomical. Another conventional method involves first precipitating indium at pH 3.0 to 4.5 from the solution generated by reductive leaching of the zinc residue by the addition of zinc calcine and roaster dust as neutralizing agents and then re-leaching indium from the precipitate (Lin and Liu, 2006; Xie, 2008; Javad Koleini et al., 2010). In this method, filtration of the precipitate is extremely slow owing to the formation of iron hydroxide and colloidal silica, and indium recovery is usually less than 70%.

Solvent extraction is commonly used for extraction and separation of indium from various indium-containing solutions. Extractants employed include di(2-ethylhexyl)phosphoric acid (D2EHPA) (Lee et al., 2002; Tsai and Tsai, 2012; Wang et al., 2003; Yang et al., 2013), D2EHPA with tributylphosphate (TBP) (Virolainen et al., 2011), 2-ethylhexyl 2-ethylhexylphosphonic acid (EHEHPA) (Liu et al., 2006; Kang et al., 2011), CYANEX 272 (Gupta et al., 2007), CYANEX 923 (Gupta et al., 2004), LIX 973N (Alguacial, 1999), sec-nonylphenoxyacetic acid and a trialkyl amine (Fan et al., 2010), and sec-octylphenoxyacetic acid and the primary amine N1923 (Ma et al., 2011). Among these, organophosphorus extractants are the most popular and are used in practical applications because they have high loading capacities for indium and good selectivity for indium over other metal ions. Sato (1975) and Sato and Sato (1992) reported comprehensively on the extraction of indium by D2EHPA and EHEHPA from H_2SO_4, HCl, and HNO_3 solutions. They found that the extraction of indium occurs in the order $HNO_3 > H_2SO_4 > HCl$ for acid concentrations below 2 mol/L, but that the order is reversed in

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concentrated acids. They also found that D2EHPA is a better extractant than EHEHPA. Although extraction and separation of indium by solvent extraction has been widely reported, few studies have considered direct extraction from actual zinc residue leach solutions which contain very low concentrations of indium.

A direct solvent-extraction process avoids the intermediate precipitation, solid–liquid separation, and re-leach steps of traditional indium recovery processes, potentially leading to lower capital and operating costs. This approach has been applied in the recovery of nickel and cobalt from laterite leach solutions (Donegan, 2006; Cheng et al., 2010a, 2010b), but has not been considered for indium recovery. The present study investigates the direct solvent extraction of indium by D2EHPA from a solution generated by the reductive leaching of a zinc residue. Parameters including contact time, initial aqueous pH, extractant concentration, and aqueous-to-organic volumetric phase ratio (A:O) were studied. The aim is to provide a new method of direct solvent extraction for indium extraction that can replace the traditional processes.

2. Experimental

2.1. Materials and chemicals

Zinc residue (from Yunnan Province, China) was the indium source employed. Spent zinc electrolyte was used as the leachate and zinc concentrate was used as the reductant. The feed solution was generated by reductive leaching of the zinc residue in 190 g/L H_2SO_4 at 90 °C, using a liquid–solid ratio of 7 mL/g, a mass ratio of zinc residue to zinc concentrate of 1:0.35, and a reaction time of 3 h. The chemical components of the zinc residue, zinc concentrate, and the reductive leaching solution are listed in Table 1.

Commercial D2EHPA was purchased from Luoyang Zhongda Chemical Co., Ltd, China, and used without further purification. The extractant was dissolved in sulfonated kerosene to achieve the required concentration. Commercial iron powder with a specific surface area of 2.10 m^2/g was used for copper cementation and ferric iron reduction. All other reagents and chemicals were of analytical-reagent grade.

The concentrations of Fe^{2+} and H_2SO_4 were determined by titration. Zn, Fe, Cd, Cu, and As were determined by inductively coupled plasma optical emission spectroscopy (ICP–OES). Indium was determined by ICP with mass spectrometric detection (ICP–MS).

2.2. Solvent extraction procedure

Extraction and stripping experiments were carried out by contacting the organic and aqueous phases at given volume ratios in 125 ml mechanically agitated extractors. After equilibration, the two phases were separated by means of a separation funnel. Countercurrent simulation experiments were performed in a box-style mixer–settler unit. The active mixer volume was 300 mL and the settler volume was 1200 mL.

Metal ion concentrations in the aqueous phases before and after extraction were determined by ICP–OES and ICP–MS, while metal contents in the organic phases were obtained by mass balance.

The distribution ratio, D, was calculated as the ratio of the concentration of metal present in the organic phase to that in the aqueous phase at equilibrium. From the D values, extraction efficiency is calculated from $E(\%) = D \times 100 / (D + (V_{aq} / V_{org}))$, where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively. Separation factors

were calculated from $\beta = D_{In} / D_{Me}$, where D_{In} and D_{Me} are the distribution ratios of indium and the impurity metals, respectively.

3. Results and discussion

3.1. Copper cementation

The objective of copper cementation is to remove copper and reduce the remaining ferric iron to the ferrous state by reaction with iron powder. D2EHPA extracts ferric iron under the same conditions as indium, but the ferrous state is hardly extracted: it is therefore necessary to reduce ferric iron to the ferrous state before indium extraction. Fig. 1 shows the effect of iron powder addition on the efficiencies of copper removal, ferric iron reduction, and indium co-precipitation. Iron powder is an effective reductant for removing copper and reduces ferric iron to the ferrous state in zinc sulfate solution. The copper removal and ferric iron reduction efficiencies increased as the iron powder addition increased from 3.0 g/L to 3.5 g/L, but thereafter reached a plateau. At an iron addition of 3.0 g/L, copper removal was 84.5% and ferric iron reduction efficiency was 89.5%; at an iron addition of 3.5 g/L, copper removal was 99.9% and ferric iron reduction efficiency was 99.7%. A further increase in the iron addition did not give any obvious improvements. However, indium co-precipitation increases with increasing iron addition—from 0.8% to 3.9% as the iron addition increased from 3.0 g/L to 4.5 g/L. In subsequent experiments, the reductive leach solution was pre-treated with 3.5 g/L iron powder to remove copper and reduce ferric iron to the ferrous state, then used as the feed solution for the solvent-extraction experiments.

3.2. Solvent extraction of indium

3.2.1. Effect of contact time

The effects of experimental parameters, such as contact time, aqueous pH, D2EHPA concentration, and phase ratio, were investigated to determine the optimum operating conditions. Fig. 2 shows the effect of contact time on the indium extraction efficiency and phase separation time. It is observed that 2 min is adequate to reach equilibrium at an agitation speed of 800 rpm. Phase separation occurred quickly: within 35 s, the two phases separated completely. There was no crud or third-phase formation during any extraction experiments. A contact time of 3 min and agitation speed of 800 rpm were adopted to ensure complete equilibrium.
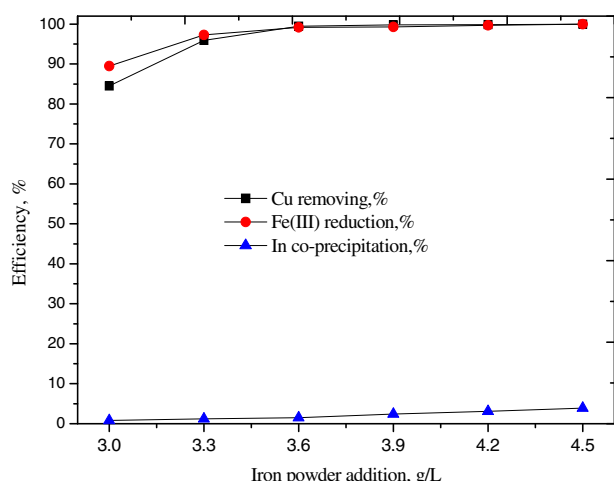
3.2.2. Effect of initial pH and D2EHPA concentration

The effect of initial pH on indium extraction at different D2EHPA concentrations is shown in Fig. 3. Extraction efficiency increases with increasing initial pH. Low extraction efficiency was achieved at pH < 0.25 because the high H^+ concentration prevents extraction of the In^{3+} cation. The optimum initial pH for indium extraction occurs from pH 0.5 to 1.5. Above pH 1.5, extraction efficiency slowly decreased, possibly caused by zinc co-extraction and hydrolysis of the indium ions in this pH range.

Fig. 3 also shows that indium extraction increases with increasing D2EHPA concentration. At an initial pH of 0.5, indium extraction increased from 56.2% to 88.1% with an increase of D2EHPA concentration from 5% to 20% (v/v). Further increasing extractant concentration to 30% gave only a slight increase in extraction, but the excess extractant co-extracts zinc and iron. Because the pH of the leach solution was about

Table 1
Chemical components of zinc residue, zinc concentrate and the reductive leaching solution.

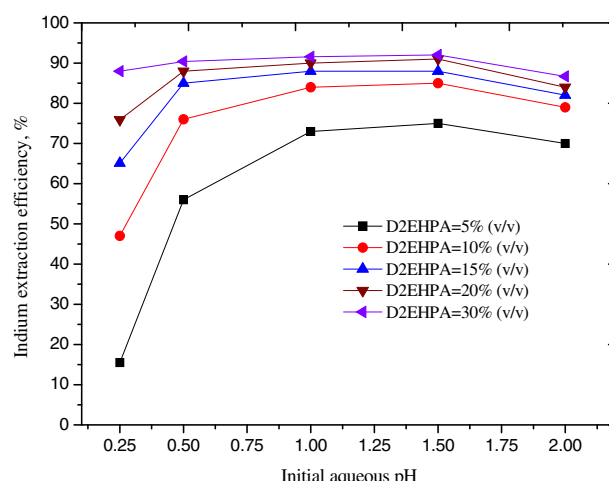| Component	Zn	Fe	Cu	Cd	SiO$_2$	As	In	Fe^{2+}
Zinc residue (wt.%)	25.94	26.58	1.24	0.087	2.68	0.48	560 g/t	/
Zinc concentrate (wt.%)	44.77	16.00	0.58	0.16	1.97	0.33	334.5 g/t	/
Reductive leach solution (g/L)	74.15	35.61	1.45	0.15	0.09	0.35	130 mg/L	32.06

Fig. 1. Effect of iron powder addition on copper removal, ferric iron reduction, and indium co-precipitation efficiencies.

0.5, an initial pH of 0.5 and D2EHPA concentration of 20% were chosen for the following tests.

3.2.3. Effect of phase ratio

Fig. 4 shows the effect of A:O on the indium extraction efficiency at different D2EHPA concentrations. Under the experimental conditions
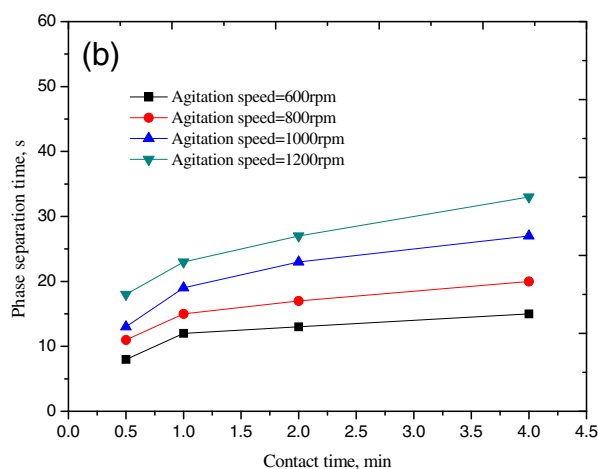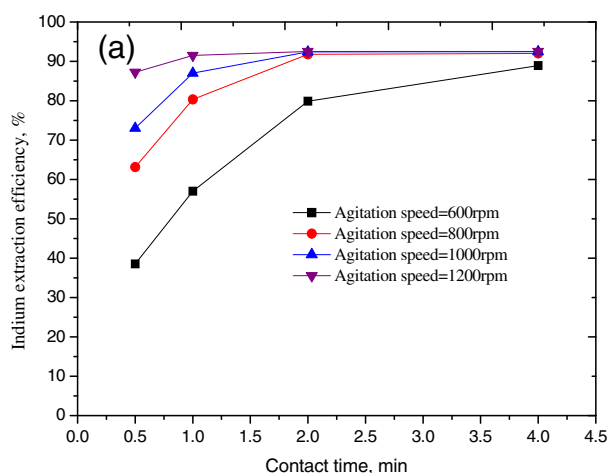

Fig. 2. Effect of contact time on (a) indium extraction efficiency and (b) phase separation time.

Fig. 3. Effect of initial pH on indium extraction efficiency at different D2EHPA concentrations.
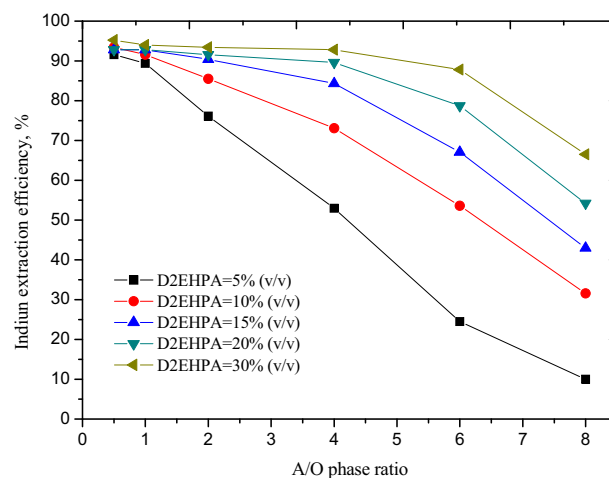
employed, indium extraction decreased with increasing A:O, significantly so at A:O > 6.0. Because a higher A:O is beneficial to concentrating indium in the organic phase, a phase ratio of 6.0 was chosen to ensure maximum indium enrichment of the organic phase.

3.2.4. Extraction isotherm

An extraction isotherm was prepared to determine the number of stages required for quantitative extraction of indium at the chosen A:O. Aqueous and organic phases were contacted at A:O from 1:2 to 10:1, while keeping the other experimental parameters constant (pH 0.5; 20% D2EHPA; total volume). After separation, the two phases were analyzed and McCabe–Thiele diagrams plotted (Fig. 5). Indium was completely extracted in three stages at an A:O of 6.0. To confirm this, a three-stage countercurrent simulation study was carried out at the above conditions. The feed liquid contained 128 mg/L indium, 74.5 g/L zinc, and 39.3 g/L iron, and the corresponding raffinate contained 5.0 mg/L indium, 74.0 g/L zinc, and 39.1 g/L iron, confirming 96.1% indium extraction with negligible co-extraction of zinc or iron. A loaded organic phase containing 738 mg/L of indium was generated for the stripping study. The β values of indium with respect to zinc and iron are 3640 and 4809, respectively, indicating that complete separation of indium from these metals is obtained by solvent extraction.

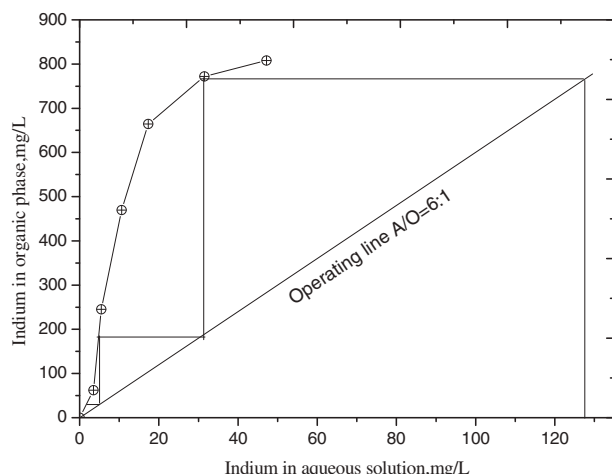Fig. 4. Effect of A:O phase ratio on indium extraction efficiency at different D2EHPA concentrations.

Fig. 5. McCabe–Thiele plot for the extraction of indium.

3.3. Stripping of indium

3.3.1. Effect of HCl concentration and phase ratio

The indium-loaded organic phase was stripped with different HCl concentrations at various phase ratios. The results (Fig. 6) show that indium stripping increased with increasing HCl concentration, but the residual HCl in the strip solution also increases, which requires greater consumption of zinc or aluminum during the subsequent indium cementation step. The optimum HCl concentration was therefore determined by considering both the indium stripping efficiency and the residual acid concentration in the strip solution: 4 mol/L HCl was chosen. Fig. 6 also shows that indium stripping decreased with decreasing phase ratio: at an A:O of 1:1, 99.2% of indium was stripped by 4 mol/L HCl, but stripping dropped to 49.1% at an A:O of 1:10. A higher phase ratio benefits enrichment of indium in the strip solution: use of the 1:1 phase ratio gave only 735 mg/L indium in the strip solution, but this increased to 4400 mg/L at an A:O of 1:6. The most suitable phase ratio was therefore determined by considering both the stripping efficiency and indium concentration in the strip solution: 4 mol/L HCl and an A:O of 1:6 were chosen.

3.3.2. Stripping isotherm

A stripping isotherm for indium was prepared to determine the number of stages required for stripping at the chosen phase ratio. The
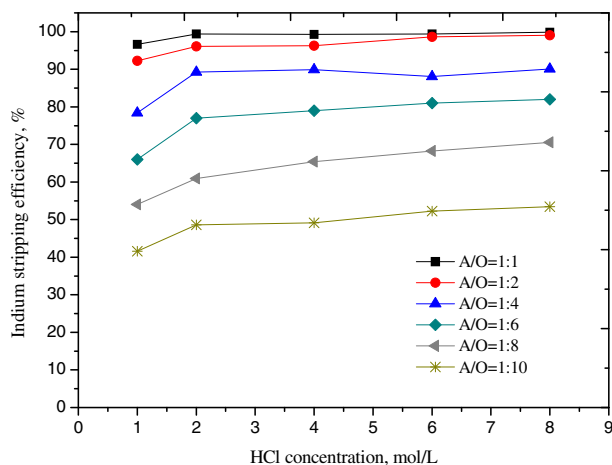
indium-loaded D2EHPA and 4 mol/L HCl were conducted at different phase ratios (A:O = 1:1 to 1:10), while keeping the total volume constant. After separation, both phases were analyzed for metal concentration and the McCabe–Thiele diagram (Fig. 7) constructed. The results indicated >99% indium stripping efficiency in three countercurrent stages at an A:O of 1:6. To confirm the above prediction, a three-stage countercurrent simulation study was performed. The final strip solution contained 4350 mg/L indium, indicating that almost all of the indium present in the loaded organic phase was stripped.

Based on the extraction and stripping isotherms described in Figs. 5 and 7, a scheme for direct solvent extraction of indium by D2EHPA from solutions generated by the reductive leach of zinc residues is presented (Fig. 8). The McCabe–Thiele plot in Fig. 5 shows indium extraction with three countercurrent stages at an A:O of 6:1. An organic phase containing 738 mg/L of indium can be achieved, starting from 128 mg/L indium in the feed solution and giving a recovery of 96.1%. A corresponding analysis was carried out for stripping of the loaded D2EHPA with 4 mol/L HCl. According to the McCabe–Thiele plot, an indium loading of 738 mg/L can be stripped to 12 mg/L at an A:O of 1:6 in three countercurrent stages (Fig. 7). In this process, the indium concentration in the strip solution was about 4400 mg/L, which is relatively low for subsequent indium recovery by cementation. To produce a higher concentration, 60% of the strip solution was recycled to stripping with the addition of HCl for the re-stripping of indium, while the other 40% of the strip solution was discharged for indium recovery. To ensure complete stripping, four countercurrent stages of stripping are adopted in the suggested flow sheet (Fig. 8). This process yielded a strip solution containing 11,000 mg/L of indium, giving an enrichment of 85 times compared with the indium concentration in the reductive leach solution. Indium in the resultant strip solution can be recovered by cementation (Nikov et al., 1994).

4. Conclusions

Direct solvent extraction of indium from a solution generated by the reductive leaching of a zinc residue produced in a zinc hydrometallurgical process was carried out using D2EHPA. The following conclusions are drawn from the present study:

1) Indium is preferentially extracted from the reductive leach solution using 20% D2EHPA, and is quantitative using three stages of countercurrent extraction at an A:O of 6:1 and initial solution pH of 0.5. 96.1% of indium is extracted, while negligible concentrations of zinc and iron are co-extracted. Separation factors of indium with respect to zinc and iron are 3640 and 4809, respectively.

2) A stripping isotherm using 4 mol/L HCl predicted optimum stripping conditions of three stages at an A:O of 1:6. These conditions were confirmed by a countercurrent simulation study.
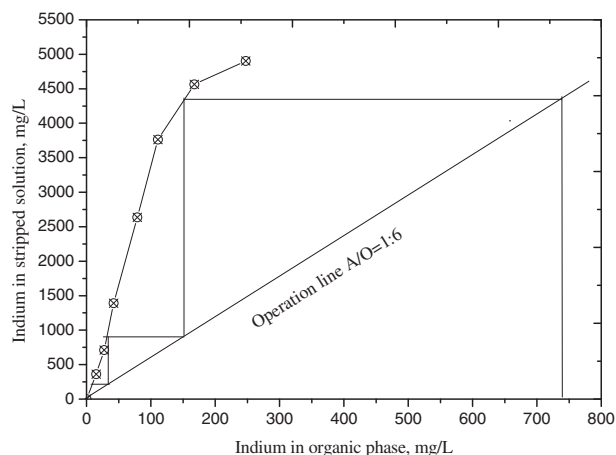

Fig. 6. Effect of hydrochloric acid concentration on the stripping of indium at different A/O phase ratios.

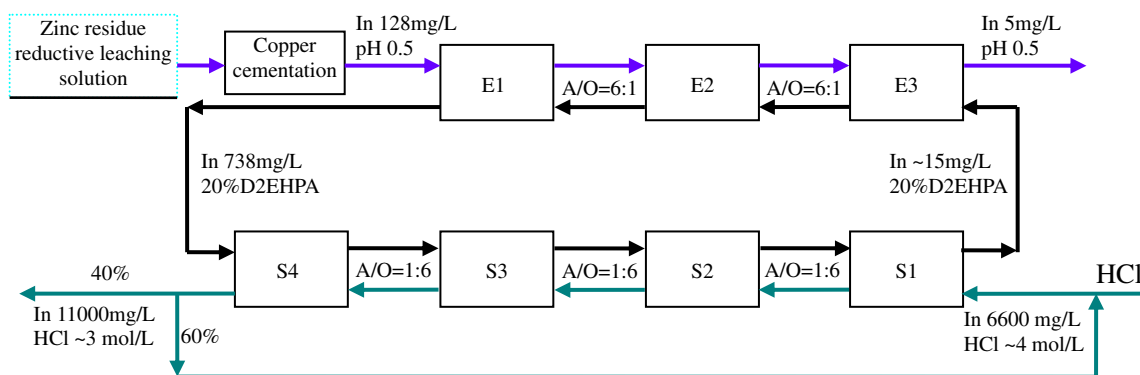Fig. 7. McCabe–Thiele plot for the stripping of indium.

Fig. 8. Suggested flow sheet for the direct solvent extraction of indium from a zinc residue reductive leach solution by D2EHPA.

3) A scheme for direct solvent extraction of indium from a zinc residue reductive leach solution by D2EHPA is given. By recycling 60% of the strip solution for the re-stripping of indium, four countercurrent stages yielded a strip solution containing 11 g/L of indium and achieved greater than 96% recovery.
4) Direct solvent extraction using D2EHPA is an effective method for the concentration and recovery of indium from low concentration solutions, and is applicable to recovering indium from zinc residue reductive leach solutions.

Acknowledgments

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