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Removal and recovery of arsenic from concentrated sulfuric acid by solvent extraction

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Abstract

Arsenic-contaminated sulfuric acid solutions are produced in large quantities as by-product during pyrometallurgical processing of sulfide minerals. Options for re-using such acid solutions are increased if the arsenic is removed and recovered as a product. The performances of tributyl phosphate and a mixture of 6 wt-% 1,2-octanediol in 2-ethylhexanol were studied in liquid-liquid extraction of arsenic from an industrial solution containing 10.4 M H₂SO₄. It was found that, due to the complex phase equilibria, a process design based on conventional batch equilibrium data did not describe the countercurrent processes accurately. A countercurrent flowsheet utilizing undiluted tributyl phosphate was investigated by pseudo-countercurrent extractions. 83.7 % extraction of arsenic and 31.4 % coextraction of H₂SO₄ was obtained in three-stage countercurrent extraction operated at a solvent-to-feed ratio of 0.79. Two-stage countercurrent scrubbing with pure water at O/A = 4.03 back-extracted 83.6 % of H₂SO₄ and 24.9 % of arsenic. 100 % and 89.7 % back-extraction was achieved in four-stage stripping at O/A = 2.01 for H₂SO₄ and arsenic, respectively. The effects of varying the flowsheet and operating parameters on separation efficiency are discussed.

Keywords

Liquid-liquid extraction; Solvent extraction; Arsenic; Sulfuric acid; Pseudo-countercurrent method; Recycling

1 Introduction

Utilization of sulfide minerals in the metals refining industry produces by-product H_2SO_4 solutions that contain arsenic and other impurities. In copper production, for instance, pyrometallurgical treatments do not remove the impurities completely, and they thus end up in cast copper anodes. During electrolytic purification of copper, arsenic dissolves in the H_2SO_4 electrolyte from the anodes with other impurities. These impurities decrease the quality of the product cathodes and lower the efficiency of the electrolysis cell. Furthermore, extremely toxic and lethal arsine gas, AsH_3 , may form if levels of arsenic get sufficiently high in the electrolyte [1].

Partial replacement of the electrolyte with fresh sulfuric acid solution can alleviate the problems caused by impurities. The electrolyte bleed is then directed to separation processes where the impurities or by-products can be treated and recovered. Copper electrolyte bleeds contain significant amounts of nickel, which can be removed by evaporative crystallization to produce crude nickel sulfate. Evaporation concentrates both H_2SO_4 and arsenic, and the resulting concentrated H_2SO_4 solution can be recycled back to electrolysis or sent for effluent treatment and disposal [1].

Flue gases from copper smelters contain volatilized arsenic. During gas cleaning, the arsenic ends up in electrostatic precipitator (ESP) dust and also into the H_2SO_4 solutions that circulate in wet gas scrubbers. Use of relatively concentrated H_2SO_4 in washing towers is encouraged by the high solubility of arsenic in H_2SO_4 [2]. Most of the ESP dust is circulated back to the smelter for a more complete recovery of raw materials but a fraction of the dust is leached with H_2SO_4 to prevent accumulation of impurities in the copper refining process [3–6]. The origins of arsenic-contaminated H_2SO_4 solutions are summarized in Fig. 1, which is simplified from the publications by Szymanowski (1998) [1], Dalewski (1999) [2] and Nazari *et al.* (2017) [3]. It should be noted that potential sources of arsenic-contaminated acids are not limited to copper refineries.

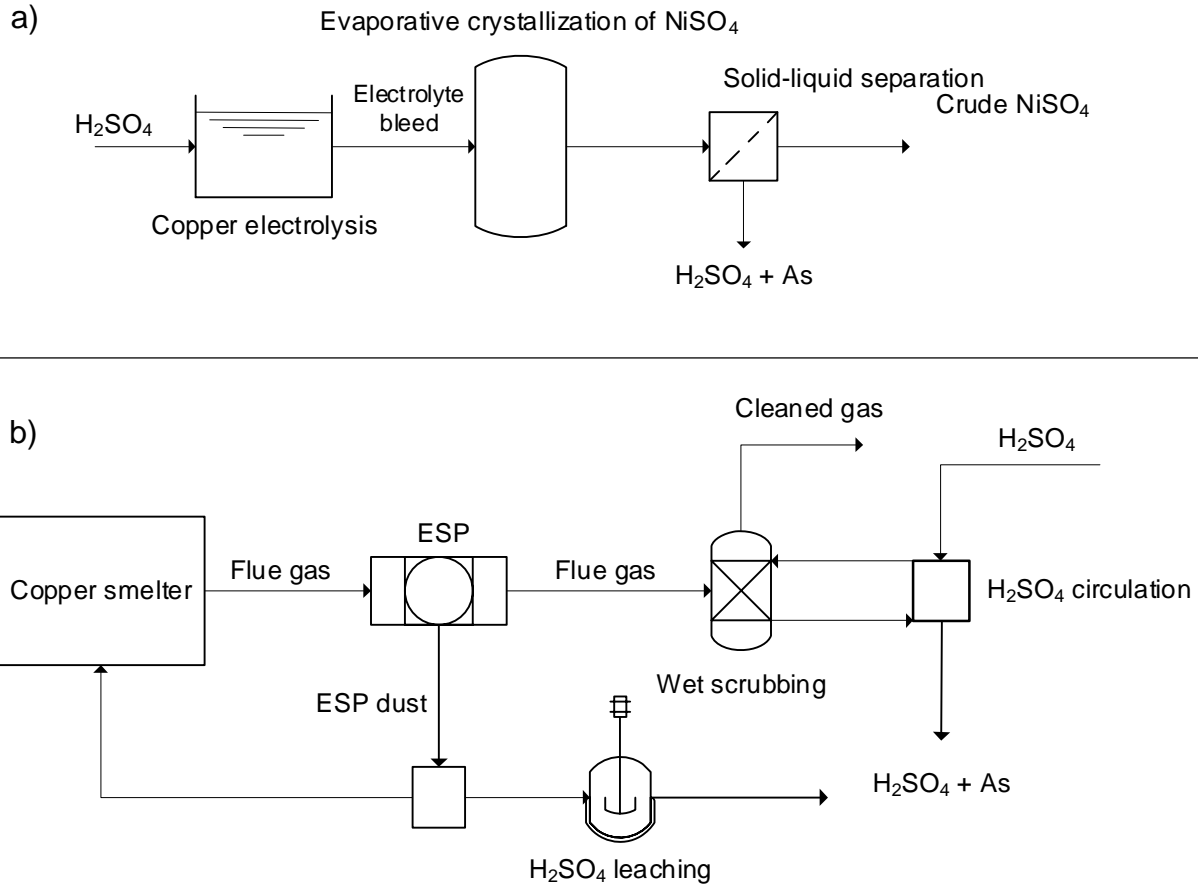


Figure 1 Schematic diagrams of the formation of arsenic-bearing concentrated H_2SO_4 solutions in copper refineries. a) Copper electrolyte bleed [1] b) Flue gas treatment in a copper smelter [2,6].

Arsenic was recently listed in the ‘Final List of Critical Minerals 2018’ by the US Department of the Interior (DOI) [7]. To promote a circular economy, the recovery of arsenic as a product should be considered instead of precipitating arsenic as impure arsenites or arsenates. Concentrated H_2SO_4 solutions, in particular, offer the possibility for producing H_2SO_4 intermediate with significantly less or no arsenic and an arsenic-rich aqueous stream that is suitable for crystallization of As_2O_3 .

The applicability of liquid-liquid extraction (LLE) for removal of arsenic from H_2SO_4 solutions has been examined by several authors (Table I). In purification of copper electrolytes, an arsenic extraction process can be located: 1) directly after copper electrolysis; 2) after decopperizing treatment for the bleed (*e.g.* liberator electrolysis); or 3) after evaporation crystallization of crude NiSO_4 . If the extraction is done before evaporation, the size of the required extraction equipment

will be larger than if the extraction is done after evaporation. On the other hand, highly concentrated H_2SO_4 solutions demand more corrosion-resistant materials [15].

Table I Literature on liquid-liquid extraction of arsenic from H_2SO_4 solutions.

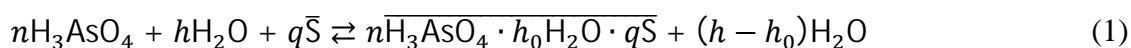
Extractant(s)	[As] ₀ [g dm ⁻³]	[Ni] ₀ [g dm ⁻³]	[Cu] ₀ [g dm ⁻³]	[H ₂ SO ₄] ₀ [g dm ⁻³]	Reference
Cyanex 301, 923, 925 Hydroxamic acids 2-ethylhexane-1,3-diol	2.5	–	–	50–200	[8,9]
Cyanex 923	0.63–5	–	–	50–200	[10,11]
DBBP+D2EHPA	3–7.6	4.6–8.4	30–31.3	160–200	[12]
TBP	28	34.7	16.6	600	[13]
TBP	10	16	65	200–600	[14]
TBP	15	0.4	8.7	200–600	[15]
TBP, D2EHPA, TAPO, HBPTA, D2EHMP	6.2	21.7	42.3	< 400	[16]
HBPTA, TBP	4–5	–	–	≤ 300	[17]
Aliphatic alcohols	6–10.5	6–10	40–50	150–300	[18,19]
Alkylated polyphenols	5.9	–	45	200	[20,21]
NMPL	0.075	–	–	137–196	[22]
Trioctylphosphine oxide	2.3	18	28.3	187.2	[23]
Hydroxamic acids	10.4–21.5	9.6–21.5	32–54.3	153–225	[24,25]
Mixtures of NOPCs and aliphatic alcohols	90–120	–	30	110–145	[26]
NOPCs, mainly TBP	3.9–11.5	12.3–14.5	8.7–33.1	100–400	[27]
TBP, DBBP, DPPP, TAPOs	1.4–15.5	–	35–45	140–220	[28,29]

D2EHMP = bis(2-ethylhexyl) methylphosphonate
DBBP = dibutyl butylphosphonate
DPPP = dipentyl pentylphosphonate
HBPTA = hexabutylphosphoric triamide
NMPL = 1-(2,6-dimethylheptyl-4-oxy)-3 methyl-1-oxo- Δ^3 -phospholen
NOPC = neutral organophosphorus compound
TAPO = trialkylphosphine oxide

In previous research, most authors have focused on extracting arsenic from non-concentrated copper electrolyte bleeds (Table I). Published results for pre-concentrated copper electrolytes are limited to work reported by De Schepper & Van Peteghem [13] and Navarro & Alguacil [14].

Demirkiran & Rice [15] studied extraction at $600 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$ feed concentration with synthetic solutions but countercurrent results were reported for non-concentrated copper electrolyte. Concentrating the solution before extraction to H_2SO_4 levels higher than 6 M aims to reduce equipment size further, yield high concentration of arsenic in the stripping raffinate, and enable small volumetric throughput of water and tributyl phosphate (TBP) in the extraction process.

Precise mechanisms and stoichiometry of solvation in extraction of arsenic are not very well known. Travkin *et al.* [16] have described the extraction of arsenic(V) with Eq. (1)



where S denotes an extractant molecule, and n , h , h_0 and q are stoichiometric constants that depend on the reaction conditions and extractant. When the feed solution contains H_2SO_4 , it is co-extracted and associated in the complex [16]. TBP is known to extract only arsenic(V) in significant amounts [30] but alcohols and glycols extract also arsenic(III) [1, 18–21]. $D(\text{As})$ is known to decrease with several solvating extractants when temperature is increased [16].

It is generally agreed that increasing H_2SO_4 concentration in the feed enhances the extraction of arsenic [1, 8–12, 14–17, 27]. Also, the more H_2SO_4 in the feed, the more aggressive becomes the co-extraction of H_2SO_4 . Co-extraction of H_2SO_4 and water causes expansion of the organic phase and simultaneous shrinkage of the aqueous phase, *i.e.* phase ratio changes during extraction. This phenomenon is not significant in extractions with 2–3 M H_2SO_4 solutions, since the absolute amount of co-extracted H_2SO_4 and water are relatively low. Another limitation caused by very high H_2SO_4 concentration in the feed is that neutral organophosphorus compounds (NOPCs) must be used without kerosene-based diluents. Otherwise the system will split into three phases. Third phase formation was also experimentally verified in current study.

To the best of our knowledge, results on extraction of arsenic from extremely concentrated (*i.e.* 10 M or higher) H_2SO_4 solutions have not been published previously and comparisons of TBP and aliphatic alcohols in extraction of arsenic from the same feed solution are missing. Moreover, the performance of alcohols has been reported only for the non-concentrated H_2SO_4 solutions, perhaps

due to their reactivity. According to speciation calculations by MEDUSA [31], the fraction of H_3AsO_4 in aqueous H_2SO_4 solution is sensitive to changes in redox-potential (see section 3, Fig. 10). Design methods and process parameters that are suitable for non-concentrated copper electrolytes are not necessarily applicable with highly concentrated H_2SO_4 solutions. Inconsistencies between McCabe–Thiele analyses and batch countercurrent simulations were reported already at $2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ [15]. Process design by McCabe–Thiele or Hunter–Nash methods is challenging, since the apparent $D(\text{As})$ values change with the speciation.

In this work, the separation of arsenic and H_2SO_4 from an industrial 10 M H_2SO_4 solution using undiluted TBP is studied. A flowsheet involving countercurrent extraction, H_2SO_4 scrubbing and arsenic stripping steps [13] is investigated by pseudo-countercurrent (pseudo-cc) method [32,33]. Pseudo-cc results are compared with the conventional McCabe-Thiele or Hunter-Nash –type graphical designs that utilize conventionally determined equilibrium curves. Differences in performance of TBP and the mixture of 1,2-octanediol and 2-ethylhexanol are discussed.

2 Experimental

Two shipments of 10.4 M H_2SO_4 solution were received from industry for the extraction studies. Compositions of these acid batches are given in Table II, and theoretical speciation analysis is shown in Fig. 2, where speciation at $\log([\text{H}^+]_{\text{tot}}) \approx 1.3$ should approximately represent the feed solution. Only arsenic and nickel were considered in speciation calculation in Fig. 2, and the metals at ppm-levels were neglected. Ionic strength was approximated iteratively in all speciation calculations.

Table II Compositions of the feed solutions.

	Shipment #1	Shipment #2
$c(\text{H}_2\text{SO}_4)$ [g dm ⁻³]	1022.2	963.3
$c(\text{As})$ [g dm ⁻³]	23.9	32.5
$c(\text{As}^{3+})$ [%]	9.2	7.1
$c(\text{Ni})$ [g dm ⁻³]	2.1	2.6
$c(\text{Cu})$ [ppm]	2.5	18.9
$c(\text{Zn})$ [ppm]	0.8	< LOD
$c(\text{Cd})$ [ppm]	< LOD	0.1
$c(\text{Sb})$ [ppm]	117.3	187.0
$c(\text{Hg})$ [ppm]	0.7	2.0
$c(\text{Pb})$ [ppm]	1.1	2.0
$c(\text{Bi})$ [ppm]	4.9	43.3

LOD = Limit of detection

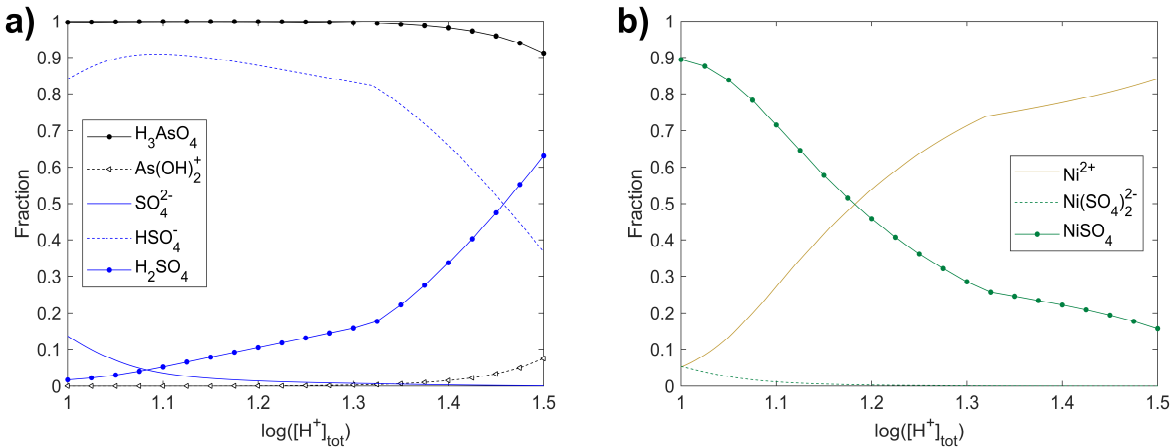


Figure 2 Effect of proton concentration on speciation of: a) arsenic and H_2SO_4 ; and b) nickel in the feed solution. Constructed with MEDUSA [31] using following parameters: $c(\text{SO}_4^{2-})_{\text{tot}} = 10 \text{ M}$, $c(\text{Ni}^{2+})_{\text{tot}} = 0.036 \text{ M}$, $c(\text{AsO}_4^{3-})_{\text{tot}} = 0.32 \text{ M}$, $E_h = +0.71 \text{ V}$ and $T = 25 \text{ }^\circ\text{C}$.

2.1 Chemicals

97 % tributyl phosphate (TBP) ($M = 266.31 \text{ g mol}^{-1}$), ≥ 90 % dibutyl butyl phosphonate (DBBP) ($M = 250.31 \text{ g mol}^{-1}$), ≥ 99 % 2-ethyl-1-hexanol ($M = 130.23 \text{ g mol}^{-1}$) and 98 % 1,2-octanediol ($M = 146.23 \text{ g mol}^{-1}$) were obtained from Merck KGaA (Sigma-Aldrich). A commercial mixture of trialkylphosphine oxides (Cyanex 923) containing mainly *n*-octyl- and *n*-hexyl hydrocarbon

chains was supplied by Cytec (now Solvay). Aliphatic hydrocarbon mixture Exxsol D80 (supplied by Exxon Mobil) was used in preliminary tests with the NOPCs. All chemicals were used as received.

Dilution of TBP, DBBP and Cyanex 923 in Exxsol D80 resulted in third phase formation when extraction from 10.4 M H₂SO₄ solution was attempted. After the observed problem of third phase formations with diluted NOPCs, 97 vol-% TBP was used in the experiments without dilution and it is referred to as undiluted TBP in this text. Cyanex 923 was too viscous in room temperature (21 ± 1 °C) to be used without dilution, and DBBP was not available in sufficient quantities. 6 wt-% solution of 1,2-octanediol in 2-ethylhexanol was prepared for the experiments. The composition of the alcohol mixture was based on works by Baradel & Guerriero [19] and Szymanowski [1]. Deionized and RO-filtered water was used for back-extractions from the loaded extractants.

2.2 Analytical methods

Total concentration of arsenic and metal concentrations were measured from aqueous samples using ICP-MS (Agilent 7900). Samples from the organic phases were back-extracted with pure water at A/O = 30, and concentrations in the back-extraction raffinates were measured to obtain the organic phase equilibrium concentrations. As(III) concentrations in the feed solution were analyzed in an external accredited laboratory. H₂SO₄ concentrations in raffinate samples were determined by acid-base titration with NaOH, and concentrations of H₂SO₄ in the organic phases were calculated from mass balance. Parallel determination of total sulfur with ICP-MS was in good agreement with mass balance calculations in conventional batch extraction experiments. Deviations between the determination by NaOH-titration and ICP-MS analysis were found for samples from scrubbing and stripping experiments. Simultaneous neutralization of H₃AsO₄ became significant as acidity was adequately low in these samples, which affected NaOH consumption in titration. Therefore, ICP-MS data was used in calculation of the pseudo-countercurrent results. Phase densities were measured at 23 °C using an Anton Paar DMA4500 density meter. A Mettler-Toledo LE-150 ORP Ag/AgCl electrode was used for redox potential measurements.

2.3 Experiments

All extraction experiments were performed in glass separation funnels at 21 ± 1 °C. Phases were mixed by using an orbital shaker. Equilibration time of 20 minutes and shaking rate of 300 min^{-1} were used. The phases were separated by gravity and samples were taken after both phases were considered clear by visual observation. As phase separation problems occurred in certain experiments with the alcohol mixture, phase disengagement was aided by centrifugation for 10 minutes at 4000 min^{-1} . Loading and stripping isotherms were determined by carrying out several batch extractions with different O/A ratios. In order to quantify the change in phase weights and volumes, separation funnels were weighed before and after each addition or removal of a phase.

2.3.1 Pseudo-countercurrent extractions

Separation of arsenic and sulfuric acid in countercurrent liquid-liquid extraction cascades was experimentally studied by batch extractions according to a pseudo-countercurrent (pseudo-cc) scheme (Fig. 3) described by Haghghi *et al.* [32]. After several consecutive cycles, the system approaches conditions similar to an actual countercurrent cascade (Fig. 4). Blocks in Fig. 3 represent one batch extraction experiment, and approach to the steady state was monitored by analyzing the cascade outlet streams as reported by Matveev *et al.* (2018) [34]. Steady-state was assumed when concentrations in the outlet streams, *i.e.* $E_{1,n}$ and $R_{3,n}$ in Fig. 3, remained constant in consecutive cycles. Table III summarizes the pseudo-cc extractions done in this work.

Table III Pseudo-countercurrent extractions.

	Run 1	Run 2	Run 3	Run 4	Run 5
O/A	0.8	4	0.5	2	2
Type	extraction	scrubbing	stripping	stripping	stripping
Stages	3	2	2	2	4
Cycles	9	6	6	6	13
Extractions	24	11	11	11	46

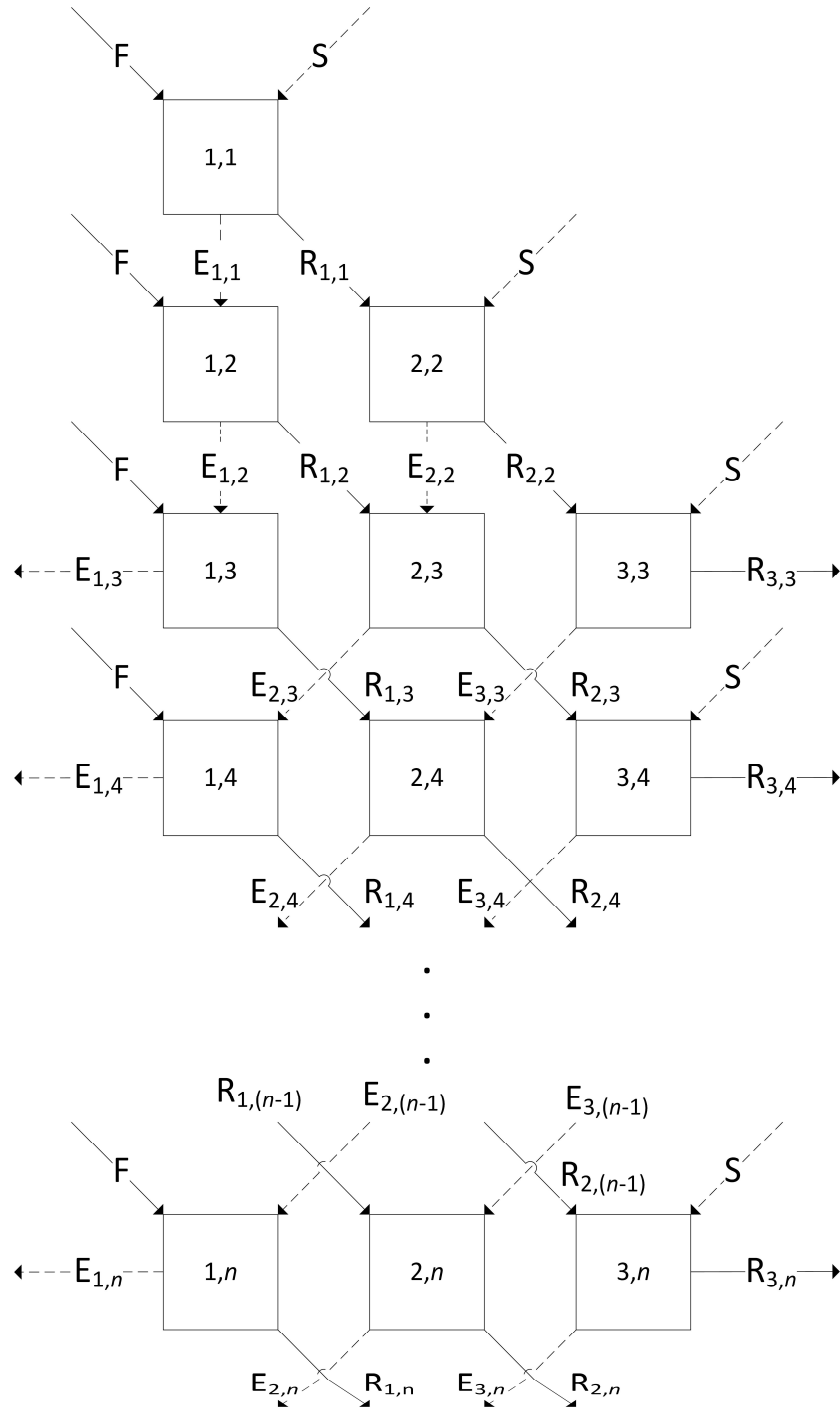


Figure 3 Pseudo-countercurrent scheme for three extraction stages. n is the number of cycles. E = extract, F = feed, R = raffinate, and S = solvent.

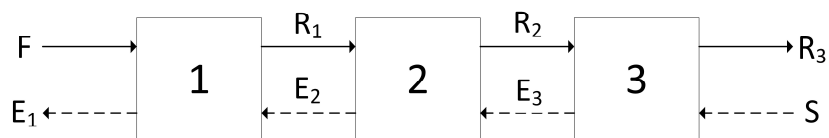


Figure 4 Schematic diagram of continuous three-stage countercurrent extraction.
E = extract, F = feed, R = raffinate, S = solvent.

3 Results and discussion

Speciation calculations (Fig. 5) showed that fractions of H_3AsO_4 , $\text{As}(\text{OH})_3$ and $\text{As}(\text{OH})_2^+$ in concentrated H_2SO_4 solutions are sensitive to changes in redox potential. The fraction of extractable H_3AsO_4 should remain high also in very concentrated H_2SO_4 providing that the redox potential of the solution is +0.65 V or above (Fig. 5a). The fraction of H_2AsO_4^- in mildly acidic solutions seems to be unaffected by changes in redox potential (Fig. 5d). The same observation was made for HAsO_4^{2-} (plot not shown).

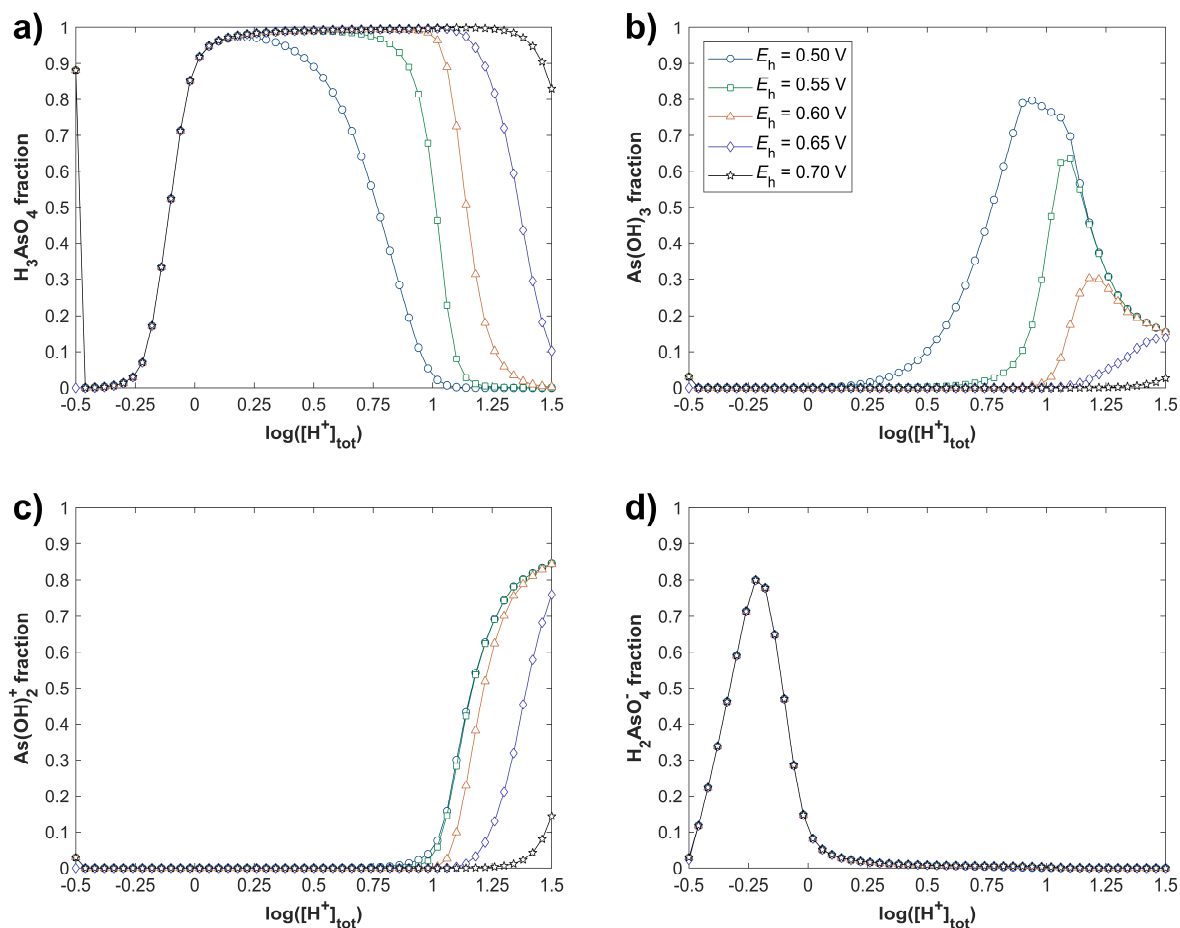


Figure 5 Effect of redox potential, E_h , on speciation of arsenic in H_2SO_4 solutions at 25 °C. Calculated with MEDUSA [31] using iterated ionic strength; $c(AsO_4^{3-})_{\text{tot}} = 0.31$ M; $c(SO_4^{2-})_{\text{tot}} = 10$ M.

3.1 Extraction of arsenic and H_2SO_4

97 vol-% TBP and the mixture of 6 wt-% 1,2-octanediol in 2-ethylhexanol behaved quite similarly in extraction (Table IV, Fig. 6). Percentages of arsenic and H_2SO_4 extracted by TBP and the alcohol mixture were practically the same for both extractants (Fig. 7). However, 22.5 g dm^{-3} peak loading concentration of arsenic in the alcohol mixture is slightly lower than the 26.4 g dm^{-3} measured for TBP (Fig. 6).

Mass balance calculations showed a 1:2:1 ratio of $H_2SO_4:H_2O:TBP$ in the loaded organic phase, when $c(H_2SO_4)_{\text{org}}$ was $200\text{--}300 \text{ g dm}^{-3}$. When $c(H_2SO_4)_{\text{org}}$ decreased below 15 g dm^{-3} in stripping, the stoichiometric ratio $H_2O:TBP$ was 7:1. Respectively, H_2O :alcohol ratio was 1:1

when there was 200–370 g dm⁻³ H₂SO₄ in the loaded alcohol phase, but H₂SO₄:alcohol ratio varied between 0.4–0.9. Loading isotherms for H₂SO₄ (Fig. 6b) are linear, and the slopes of the isotherms are quite similar to those reported by Gromov *et al.* for 2-ethyl-1-hexanol [35].

Arsenic was more selectively extracted by TBP at O/A between 0.1–1, whereas at O/A ratios 2 and 3.5 the alcohol mixture was more selective to arsenic. $D(\text{As})$ of approximately 2.7 published by Navarro & Alguacil [14] is probably the highest reported for undiluted TBP. It was obtained with a feed containing 18 g dm⁻³ arsenic and 600 g dm⁻³ H₂SO₄ [14]. Typical $D(\text{As})$ values for TBP have ranged between 0.4–1.7 for feed solutions with 1–3 M H₂SO₄ [14–17, 29]. For 10.4 M H₂SO₄ solution containing 23.9 g dm⁻³ arsenic, the highest $D(\text{As})$ in the current experiments was 1.31 (Table IV). The probable reason for lower $D(\text{As})$ compared with Navarro's & Alguacil's [14] results is that the feed in current study contained higher amount of undissociated H₂SO₄ (Fig. 2a). The higher amount of undissociated H₂SO₄ makes competition between H₂SO₄ and H₃AsO₄ more aggressive. Together with possible differences in redox potential, the greater amount of undissociated H₂SO₄ explains the lower $D(\text{As})$ in the current study (Fig. 5).

$D(\text{As})$ values of aliphatic alcohols are available in the literature only for 150–200 g dm⁻³ H₂SO₄ solutions [1,8,21]. Iberhan & Wósniewski [8] published a $D(\text{As(V)})$ value of approximately 0.4 for 2-ethylhexane-1,3-diol with 150 g dm⁻³ H₂SO₄. In the current study $D(\text{As})$ ranged from 0.9 to 1.5 for 6 wt-% 1,2-octanediol in 2-ethylhexanol. As with TBP, the overall distribution coefficients of arsenic are very dependent on the feed composition.

Table IV Comparison of TBP and alcohol mixture in extraction of arsenic and H_2SO_4 from feed solution containing 23.9 g dm^{-3} of arsenic and 1022.2 g dm^{-3} of H_2SO_4 .

O/A	TBP			6 wt-% 1,2-octanediol in 2-ethylhexanol		
	$D(\text{As})$	$D(\text{H}_2\text{SO}_4)$	$\beta(\text{As}/\text{H}_2\text{SO}_4)$	$D(\text{As})$	$D(\text{H}_2\text{SO}_4)$	$\beta(\text{As}/\text{H}_2\text{SO}_4)$
0.1	1.22	0.34	3.54	1.01	0.37	2.74
0.125	1.27	0.36	3.50	1.07	0.38	2.79
0.25	1.24	0.34	3.68	1.02	0.37	2.72
0.5	1.28	0.33	3.92	1.03	0.36	2.88
0.8	1.31	0.32	4.07	0.93	0.35	2.64
1	1.22	0.31	3.92	1.14	0.35	3.26
2	1.04	0.30	3.41	1.31	0.31	4.20
3.5	0.74	0.30	2.46	1.52	0.29	5.19

$$\beta(\text{As}/\text{H}_2\text{SO}_4) = D(\text{As})/D(\text{H}_2\text{SO}_4)$$

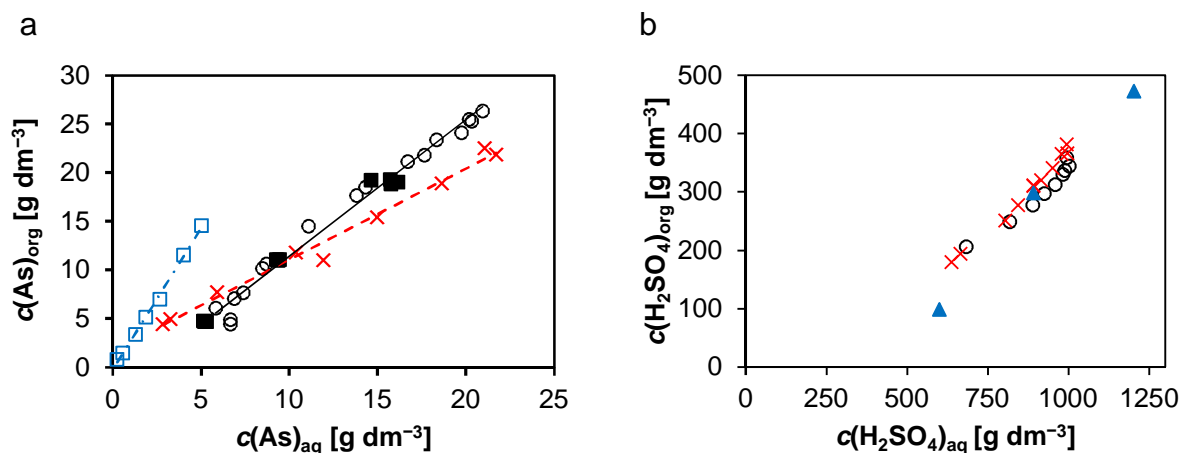


Figure 6 Loading isotherms for extraction of arsenic (a) and H_2SO_4 (b) from feed solution containing 23.9 g dm^{-3} arsenic and 1022.2 g dm^{-3} H_2SO_4 . Undiluted TBP (circles), undiluted TBP in pseudo-cc extraction (filled squares), 6 wt-% 1,2-octanediol in 2-ethylhexanol (crosses), undiluted TBP & 600 g dm^{-3} H_2SO_4 in the feed [14] (hollow squares), 2-ethylhexanol [35] (triangles).

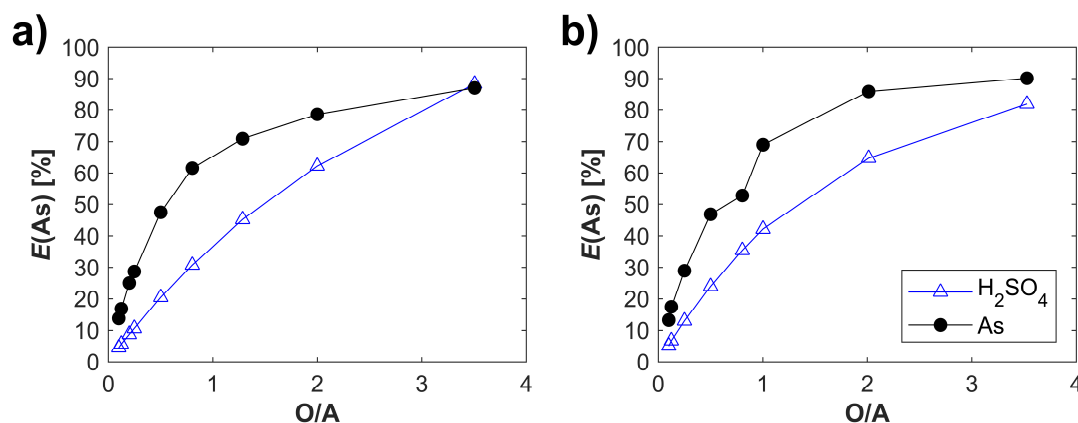


Figure 7 Percentages of arsenic and H₂SO₄ extracted from feed solution containing 23.9 g dm⁻³ of arsenic and 1022.2 g dm⁻³ of H₂SO₄: a) 97 vol-% TBP; b) 6 wt-% 1,2-octanediol in 2-ethylhexanol.

3.1.1 Phase behavior

Change in phase ratio, $\Delta(O/A)$, with alcohol mixture at initial O/A ratios between 0.1–1.5 is slightly more extensive than $\Delta(O/A)$ for TBP (Fig. 8a). The more extensive $\Delta(O/A)$ can explain the slightly more gradual loading isotherm (Fig. 6a). Because of the changes in phase ratios, percentages of extraction are not precisely deducible from distribution coefficients alone.

The feed acid became completely miscible with TBP at initial O/A = 6.5. With complete or near-complete uptake of feed acid into the organic phase there would be little or no raffinate stream coming from the extraction stages. Therefore, O/A ratios above 4 were not tested with the alcohol mixture after miscibility observations with TBP. In general, phase behavior at room temperature favors the use of TBP. Samples from backextraction analyses (A/O = 30) of the alcohol mixture had to be centrifuged, since the backextracted samples were still hazy four days after shaking. In the case of TBP, backextracted organic samples were separated by gravity and no centrifugation was required. Baradel *et al.* [20] reported that raising the temperature provides faster phase separation, which could improve phase behavior of the alcohol mixture. On the other hand, increasing the temperature would also increase the reactivity of the alcohols (see section 3.2.1).

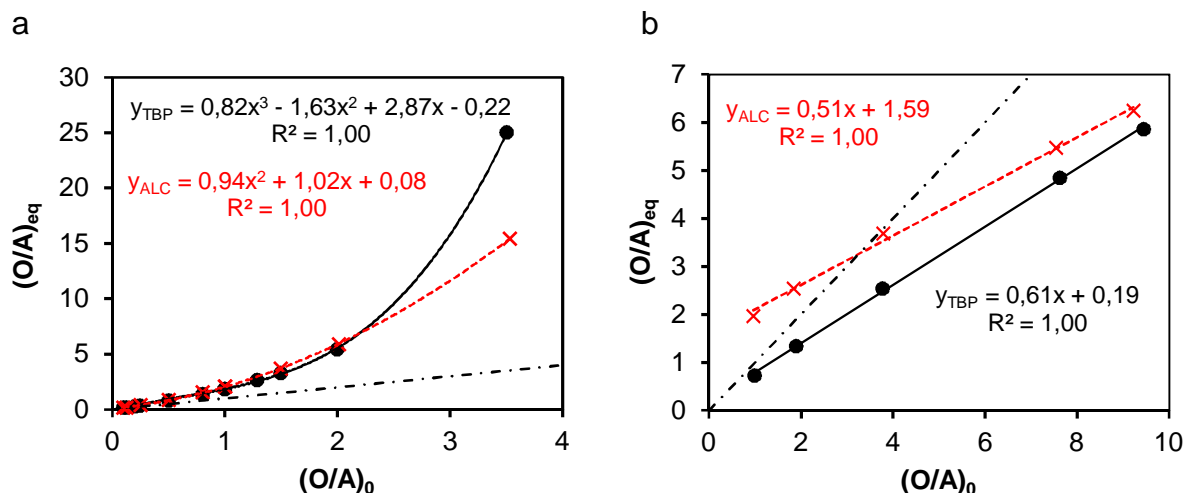


Figure 8 Changes in O/A ratios in extraction (a) and scrubbing (b) of arsenic and H₂SO₄ from feed solution Shipment #1. 97 vol-% TBP (circles), 6 wt-% 1,2-octanediol in 2-ethylhexanol (crosses). Dash-dot line represents constant phase ratio.

3.1.2 Extraction performance in countercurrent operation

McCabe–Thiele interpolation with linear operating lines has been used by several authors [11, 14, 15] in evaluation and development of LLE flowsheets for separating arsenic and H₂SO₄ from dilute to moderately concentrated H₂SO₄. The requirement for a linear operating line would be that O/A ratios remain constant between the stages and no speciation changes take place in the system [36]. Demirkiran & Rice [15] have already reported inconsistencies between McCabe–Thiele constructions and experimental results. Therefore, pseudo-cc extractions by TBP were used to study the distributions in countercurrent cascades. Due to the unpredictable phase behavior of 1,2-octanediol and 2-ethylhexanol in back-extraction and better **phase** separation observed with TBP, the alcohol mixture was not investigated by pseudo-cc method.

Three stages with O/A = 0.8 (**higher $\beta(\text{As}/\text{H}_2\text{SO}_4)$ for TBP, see Table IV**) was selected to study countercurrent extraction, since 95 % extraction of arsenic with three countercurrent extraction stages operating at O/A = 1.17 was reported earlier by Navarro & Alguacil [14]. Even such a low number of stages is enough to reveal possible curvature in an operating line. Initial O/A = 0.8 produced an equilibrium O/A of 1.38 in conventional batch experiments (Fig. 8a), and thus using O/A = 0.8 does not lower the volume of the raffinate too much.

Concentration profiles for arsenic and H_2SO_4 in three-stage pseudo-cc extraction are given in Table V and Fig. 9b. In Table V the feed solution entered at stage 1, and TBP at stage 3, respectively. V_0 values indicate the initial phase volumes of the stages and V_t is used to describe the volumes at equilibrium. 83.7 % of the arsenic and 31.4 % of the H_2SO_4 were extracted at $O/A = 0.79$. The percentage of arsenic extracted is somewhat lower than reported in [14] for $O/A = 1.17$. Arsenic is significantly extracted in all stages, but the concentration profiles of the cascade show that most of the H_2SO_4 extraction occurs in stage 3 where TBP is fed (Table V). Additional extraction stages should therefore enhance the separation and increase $E(\text{As})$, since cumulative $E(\text{H}_2\text{SO}_4)$ remains practically constant in the stages that follow the TBP feeding stage. Enhancement in separation is seen also from the increase in $\beta(\text{As}/\text{H}_2\text{SO}_4)$ and $D(\text{As})$ from stage 3 to stage 1. After three-stage extraction, TBP contained 19.24 g dm^{-3} arsenic and 292 g dm^{-3} H_2SO_4 . Respectively, the raffinate composition was 5.14 g dm^{-3} arsenic and 905 g dm^{-3} H_2SO_4 .

Table V Results of three-stage pseudo-cc extraction. The feed solution contained 23.9 g dm^{-3} arsenic and 1022.2 g dm^{-3} H_2SO_4 . $O/A = 0.79$ (in); $E/R = 1.43$ (out).

Stage	1	2	3
$V_{0,\text{aq}}$ [cm^3]	124.7	121.8	111.5
$V_{0,\text{org}}$ [cm^3]	124.7	125.3	99.0
$V_{0,\text{tot}}$ [cm^3]	249.5	244.8	213.6
O/A	1.00	1.03	0.89
$V_{t,\text{aq}}$ [cm^3]	123.6	118.2	87.6
$V_{t,\text{org}}$ [cm^3]	125.7	129.0	121.3
$V_{t,\text{tot}}$ [cm^3]	249.6	245.2	214.3
E/R	1.02	1.09	1.38
$D(\text{As})$	1.31	1.20	0.93
$D(\text{H}_2\text{SO}_4)$	0.29	0.29	0.28
$\beta(\text{As}/\text{H}_2\text{SO}_4)$	4.56	4.09	3.31
$c(\text{As})_{\text{aq}}$ [g dm^{-3}]	14.65	9.26	5.14
$c(\text{As})_{\text{org}}$ [g dm^{-3}]	19.24	11.14	4.78
$c(\text{H}_2\text{SO}_4)_{\text{aq}}$ [g dm^{-3}]	1015.0	994.4	904.9
$c(\text{H}_2\text{SO}_4)_{\text{org}}$ [g dm^{-3}]	292.1	292.9	254.2

Simplified McCabe–Thiele analysis suggests that five stages are required to extract 83.7 % of the arsenic at $O/A = 0.79$ (Fig. 9a). The pseudo-cc steady-state compositions indicate that such extraction results could be achieved in only three countercurrent stages (Fig. 9b). The McCabe–Thiele analysis in Fig. 9a was constructed by utilizing conventional batch experiment data and assuming constant phase ratio. The percentage of extraction was set to 83.7 %, which was achieved in real pseudo-cc experiments. There were probably no significant changes in the aqueous speciation during extraction, as the equilibrium line remained fixed in the pseudo-cc experiments (Fig. 6a and Fig. 9). Theoretical McCabe–Thiele diagram (Fig. 9a) predicted a higher number of stages because curvature in the operating line was not considered.

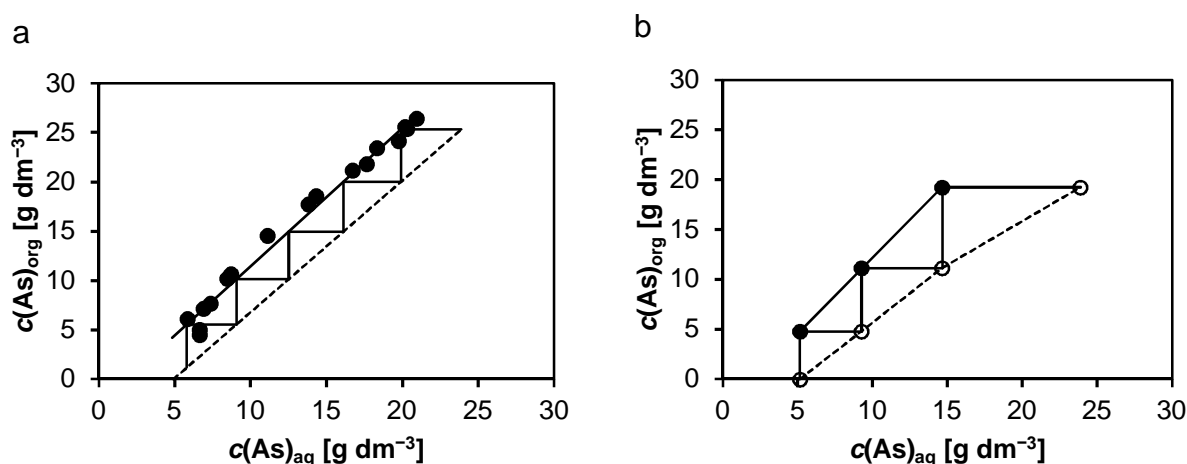


Figure 9 Comparison of theoretical McCabe-Thiele analysis (a) with the experimental results (b). $O/A = 0.79$ and 83.7 % removal of arsenic. $c_0(\text{As})_{\text{aq}} = 23.9 \text{ g dm}^{-3}$ and $c_0(\text{As})_{\text{org}} = 0$.

3.2 Back-extraction

Separation of arsenic and H_2SO_4 in back-extraction is based on the different strength of the acids. As a stronger acid H_2SO_4 dissociates at higher proton concentration than H_3AsO_4 (Fig. 10). Protons and anions which are formed by dissociation have much stronger affinity to water, and they are back-extracted more aggressively than the undissociated acids. According to theoretical calculations (Fig. 10), the first dissociation of H_3AsO_4 starts approximately when $\log([\text{H}^+]) = 0.5$ in the raffinate. At this proton concentration there is no undissociated H_2SO_4 in the aqueous solution.

Theoretically it would be favorable to increase O/A ratio stage by stage in H_2SO_4 scrubbing so that $0.5 \leq \log([\text{H}^+]) \leq 1$ in the back-extraction raffinates. This type of fractional extraction could be attempted to separate the acids completely. If the fractional extraction approach turns out to be non-feasible in practice, at least bulk separation can be done by solvent extraction to produce a relatively low volume of arsenic-rich solution whose total concentration of SO_4^{2-} is significantly lower. It can be concluded from Fig. 5a and Fig. 10 that co-extraction of H_2SO_4 does not lower the separation efficiency as long as the redox potential is sufficiently high in the initial feed solution.

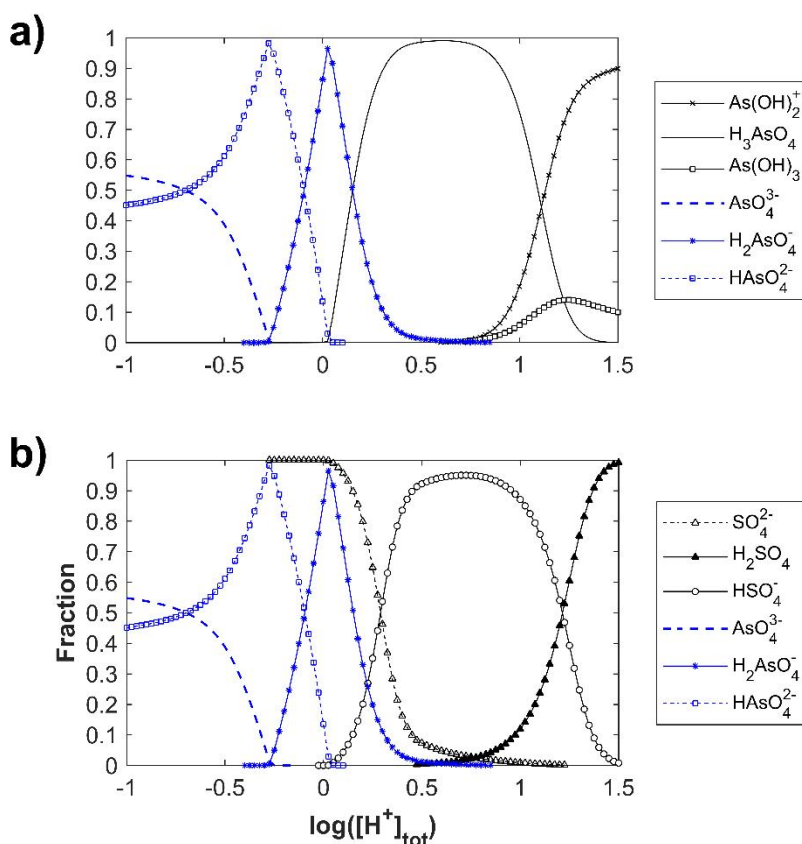


Figure 10 Effect of proton concentration on speciation of H_3AsO_4 and H_2SO_4 . Calculated by MEDUSA [31]. Input parameters for MEDUSA are the same as were measured for stripping raffinate in the pseudo-cc experiments (section 3.2.2): $E_h = +649$ mV; $c(\text{AsO}_4^{3-})_{\text{tot}} = 0.536$ M; $c(\text{SO}_4^{2-})_{\text{tot}} = 0.653$ M; $T = 25$ °C; iterated ionic strength.

3.2.1 Scrubbing

Organic phases were prepared for the batch scrubbing experiments by loading both extractants with the feed solution from Shipment #1 at O/A = 0.1. Water scrubbing of loaded TBP exhibited

very similar behavior to that reported by Navarro & Alguacil [14]. 17.2 % of arsenic and 59.3 % of H_2SO_4 were back-extracted at $\text{O/A} = 3.77$ (Fig. 11). Selectivity towards H_2SO_4 with $\text{O/A} \approx 4$ and above was maintained in consecutive scrubbing treatment. Back-extraction with water is more selective to H_2SO_4 until the acidity of the system gets sufficiently low (Fig. 10). Separation of arsenic and H_2SO_4 by TBP is clearly better than by the mixture of 1,2-octanediol and 2-ethylhexanol. Moreover, phase separation times were longer for the alcohol mixture.

Another issue with using the mixture of 1,2-octanediol in 2-ethylhexanol is the reactivity of the alcohols. Etherification of 2-ethylhexanol is likely to occur, especially at slightly elevated temperatures [37]. The redox potential of the feed solution was approximately +710 mV vs. SHE at +21 °C and it is questionable whether the oxidation reactions of alcohols are negligible under such conditions. Coupled with possible reactions of the diol, the resulting mixture has practically an unknown composition. The reaction products themselves probably have extractive properties but their mutual solubilities with water are likely different compared with the original alcohol constituents [38]. Water-miscible reaction products would explain the observed difficulties in back-extraction of the organic samples (section 3.1.1).

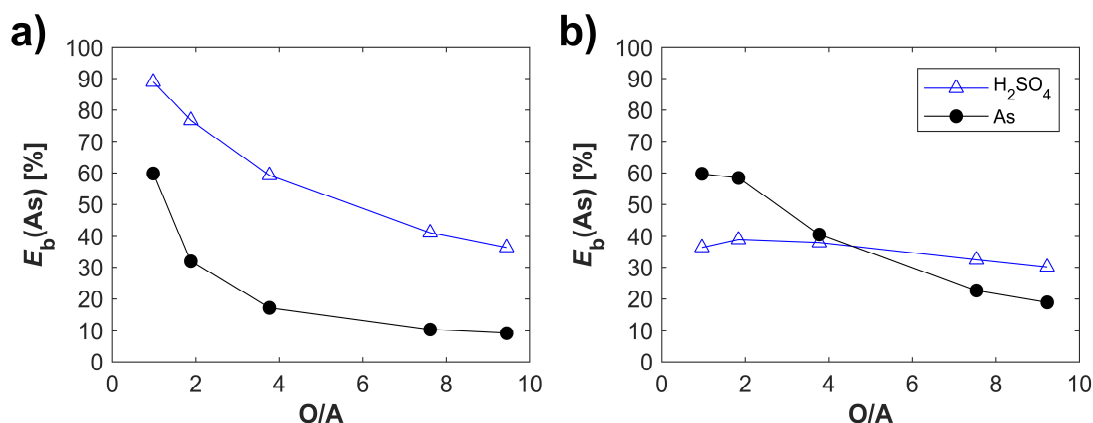


Figure 11 Back-extraction percentages in scrubbing of the loaded extractants. a) 97 vol-% TBP with 25.3 g dm⁻³ arsenic and 330 g dm⁻³ H_2SO_4 . b) 6 wt-% 1,2-octanediol in 2-ethylhexanol with 21.9 g dm⁻³ arsenic and 390 g dm⁻³ H_2SO_4 .

In scrubbing of the loaded TBP, O/A ratios decreased as expected, due to back-extraction of H_2SO_4 (Fig. 8b). However, in scrubbing of the loaded alcohol mixture with initial O/A ratios of 1

and 2, the O/A ratios increased, suggesting that some H₂O was still extracted to the organic phase. The scrubbing raffinates were quite concentrated H₂SO₄ solutions up to 750 g dm⁻³ but they also contained significant amounts of arsenic, especially the raffinates from scrubbing of the alcohol mixture (Table VI). Scrubbing raffinates can be recycled back to extraction stages.

As the literature [1,8,15,16] suggests, if the As(V) species are predominant and in an extractable form of H₃AsO₄ in the solution, arsenic can be extracted to the organic phase with co-extraction of H₂SO₄. More complete separation can be achieved in subsequent scrubbing and stripping stages (Fig. 10). However, if extraction is performed from H₂SO₄ solutions in which As(III) species are dominant, in principle H₂SO₄ should be more selectively extracted by TBP. SO₂ absorption can be used to reduce As(V) species to As(III) [1,15,27], which is what happens in certain types of gas scrubbing.

Table VI Distribution of arsenic and H₂SO₄ in water scrubbing of loaded TBP (25.3 g dm⁻³ arsenic and 330 g dm⁻³ H₂SO₄) and a mixture of 1,2-octanediol and 2-ethylhexanol (21.9 g dm⁻³ arsenic and 390 g dm⁻³ H₂SO₄).

O/A	TBP				6 wt-% 1,2-octanediol in 2-ethylhexanol			
	[As] _{aq} [g dm ⁻³]	[As] _{org} [g dm ⁻³]	[H ₂ SO ₄] _{aq} [g dm ⁻³]	[H ₂ SO ₄] _{org} [g dm ⁻³]	[As] _{aq} [g dm ⁻³]	[As] _{org} [g dm ⁻³]	[H ₂ SO ₄] _{aq} [g dm ⁻³]	[H ₂ SO ₄] _{org} [g dm ⁻³]
1	13.08	12.2	253.7	43.8	19.3	6.6	196.8	174.9
2	12.58	20.0	393.5	88.8	29.8	8.3	331.8	204.7
4	12.38	23.4	555.3	150.3	33.3	13.2	521.0	231.4
8	13.81	24.4	710.3	209.4	28.5	17.9	688.0	260.8
10	14.71	24.5	752.4	224.4	27.3	18.8	730.8	270.7

TBP was loaded for the pseudo-cc scrubbing and stripping experiments by contacting it with the feed acid from Shipment #2 at O/A = 0.1. TBP prepared in this way contained initially 35.3 g dm⁻³ of arsenic and 284.2 g dm⁻³ of H₂SO₄ (Table VII). Two-stage scrubbing with an O/A ratio of 4.03 back-extracted 24.9 % of arsenic and 83.6 % of H₂SO₄. Concentrations in the scrubbed TBP were 30.5 g dm⁻³ and 53.5 g dm⁻³ for arsenic and H₂SO₄, respectively. The composition of the scrubbed TBP is promising for producing an arsenic-rich stripping raffinate, although the scrubbing could be optimized further. The addition of a third scrubbing stage would enhance the separation. With three scrubbing stages, there could also be room for increasing the O/A while maintaining near-complete scrubbing of H₂SO₄. In the two-stage scrubbing, the volume of the aqueous phase

expanded from 19.6 cm³ to 29.2 cm³, and it contained 21.6 g dm⁻³ of arsenic and 670.4 g dm⁻³ of H₂SO₄. Increase in O/A would result in a smaller volume of more concentrated scrubbing raffinate, which would make smaller change to the extraction stage feed when recycled.

3.2.2 Pseudo-countercurrent stripping of loaded and scrubbed TBP

The organic phase for the stripping experiments was prepared by scrubbing loaded TBP twice with an aliquot of pure water equivalent to O/A = 4 in single contact. TBP produced by this method contained 25 g dm⁻³ and 35 g dm⁻³ of arsenic and H₂SO₄, respectively.

Results from pseudo-cc back-extraction experiments are summarized in Table VII. 89.7 % of arsenic was stripped in four countercurrent stages at O/A = 2, yielding a raffinate with 40 g dm⁻³ arsenic and 64 g dm⁻³ H₂SO₄. Total sulfur in stripped TBP was below the detection limit of the back-extraction-ICP-MS determination (Table VII), and hence it was assumed that all H₂SO₄ was stripped. Arsenic concentration in stripped TBP was 2.7 g dm⁻³.

Two-stage stripping with pure water is enough to back-extract arsenic almost completely (98.6 %) at O/A = 0.5. The resulting stripping raffinate at O/A = 0.5 contained 11.7 g dm⁻³ of arsenic and 14.1 g dm⁻³ of H₂SO₄, whereas with O/A = 2 the concentrations in stripping raffinate were 32.3 g dm⁻³ and 66 g dm⁻³ for arsenic and H₂SO₄, respectively. However, with O/A = 2, back-extraction of arsenic was lowered to 75 %. Complete stripping of arsenic requires either the deployment of a sufficient number of stages or decreasing O/A, but a decrease in O/A dilutes the raffinate.

Stripping efficiency and phase separation could be further improved by increasing temperature. Travkin *et al.* [16] reported a significant decrease in $D(\text{As(V)})$ from over 0.9 at 20 °C to approximately 0.4 at 65 °C. In this work, phase separation by gravity was successful in the experiments at room temperature but overnight settling was required to get rid of haziness in the aqueous phase. Instead of using pure water, dilute saline solution containing *e.g.* Na₂SO₄, Na₂CO₃ or dilute H₂SO₄ can be used for stripping to facilitate phase separation [1,15].

Table VII Results from pseudo-countercurrent back-extraction experiments.

Target	Scrubbing		Stripping		Stripping		Stripping			
$c_0(\text{H}_2\text{SO}_4)_{\text{org}}$ [g dm ⁻³]	284.2		35.0		35.0		35.0			
$c_0(\text{As})_{\text{org}}$ [g dm ⁻³]	35.3		25.0		25.0		25.0			
O/A (in)	4.03		0.5		2.01		2.01			
E/R	2.33		0.45		1.87		1.83			
$E(\text{As})$ [%]	24.9		98.6		75.0		89.7			
$E(\text{H}_2\text{SO}_4)$ [%]	83.6		100		99.6		100			
Stage	1	2	1	2	1	2	1	2	3	4
$V_{0,\text{aq}}$ [cm ³]	19.6	24.4	99.7	97.5	29.6	30.6	29.8	30.0	29.9	30.3
$V_{0,\text{org}}$ [cm ³]	72.8	79.2	47.4	49.4	58.1	59.7	57.4	58.2	58.2	59.8
$V_{0,\text{tot}}$ [cm ³]	92.4	103.6	147.0	146.9	87.7	90.3	87.1	88.1	88.1	90.1
O/A (stagewise)	3.71	3.24	0.48	0.51	1.96	1.95	1.93	1.94	1.95	1.98
$V_{\text{eq},\text{aq}}$ [cm ³]	24.1	29.2	97.5	103.9	30.1	31.6	30.2	30.4	30.2	31.2
$V_{\text{eq},\text{org}}$ [cm ³]	68.1	73.5	46.9	47.5	59.1	56.3	57.0	57.7	57.9	58.8
$V_{\text{eq},\text{tot}}$ [cm ³]	92.2	102.8	144.3	151.4	89.2	87.9	87.1	88.1	88.1	90.0
E/R (stagewise)	2.83	2.52	0.48	0.46	1.96	1.78	1.89	1.89	1.91	1.88
$D(\text{As})$	1.31	1.64	0.21	0.34	0.37	0.57	0.27	0.35	0.43	0.58
$D(\text{H}_2\text{SO}_4)$	0.16	0.25	–	–	–	–	–	–	–	0.03
$\beta(\text{As}/\text{H}_2\text{SO}_4)$	8.23	6.68	–	–	–	–	–	–	–	17.35
$c(\text{As})_{\text{aq}}$ [g dm ⁻³]	23.33	21.59	1.79	11.72	17.74	32.28	9.84	23.22	35.67	40.13
$c(\text{As})_{\text{org}}$ [g dm ⁻³]	30.47	35.43	0.37	4.03	6.51	18.42	2.68	8.20	15.18	23.19
$c(\text{H}_2\text{SO}_4)_{\text{aq}}$ [g dm ⁻³]	337.2	670.4	< 1.7*	14.1	3.2	66.0	< 1.3*	< 1.3*	3.1	64.0
$c(\text{H}_2\text{SO}_4)_{\text{org}}$ [g dm ⁻³]	53.5	164.8	< 5*	< 5*	< 5*	< 5*	< 2*	< 2*	< 2*	2.1
*Limit of detection										

3.2.3 Comparison of batch equilibrium data with pseudo-countercurrent data

Concentration of arsenic peaked 29 g dm^{-3} in the conventional stripping isotherm, which was determined by batch stripping by pure water and varying the O/A ratio (Fig. 12a). This stripping isotherm did not reveal the possibility of producing an aqueous stripping raffinate with over 30 g dm^{-3} of arsenic. A linear operating line drawn on the basis of 89 % back-extraction for arsenic and $O/A = 2$ intersects with both equilibrium lines. However, over-the-isotherm performance was observed in four-stage stripping at $O/A = 2$ as both the isotherm and operating line relocated in the $c(\text{As})_{\text{aq}}$ vs. $c(\text{As})_{\text{org}}$ plot. (Fig. 12c & Fig. 12d).

Two-dimensional graphical constructions (*e.g.* McCabe–Thiele and Hunter–Nash) based on the measured $c(\text{As})$ values fail to describe the separation cascades accurately. The deviations are highlighted especially at back-extraction stages, which can be explained by dissociation of H_3AsO_4 at low acidity (Fig. 10). Sharply decreasing $D(\text{As})$ in the back-extraction stages (Table VI) is in agreement with this explanation.

No established model describes the chemical equilibria of the system, and thus rigorous mass balance iterations are currently impossible. Furthermore, McCabe–Thiele and Hunter–Nash diagrams or mass balance iterations as such provide only theoretical prediction and can only serve as tools to give initial estimates for piloting studies. Pseudo-cc extraction provides information also about the practical feasibility of a process, and the equilibrium compositions of the streams can be experimentally verified. Drawbacks of the pseudo-cc method are that completing the schemes requires a lot of manual labor and recycle streams are hard to embed in the design by pseudo-cc method. The number of extractions increases rapidly when the number of countercurrent stages increases and the schemes must be replicated in order to carry out sensitivity analyses for process parameters. Despite these weaknesses it is a cost-effective intermediate design method for continuous processes involving hazardous materials or processes that require instrumentation with expensive materials.

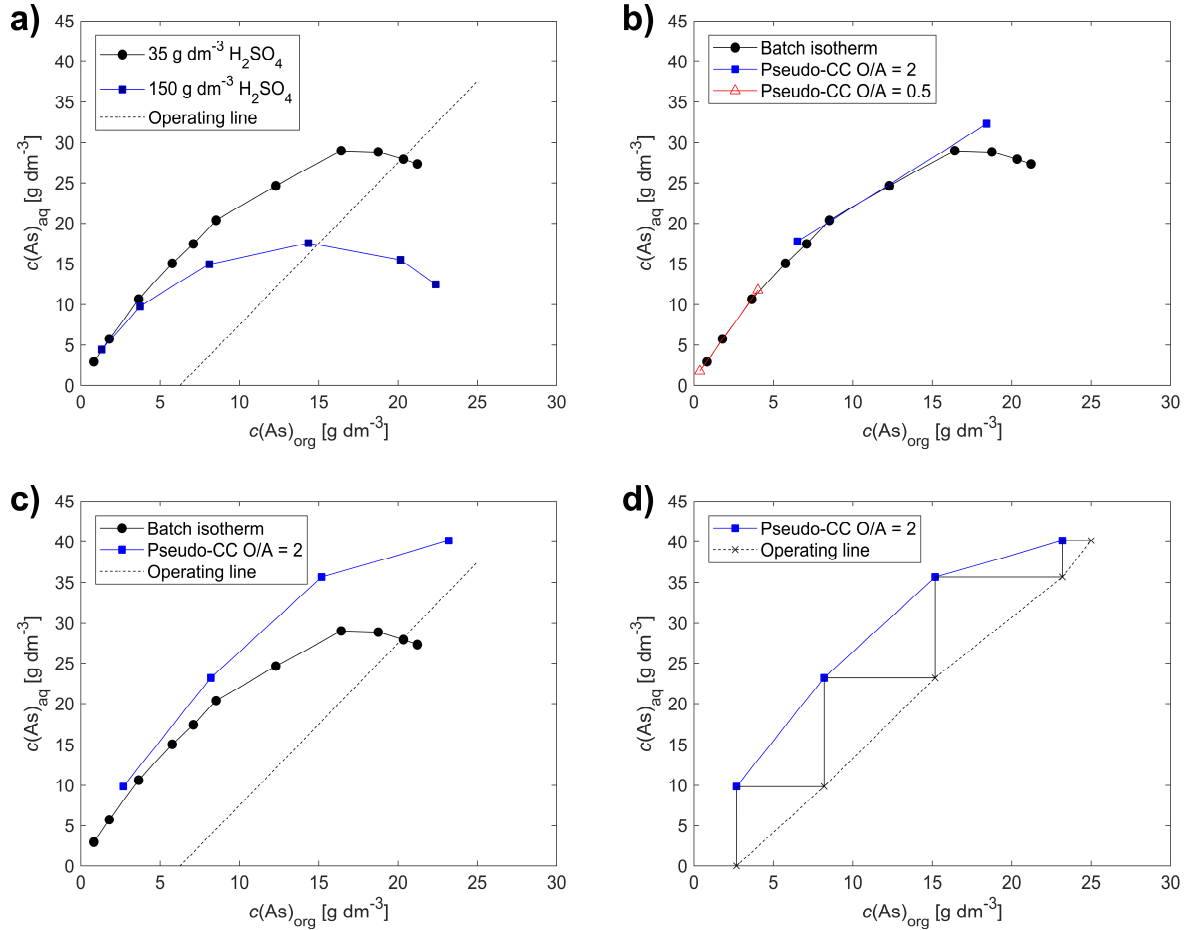


Figure 12 Arsenic distributions in batch and pseudo-cc experiments: a) influence of H_2SO_4 concentration on batch stripping isotherms; b) comparison of two-stage pseudo-cc equilibrium lines with batch isotherm; c) comparison of four-stage pseudo-cc equilibrium line with batch isotherm; d) McCabe–Thiele plot based on data from four-stage pseudo-cc stripping.

3.3 Process scheme

Pseudo-cc experiments showed that with certain adjustments and considerations, a similar flowsheet to the one patented by De Schepper & Van Peteghem [13] is suitable also for treating 10 M H_2SO_4 solutions. Calculation of the flowsheet in Fig. 13 was based on percentages of extraction and phase volume changes that were determined by pseudo-cc experiments. Recycling of expanded TBP, scrubbing raffinate and stripping raffinate bleed was not taken into account. Recycling water-containing stripped TBP and scrubbing raffinate back to extraction might lower $E(\text{As})$ slightly. 261.4 liters per time unit less water would be required if scrubbing was carried out by stripping raffinate. Use of stripping raffinate in scrubbing would also help with back-extraction

loss of arsenic during scrubbing. If only 5 % loss of arsenic is assumed in scrubbing, stripping raffinate would contain 47.6 g dm^{-3} of arsenic, which is close to the 50 g dm^{-3} presented by De Schepper & Van Peteghem [13]. However, the back-extraction percentage of H_2SO_4 would then be lower in scrubbing and it would end in the stripping raffinate without a third scrubbing stage. Treating 1000 l/t of feed acid with 790 l/t of undiluted TBP and 720 l/t of water yielded 737 l/t of raffinate with significantly lowered arsenic concentration, and 487 l/t of arsenic-rich stripping raffinate. Flow rates of stripping raffinate, inlet water and feed acid will be reduced once the recycle streams are connected.

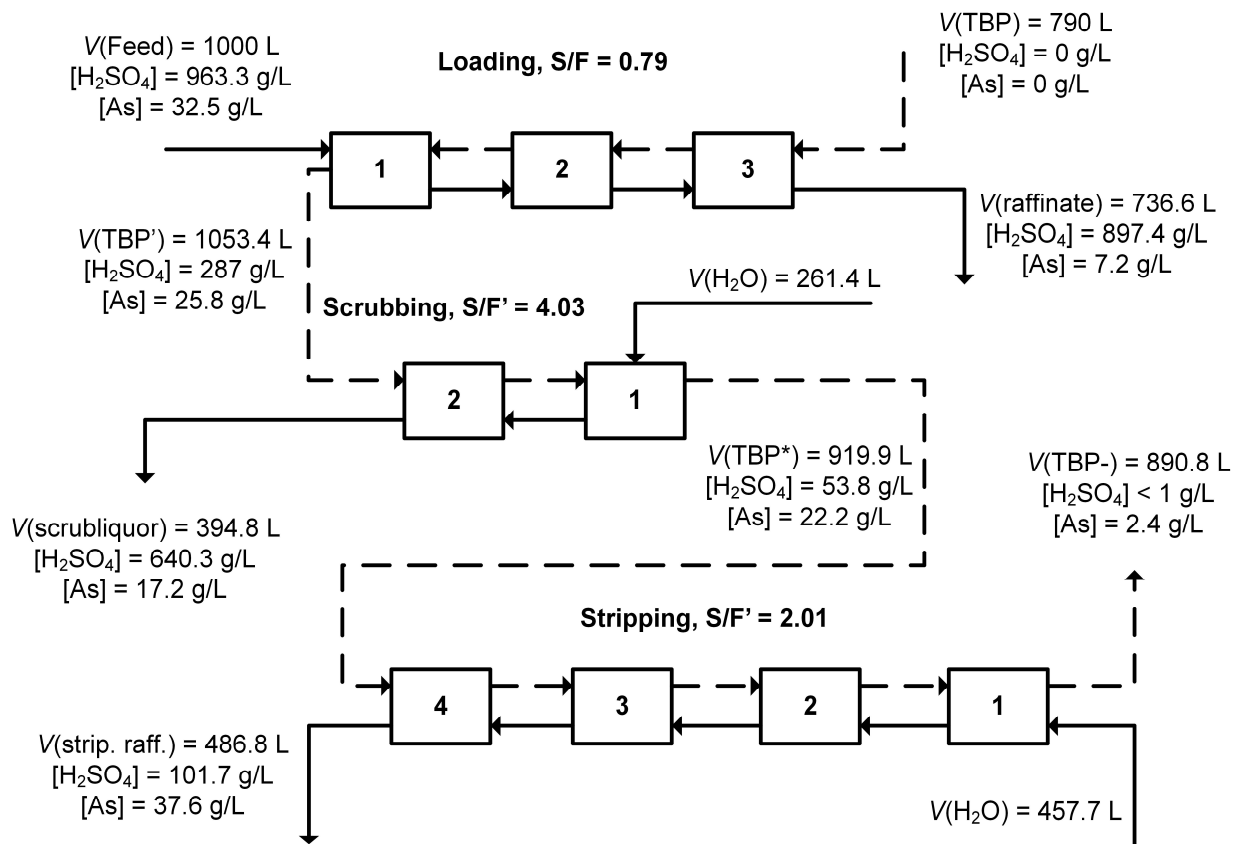


Figure 13 Flowsheet for separating arsenic and H_2SO_4 as investigated by pseudo-countercurrent experiments.

Increasing O/A in extraction would provide higher $E(\text{As})$ assuming the same number of stages but it would also decrease the throughput of the process and the $c(\text{H}_2\text{SO}_4)$ in the raffinate, as the larger amount of fed TBP would extract more H_2SO_4 and H_2O . The throughput would be lower also because higher volume of scrubbing liquor should be recycled to the extraction stages. If higher

loading of H_2SO_4 was compensated by decreasing O/A in scrubbing, the throughput of the process would again be decreased due to increased circulation to the feed.

The solvent extraction circuit discussed here aims at bulk recovery of arsenic. Raffinates of the process are classified as hazardous waste not only because of the arsenic but also because of other heavy metals [39]. The environmental limits for heavy metals in aqueous waste in the European Union are 0.15 ppm, 0.03 ppm and 0.2 ppm for arsenic, mercury and lead, respectively. For copper and nickel the limit is 0.5 ppm [39].

TBP extracts arsenic and H_2SO_4 in significant amounts but partial extraction of mercury was also noticeable in the ICP-MS results. The concentration of mercury was 4.5–8 ppm in the extracts, and it was partially back-extracted in stripping, resulting in 2–3 ppm of mercury in the stripping raffinate. Stripping raffinate requires further SO_4^{2-} removal if As_2O_3 crystallization at high purity is intended, and the mercury must be removed in possible plant operation. Raffinate from the extraction stages could be re-used in applications where the impurities can be tolerated at the levels found, *e.g.* in leaching.

4 Conclusions

Liquid-liquid extraction of arsenic and H_2SO_4 by undiluted TBP (97 vol-%) and mixture of 1,2-octanediol and 2-ethylhexanol was investigated experimentally for treating a 10.4 M industrial H_2SO_4 solution containing 32.5 g dm^{-3} arsenic. If neutral organophosphorus extractants are used, they must be used in undiluted form for such concentrated H_2SO_4 to maintain the system in two phases. Phase behavior of TBP was superior to the mixture of 1,2-octanediol and 2-ethylhexanol in back-extraction of the loaded extractants at room temperature. Moreover, TBP offered better separation of arsenic and H_2SO_4 , and the difference in separation efficiency was highlighted in scrubbing.

McCabe–Thiele analyses were shown to be inaccurate in design of liquid-liquid extraction cascades for the system at hand. The Hunter–Nash method could predict H_2SO_4 transfer with reasonable accuracy but the distribution of arsenic is more complicated to describe. Performances

of the countercurrent cascades were experimentally determined by a pseudo-countercurrent batch extraction scheme. It was shown that significantly better performance can be achieved in the stripping cascade than could be predicted from a stripping isotherm determined by conventional methods, most probably due to significant changes in aqueous speciation.

A conventional solvent extraction flowsheet utilizing TBP can also be used for very concentrated H₂SO₄ solutions. 83.7 % of arsenic was removed by undiluted TBP in three countercurrent stages with a solvent-to-feed ratio of 0.79 from a 10.4 M (1022.2 g dm⁻³) H₂SO₄ solution containing initially 23.9 g dm⁻³ arsenic. The results show that arsenic concentrations of 40–50 g dm⁻³ in the stripping raffinate can be obtained with the proposed non-optimized flowsheet.

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REFERENCES

- [1] Szymanowski, J., Removal of toxic elements from copper electrolyte by solvent extraction. *Min. Proc. Ext. Met. Rev.* 18 (1998), 389–418.
<https://doi.org/10.1080/08827509808914162>.
- [2] Dalewski, F., Removing arsenic from copper smelter gases. *JOM.* 51:9 (1999), 24–26.
<https://doi.org/10.1007/s11837-999-0153-0>.
- [3] Piret, N.L., Removal and safe disposal of arsenic in copper processing. *JOM.* 51:9 (1999), 16–17. <https://doi.org/10.1007/s11837-999-0150-3>.
- [4] Riveros, P.A., Dutrizac, J.E., Spencer, P, Arsenic disposal practices in the metallurgical industry. *Can. Metall. Quart.* 40 (2001), 395–420.
<https://doi.org/10.1179/cmqa.2001.40.4.395>.
- [5] Opio, F.K., 2013. Investigation of Fe(III)–As(III) phases and their potential for arsenic

- disposal. Queen's University, Kingston, Canada.
- [6] Nazari, A.M., Radzinski, R., Ghahreman, A., Review of arsenic metallurgy: Treatment of arsenical minerals and immobilization of arsenic. *Hydrometallurgy* 174 (2017), 258–281. <https://doi.org/10.1016/j.hydromet.2016.10.011>.
- [7] US. Department of the Interior, Final List of Critical Minerals 2018. <https://www.federalregister.gov/documents/2018/05/18/2018-10667/final-list-of-critical-minerals-2018>, Accessed: 5 October 2018.
- [8] Iberhan, L., Wiśniewski, M., Removal of arsenic(III) and arsenic(V) from sulfuric acid solution by liquid–liquid extraction, *J. Chem. Technol. Biotechnol.*, 78 (2003) 659–665. <https://doi.org/10.1002/jctb.843>.
- [9] Iberhan, L., Wiśniewski, M., Removal of arsenic(III) and arsenic(V) with Cyanex 925, Cyanex 301 and their mixtures. *Hydrometallurgy* 63 (2002) 23–30. [https://doi.org/10.1016/S0304-386X\(01\)00198-0](https://doi.org/10.1016/S0304-386X(01)00198-0).
- [10] Wiśniewski, M., Extraction of arsenic from sulphuric acid solutions by Cyanex 923, *Hydrometallurgy* 46 (1997) 235–241. [https://doi.org/10.1016/S0304-386X\(97\)90003-7](https://doi.org/10.1016/S0304-386X(97)90003-7).
- [11] Wiśniewski, M., Removal of arsenic from sulphuric acid solutions. *J. Radioanal. Nucl. Chem.* 228 (1998) 105–108. <https://doi.org/10.1007/BF02387308>.
- [12] Ballinas, M. L., San Miguel, E. R., Muños, M., Gyves, J., Arsenic(V) extraction from sulfuric acid media using DBBP-D2EHPA organic mixtures. *Ind. Eng. Chem. Res.* 42 (2003) 574–581. <https://doi.org/10.1021/ie020402a>.
- [13] De Schepper, A., Van Peteghem, A., Treatment of solutions containing impure metals, US Patent No. 4061564, December 6, 1977.
- [14] Navarro, P., Alguacil, F. J., Removal of arsenic from copper electrolytes by solvent extraction with tributylphosphate. *Can. Metall. Quart.* 35 (1996) 133–141. [https://doi.org/10.1016/0008-4433\(95\)00044-5](https://doi.org/10.1016/0008-4433(95)00044-5).
- [15] Dermirkiran, A., Rice, N.M., The extraction of arsenic (V) from copper refinery electrolytes with tri-n-butyl phosphate: II – Flowsheet development, in: K. C. Sole, P. M. Cole, J. S. Preston, D. J. Robinson (Eds.), *Proceedings of the International Solvent Extraction Conference, ISEC 2002, SAIMM, Johannesburg, 2002*, 890–895.
- [16] Travkin, V. F., Kravchenko, A. N., Miroevsky, G. P., Extraction of arsenic and antimony from sulfate solutions with organophosphorus reagents, *Tsvet. Met.* 4 (1993) 14–18.

- [17] Travkin, V.F., Glubokov, Y.M., Mironova, E.V., Yakshin, V.V., Extraction of arsenic(V) with hexabutylphosphoric triamide, *Russ. J. Appl. Chem.* 74 (2001) 1664–1667. <https://doi.org/10.1023/A:1014801117889>.
- [18] Baradel, A., Guerriero, R., Meregalli, L., Vittadini, I., Extraction of As from copper refining electrolyte, *JOM* 38:32 (1986) 32–37. <https://doi.org/10.1007/BF03257918>.
- [19] Baradel, A., Guerriero, R., Process for separating arsenic from acid solutions which contain it, US Patent No. 4737350, April 12, 1988.
- [20] Baradel, A., Guerriero, R., Meregalli, L., Vittadini, I., New extractant for arsenic separation from industrial solutions, in *ISEC '86 International Solvent Extraction Conference: Preprints, Volume II*, Dechema, Frankfurt, 1986, 401–407.
- [21] Baradel, A., Guerriero, R., Veronese, G., Process for separating arsenic from acid solutions containing it, US Patent No. 4701311, October 20, 1987.
- [22] Avila-Rodriguez, M., Barron-Zambrano, J.A., Navarro-Mendoza, R., Saucedo-Medina, T.I., Thermodynamic study of liquid-liquid extraction of arsenic(V) by NMPL from H₂SO₄ medium, *Solvent Extr. Ion Exc.* 19:3 (2001) 457–472. <https://doi.org/10.1081/SEI-100103280>.
- [23] Marr, R., Bart, H-J., Wachter, R., Method of removing arsenic from copper electrolyte, US Patent No. 4503015, March 5, 1985.
- [24] Schwab, W., Kehl, R., Common separation of contaminating elements from electrolyte solutions of valuable metals, US Patent No. 4834951, May 30, 1989.
- [25] Kehl, R., Schwab, W., Sudderth, R.B., Korkosky, G.A., Process for selective extraction of contaminant elements from mixtures of electrolytes in solution, US Patent No. 5039496, August 13, 1991.
- [26] Hiemeleers, J., De Schepper, A., Van Peteghem, A., Treatment of ores and metallic by-products containing arsenic and antimony, US Patent No. 4102976, July 25, 1978.
- [27] Totsuka, T., Sasaki, K., Nagai, K., Fundamental studies on purification of copper electrolyte, *Metallurgical Review MMIJ* 3:2 (1986) 146–154.
- [28] Dreisinger, D. B., Leong, B. J. Y., Balint, B. J., Beyad, M. H., The solvent extraction of As, Sb and Bi from copper refining electrolytes using organophosphorus reagents, in D. H. Logsdail, M. J. Slater (Eds.), *Solvent Extraction in the Process Industries Volume 3*

- Proceedings of ISEC '93, Elsevier Science Publishers Ltd., Barking, 1993, pp. 1271–1278.
- [29] Dreisinger, D. B., Leong, B. J. Y., Saito, B. R., West-Sells, P. G., The solvent extraction and ion-exchange removal of As, Sb and Bi from copper sulphate-sulphuric acid solutions, in J. B. Hiskey, G. Warren (Eds.), *Hydrometallurgy: Fundamentals, Technology and Innovations*, Society for Mining, Metallurgy and Exploration, 1993, 801–815.
- [30] Giganov, G.P., Travkin, V.F., Ankina, N.P., Extraction of arsenic from acidic solutions with tributylphosphate. *Tsvet. Met.* 8 (1978) 27–29.
- [31] KTH, Kungliga Tekniska Högskolan, School of Chemical Science and Engineering, MEDUSA, Chemical Equilibrium Diagrams, <https://www.kth.se/che/medusa/>, Updated: 26.04.2013, Accessed: 1 February 2019.
- [32] Haghghi, H.K., Moradkhani, D., Salarirad, M.M., Separation of zinc from manganese, magnesium, calcium and cadmium using batch countercurrent extraction simulation followed by scrubbing and stripping, *Hydrometallurgy* 154 (2015) 9–16.
<http://dx.doi.org/10.1016/j.hydromet.2015.03.007>.
- [33] Thornton, J.D. *Science and practice of liquid-liquid extraction Vol. 1.*, Oxford University Press, New York, 1992.
- [34] Matveev, P.I., Petrov, V.G., Egorova, B.V., Senik, N.N., Semenкова, A.S., Dubovava, O.V., Valkov, A.V., Kalmkov, S.N., Solvent extraction of rare earth elements by tri-*n*-butyl phosphate and tri-iso-amyl phosphate in the presence of Ca(NO₃)₂, *Hydrometallurgy* 175 (2018) 218–223. <https://doi.org/10.1016/j.hydromet.2017.12.007>.
- [35] Gromov, P.B., Kasikov, A.G., Shchelokova, E.A., Petrova, A.M., Regeneration of sulfuric acid from electrolyte waste of the copper - smelting plant using solvent extraction, *Hydrometallurgy* 175 (2018) 187–192.
<https://doi.org/10.1016/j.hydromet.2017.11.008>.
- [36] Wankat, P.C., *Separation Process Engineering*, second ed., Prentice Hall, Westford, 2009.
- [37] Hendrickson, J.B., Cram, D.J., Hammond, G.S., *Organic Chemistry*, third ed., McGraw-Hill, New York, 1970.
- [38] Kislik, V.S., *Solvent Extraction – Classical and Novel Approaches*, first ed., Elsevier, Oxford, 2012.

- [39] EUR-Lex, Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control), <https://eur-lex.europa.eu/eli/dir/2010/75/oj>, Accessed: 1 February 2019.