

Article

Characterisation of Parameters Influencing the Phase Separation in Copper Solvent Extraction Systems Using Oxime-Type Extractants for the Field Operation

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Abstract: Solvent extraction (SX) is one of the most widely applied hydrometallurgical processes in copper production from oxide ore. As the high-grade ore deposits have been developed and depleted, now only low-grade ore deposits are being developed and are therefore facing obstacles of extreme processing conditions. This results in leaching gangue minerals and requires a more complicated solvent extraction system. Recently, synergistic solvent extraction has been introduced to separate copper from the leached solution with high impurities. However, operational obstacles arise due to the complicated solvent extraction process, including multi-stages of extraction, and using more than one extractant in a single solvent extraction system. The phase separation in solvent extraction is one of the major issues in field operation. A poor phase separation could affect the entire process and eventually cause production loss. Therefore, in this study, the phase separation behaviours were studied in consideration of the field operation. Major parameters considered in the study were the type of diluent, temperature, mixing speed, solution pH and Oxidation Reduction Potential (ORP), and addition of impurities (flocculant and colloidal silica). The phase separation behaviours in the continuous counter-current SX system using a pilot-scale mixer-settler in the above conditions was investigated.

Keywords: copper solvent extraction; phase separation behaviour; flocculant; colloidal silica; 2-hydroxy-5-nonyl acetophenone oxime (ketoxime); 5-nonylsalicylaldoxime (aldoxime)



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1. Introduction

A solvent extraction (SX) is one of the most widely applied hydrometallurgical processes in copper production from oxide ores. Many applications have been commercialised in various conditions of the copper recovery process, typically using leaching, solvent extraction, and electrowinning (EW) [1,2]. A heap leaching (HL) to SX\EW is one of the most well-known processes for low-grade copper oxide ore processing and production [3–5]. In recent times, as high-grade copper deposits have already been developed and depleted [6,7], a newly-opened mining project has obstacles, such as a low-grade ore, a high stripping ratio, and physio-chemical impurities in the ore [8–10]. As a result, ore processing requires more extreme conditions, such as high temperatures, pressurised solvent extractions, and additives for leaching, and this leads to leaching unnecessary minerals together. Consequently, the following process is more complicated; for example, multi-stages of extractions, scrubblings, and conditionings in the SXs using more than one extractant and additive is necessary. This SX technique is known as synergistic solvent extraction (SSX) [11,12].

The SSX has advantages over the conventional SX, such as a more efficient extraction rate and better selectivity of the target metals [13]. However, using multiple extractants in a single SX system is not an easy task in the prospect of the field operation considering many factors [14], such as that it has not been commercialised for base metal production. One of the major issues is the poor phase separation, which could affect the entire SX process, eventually reducing extraction efficiency and production rate. The phase separation behaviour in common SX is affected by various factors, such as the operating conditions, the physio-chemical properties of chemicals and interfacial phenomena, and the design of the mixer-settler [15].

The phase separation behaviour in the SX system has not been widely studied. Luo, Hu [15] reported the phase separation behaviour in the copper and nickel solvent extraction process using a sulfonic acid and carboxylate ester as the extractant. The authors focused on the specific settling rate (SSR) on the loaded organic solution by considering the physicochemical parameters between the phase separation. Liu, Qiu [16] studied the phase separation dynamics in copper SX and focused on LIX984N contents in the organic phase. Due to the LIX984N's physical property, higher volume in the organic phase caused slower phase separation. A third phase formation between the organic and the aqueous phases is affected by the phase separation behaviours. Often the third phase is formed due to the precipitation of the metal sulphates or carbonates and breaking the organic structure of the extractant [17–20]. Several practitioners have studied the phase separation behaviours in the microfluidic SX system. Priest, Hashmi [21] determined the phase separation on the Y-junction in the microchannel in terms of the micro-level of the droplet contact for both organic and aqueous phases. Kriel, Holzner [22] also developed the quantitative phase separation efficiency in the Y-junction extraction chip for various inlet pressures at the micro-level of SX. Many others studied the phase disengagement characteristics on the microlevels [23–25]. However, those are fundamental studies and are not considered real-world plant operations.

Oxime-type extractants are well known as copper-specific extractants from an acidic sulphate solution due to their selectivity of copper from other base metals, especially iron contents in the solution [26]. Most widely commercialised oxime extractants are based on aldoxime and ketoxime to consider the condition of feed solution in the SX system, such as pH, ORP and temperature [27,28]. According to Kordosky [28], the selectivity of iron content in the feed solution changes depending on the reaction pH. However, physical characteristics are also different as aldoxime has a higher viscosity than ketoxime. Thus, a mixture of both oximes could also be used in the commercial SX system [2].

Therefore, in this study, the phase separation behaviour has been studied in the copper SX system using oxime-type extractants for the acidic sulphate feed solution from the oxide copper ore processing plant. Two different oxime type extractants were characterised in consideration of the field operation. Major parameters considered in this study were the type of diluent, temperature, mixing speed, solution pH and ORP, and addition of impurities (flocculant and colloidal silica). The phase separation behaviours in the continuous counter-current SX system using a pilot-scale mixer-settler at the above conditions was investigated.

2. Materials and Methods

2.1. Materials

Two different types of oxime extractants, including 2-hydroxy-5-nonylacetophenone oxime (LIX84I) and 5-nonylsalicylaldoxime (LIX860N), supplied by BASF, Inc. (Florham Park, NJ, USA), were used for the experiments. Orfom SX-12 CT (Distillates Hydrotreated Light, 100% wt) and ISD-159 (Hydrosulfurized kerosene, 100% wt) as diluents were correspondingly supplied by Chevron Phillips Chemical (The Woodlands, TX, USA) and IS Chemical Ltd. (Seoul, South Korea). A lean organic phase was prepared by dissolving 10% of the extractant into the diluent. A pregnant leach solution (PLS) containing approximately 2.1 g/L Cu and other metal values was used for an aqueous phase. The PLS was obtained

from the Boleo plant site. The chemical composition of the PLS and the organics prepared were tabulated in Table 1. All other chemicals used were of analytical grade, supplied by Sigma-Aldrich, Inc. (St. Louis, MO, USA), except Hyperfloc AF302 as flocculants, supplied by Hychem, Inc. (Tampa, FL, USA).

Table 1. The chemical composition of pregnant leach solution (PLS) and the prepared organics.

Element	Unit	Cu	Co	Zn	Mn	Fe	Si
PLS	mg/L	4150	81	429	2940	2425	122
Organic phase		Org. 1: LIX84I (10%) in ISD-159 (90%)					
		Org. 2: LIX84I (5.6%) and LIX860N (4.4%) in ISD-159 (90%)					
		Org. 3: LIX84I (5.6%) and LIX860N (4.4%) in Orfom SX-12 CT (90%)					

2.2. Experimental Procedures

A stainless-steel baffle and Teflon agitator fitted in a typical 1-litre beaker were prepared for the phase separation test to eliminate vortexing and to maximise the mixing rate of two phases during the reaction. A specific design and experimental apparatus are shown in Figure 1. For the test, the baffle was placed in the 1-litre beaker as the reactor. The agitator was fitted on an overhead stirrer (HS-30T, Daihan Scientific Co., Ltd., Wonju, South Korea) and positioned at 0.5 cm from the bottom of the reactor. Typical parameters of the test work were a 5 min reaction, temperature of 25 °C, a mixing speed of 1750 (±25) rpm, a pH 2.0, and 480 mL of an organic solution (O) and 400 mL of an aqueous solution (A) as O/A mixing ratio 1.2:1. The prepared apparatus was placed on the benchtop and 300 mL of the lean organic and the aqueous solutions were filled in the reactor, respectively. Once the reaction finished, the phase separation time was recorded using a stopwatch with a time resolution of 0.01 sec. The phase separation time defined in this study is the time at which the dispersion band disappeared after a 5 min reaction, in which the interface of two phases were visually clear, as in Figure 2. A bubble breaking time was also recorded, as all of the bubbles visually disappeared due to some of the test results showing oddly longer breaking times. The organic phase continuity was considered for all tests. The range of parameters considered in the experiment was a temperature range of 25–45 °C, a mixing speed of 1255–3000 rpm, O/A ratio 0.3–3.0, a pH 0.5–2.0, ORP 500–900 mV, and the effect of impurities, including flocculant and colloidal Si. All of the tests were triplicated to minimise any human errors. Cu extraction was monitored and calculated from the analysis of the raffinate solution. Details of all experiments are presented in the following sections. The definition of Cu extraction rate yield in this research is expressed as Equation (1).

$$\text{Cu extraction rate (\%)} = 1 - \frac{\text{raffinate Cu (mg/L)}}{\text{feed solution Cu (mg/L)}} \times 100 \quad (1)$$

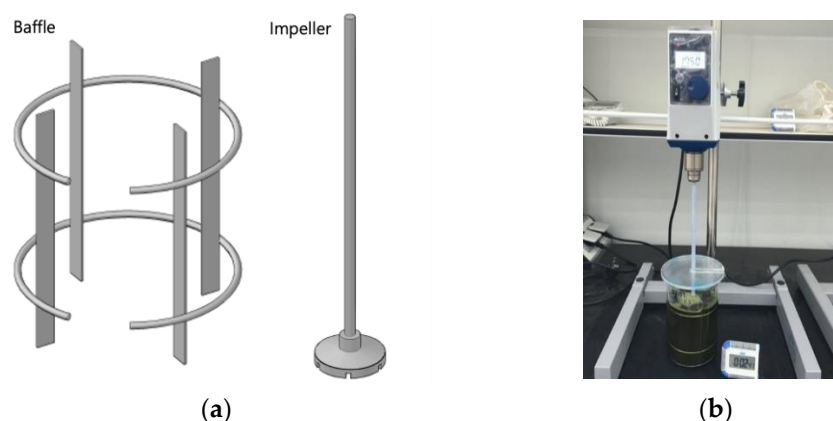


Figure 1. The schematic diagram (a) and the picture (b) of the experimental apparatus for the test.

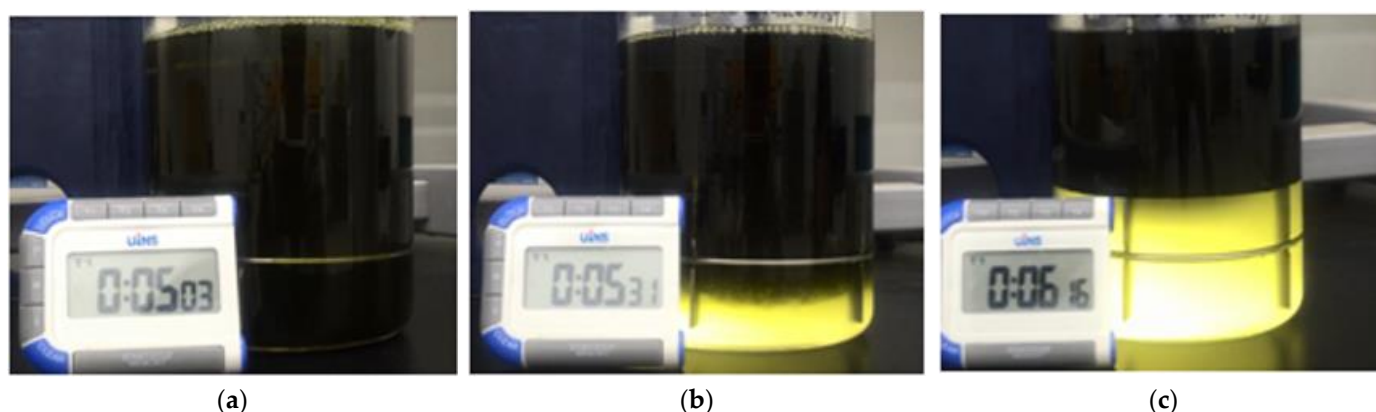


Figure 2. The example of the defined phase breaking time on the phase separation test, from left: (a) the end of reaction; (b) the mid of phase breaking; and (c) the end of phase separation time, visually clear on the interface of two phases.

2.3. Methods of Analysis

Physical characteristics of the organic sample were determined using a viscometer (DHR-1, TA Instruments, New Castle, DE, USA) and a density/specific gravity meter (DA-130N, Kyoto Electronics Manufacturing, Ltd., Kyoto, Japan). The chemical composition of all aqueous samples was analysed using the inductively coupled plasma optical emission spectrometer (ICP-OES) from PerkinElmer, Waltham, MA, USA (Optima 7300 series).

3. Results and Discussion

3.1. Physical Characteristics of the Organic Phase

The extractants and the prepared organics were characterised using the viscometer and the specific gravity meter at the temperature range 10–45 °C. From the results presented in Figure 3, the viscosity of LIX860N was exceptionally high at 302 cP (centipoise) at the lower temperature of 10–20 °C while LIX84I was below 80 cP. However, the viscosities of the prepared organics (Org. 1) were 2.0–3.8 cP as the extractant dissolved in diluent by 10:90% v/v ratio. The increasing temperature had no significant effect on changing the specific gravity for the prepared organics. The specific gravity for the extractants was 0.78–0.82 g/cm³ and 0.88–0.93 g/cm³, respectively, within the temperature range mentioned above. In general, the viscosity could be affected in the field operation in terms of the phase separation due to a higher viscosity, resulting in a slower separating time on the two phases, and similarly, by the specific gravity effects on the phases. However, most of the extractants and diluents on the market already consider these problems.

3.2. Effect of Temperature and Diluent Type

A series of tests were conducted to examine the effect of temperature on the phase separation time within the range of 25–45 °C. The results shown in Figure 4 demonstrate that the phase separation time was reduced when the temperature increased, as expected from the viscosity test. The phase separation time of the Org. 1 (using LIX84I alone) was 50 s at 25 °C and 25 s at 45 °C, while LIX860N in the organic solution increases the phase separation time as significantly as over five times at 30 °C. The bubble breaking time was observed only in Org. 2 as of 232 s at 25 °C and 117 s at 45 °C, respectively, while the bubble in Org. 1 broke instantly after the reaction. A cloudy raffinate was observed at a higher temperature from both organics, as presented in Figure 5. It assumes that the cloudy raffinate was caused by the generation of the organic microdroplets in the aqueous phase as entrainment at high temperatures. Cu extraction was monitored only in the Org. 1 reaction and was gradually increased by the temperature increasing from 97% at 25 °C to 98% at 45 °C.

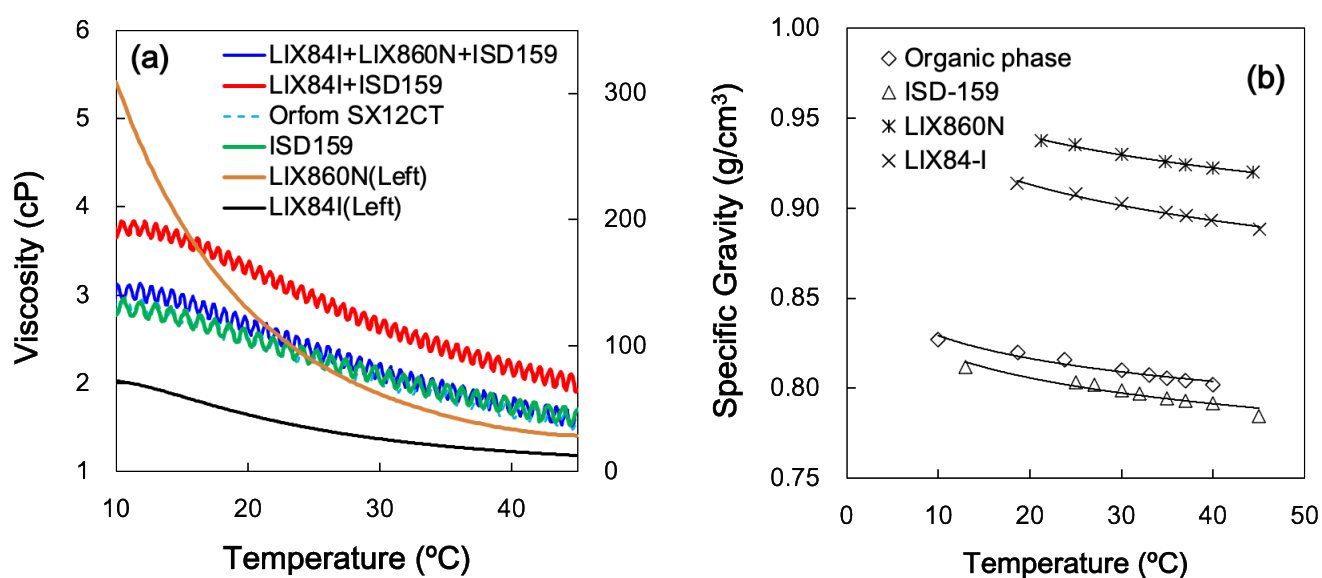


Figure 3. Physical characteristics of (a) the viscosity (left and right Y axis); and (b) the specific gravity of the extractants, the diluents and the prepared organics, respectively.

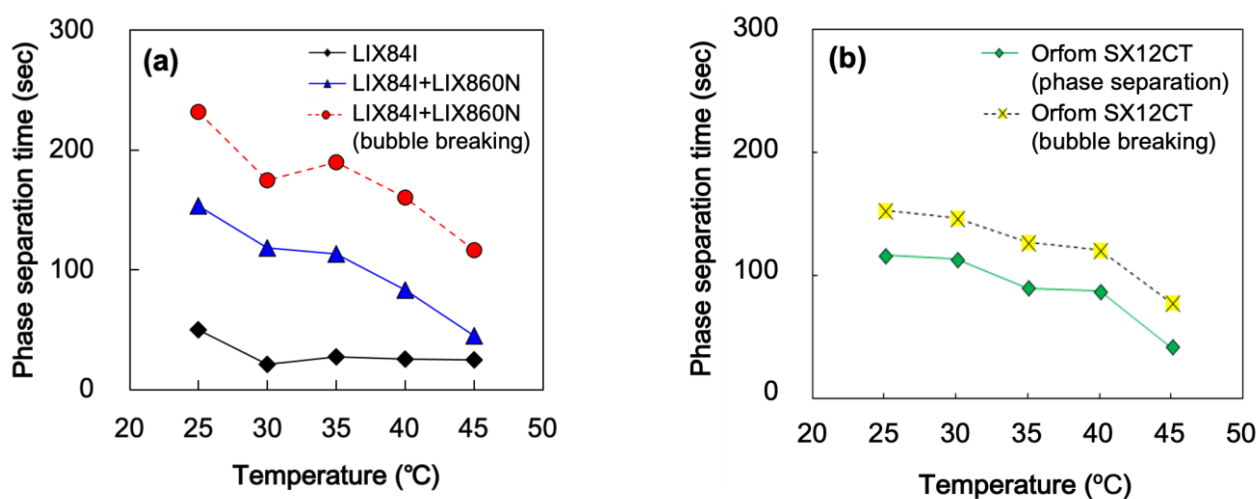


Figure 4. The effect of the temperature and diluent type on the phase separation time: (a) using ISD-159; and (b) Orfom SX-12 CT.

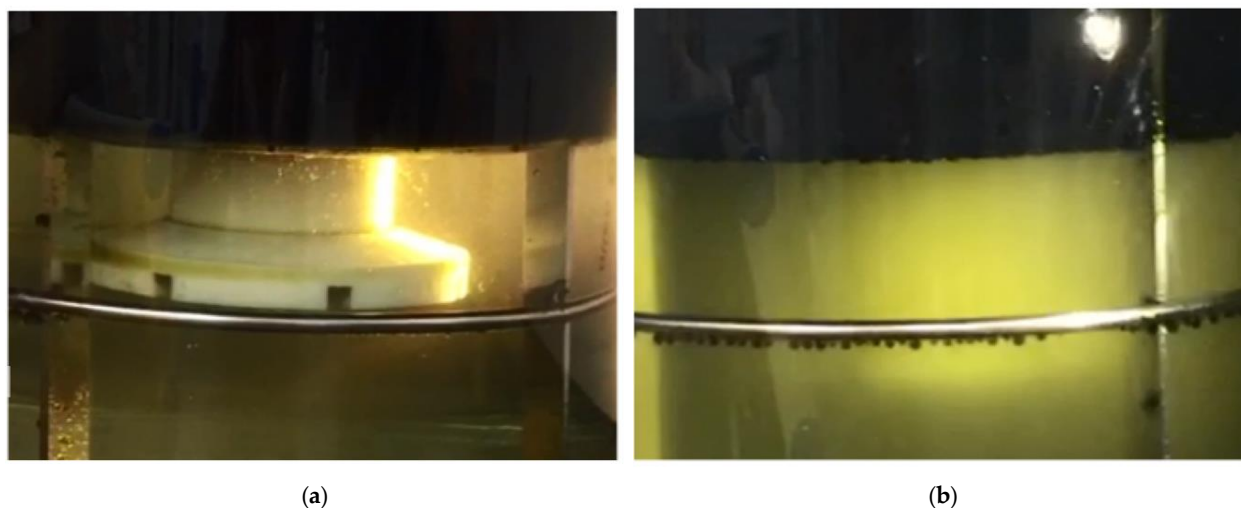


Figure 5. The comparison of the raffinate as: (a) a clear solution at 25 °C; and (b) the cloudy solution at 45 °C.

The test for the effect of diluent type at different temperatures in the range of 25–45 °C was conducted. Two organic phases were prepared using the extractant dissolved into Orfom SX-12 CT and ISD-159 diluents. From the results shown in Figure 4, the phase separation time using both diluents was similar, but using ISD-159 was slightly higher at 154 s while Orfom SX-12 CT was 117 s at 25 °C. In addition, the bubble breaking time behaves similarly to the phase separation. The bubble breaking time was considered as separate from the phase separation time in this research. However, the bubble breaking time could be affected to limit a flowrate in field operations as the continuous counter-current solvent extraction commonly used.

3.3. Effect of Mixing Speed

The effect of mixing speed on the phase separation time was investigated at a range of 1255–3000 rpm. Figure 6 shows the results of evaluating the mixing speed on the phase separation time. A dramatic increase of the phase separation time was observed at over 2000 rpm on Org. 1, while Org. 2 was relatively steady on the phase separation time. The bubble breaking time was only observed on Org. 2 and was slightly longer than the bubble breaking time when the mixing speed was over 2500 rpm. From the results, a microbubble could be generated at a high mixing speed which causes a more prolonged phase separation and bubble breaking time. Cu extraction slightly increased when increasing the mixing speed. Moreover, the phase separation and the bubble breaking time should be considered and controlled in the field operation because those are related to entrainments between two phases. The entrainment behaviours are also closely connected to other factors, as further discussed in the following section. Cu extraction slightly increased from 96% at 1255 rpm to 97.5% at 2200 rpm, and then gradually decreased to 96.5% at 3000 rpm. We determined that the mixing speed at the extraction stage in the Boleo plant was around 4.51 to 4.91 m/s. This converted to 2000 (4.66 m/s) to 2200 rpm (5.13 m/s) in the laboratory test. Thus, a higher mixing speed resulted in a lower performance index in the field operation.

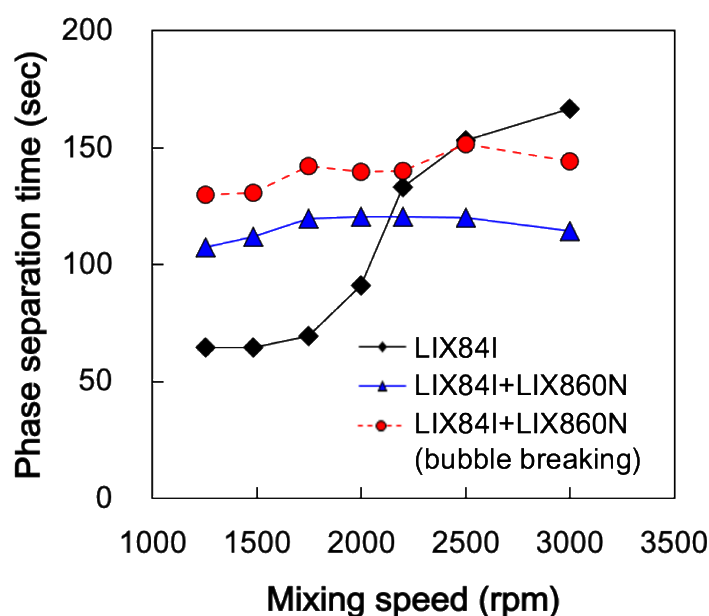


Figure 6. The effect of the mixing speed on the phase separation time.

3.4. Effect of O/A Ratio

The results of the effect of the O/A ratio on the phase separation time are shown in Figure 7. When the O/A ratio is increased, the phase separation time is also increased from 32 s at 0.3 to 91 s at 3.0 O/A ratio on the Org. 1. On the other hand, a significant increase in the phase separation time was observed on the Org. 2 at above O/A ratio 0.8 from 102 s and up to 139 s at O/A ratio 1.2, while averaging 35 s below the O/A ratio 0.8. Conversely,

the bubble breaking time decreased when the O/A ratio increased, presented as 350 s at the O/A ratio of 0.3 and 122 s at a 1.2 O/A ratio. Cu extraction was increased at a higher O/A ratio, as expected due to the physical quantity of the organic phase. The Cu extraction was 54% at 0.3, 96.5% at 1.2 and over 99% at 3.0 O/A ratio, respectively.

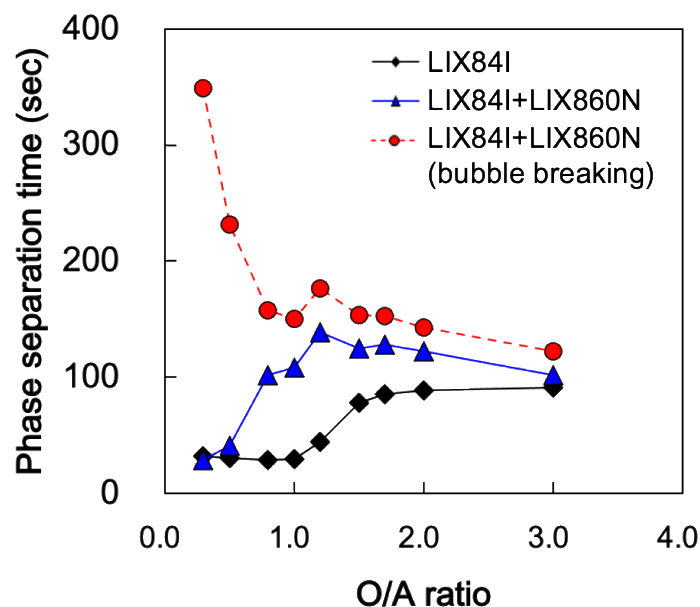


Figure 7. The effect of the O/A ratio on the phase separation time.

3.5. Effect of pH and ORP

A series of tests were conducted to evaluate the effect of pH and ORP on the phase separation time at a pH range of 0.5–2.0 and three sets of ORP at a range of 500–900 mV. The pH was controlled on the aqueous phase prior to the test and during the reaction using 2 M H_2SO_4 solution, and ORP was also measured. From the results shown in Figure 8, at a lower pH, increasing the phase separation time on Org. 1 was observed while the phase separation time decreased when increasing pH on Org. 2. Furthermore, a noticeable change of the phase separation time was shown on pH between 1.0 and 1.2 as 119 s and 83 s, respectively (Figure 8c). The bubble breaking time on Org. 2 was observed as a similar trend to the phase separation time. However, Cu extraction was significantly influenced by pH changes on Org. 1 from 48% at pH 0.5 to 73% at pH 2.0 (Figure 8d). The effect of ORP was investigated using Org. 2 only (Figure 8a,b). Changing ORP affects not only the phase separation time but also the Cu extraction. A higher ORP reduces the phase separation time slightly, but a noticeable decreasing Cu extraction rate was observed at higher ORP conditions as over 96% at < 500 mV, and 73% at < 800 mV, respectively. Generally, oxime-type extractants have a high Fe ion selectivity in acidic Cu solvent extraction systems. Specifically, ketoxime (LIX84) has a better Fe ion selectivity at pH < 2.0 while aldoxime (LIX860) is appropriate at pH > 2.0. However, aldoxime characterised the high viscosity and was relatively costly according to its manufacturer [29]. Therefore, the use of mixing extractants is ideal, depending on the operating condition of the system and the field operation.

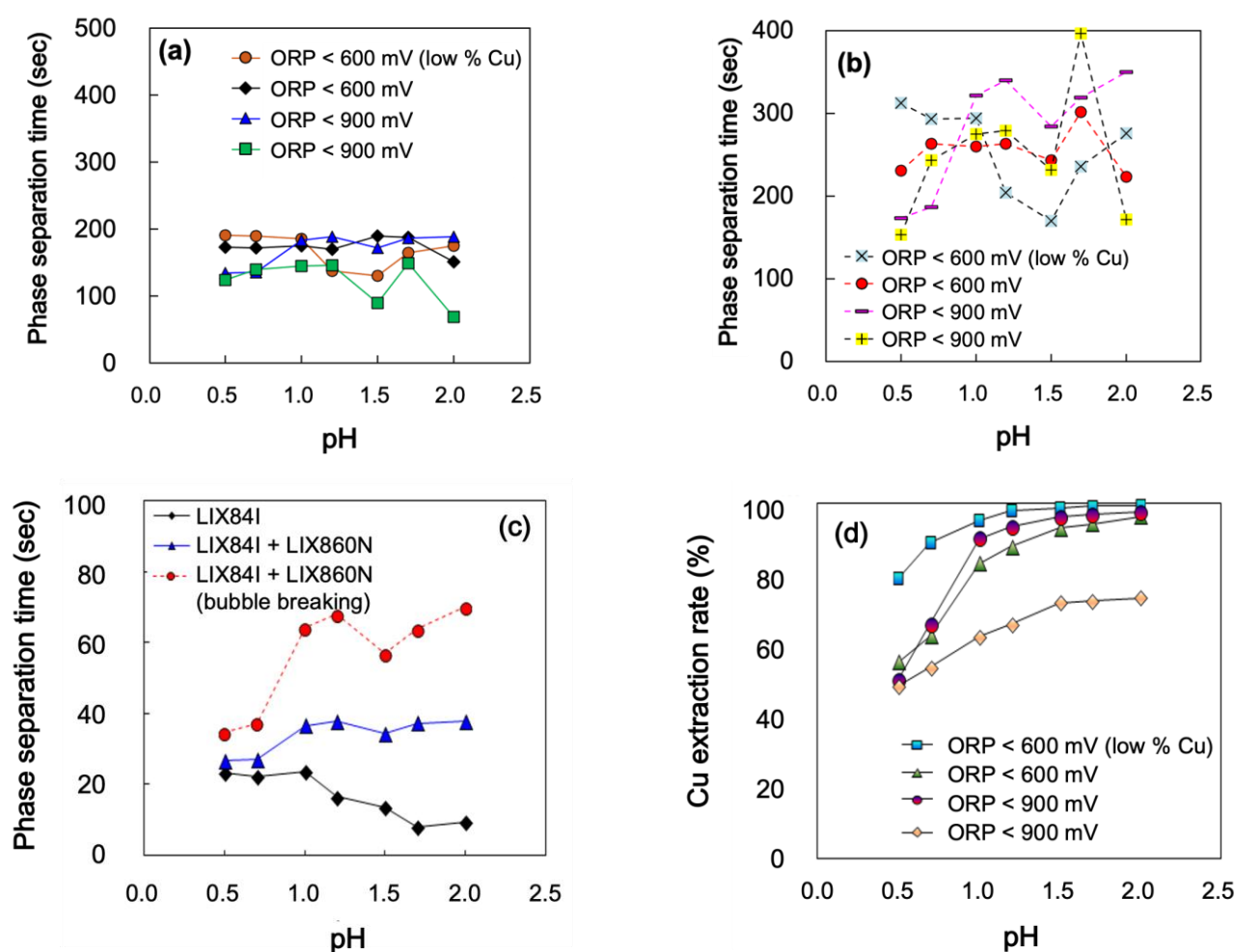


Figure 8. The effect of the ORP and pH on the phase separation time: (a) ORP at different pH; (b) bubble breaking time; (c) effect of pH; and (d) Cu extraction at different ORP and pH.

3.6. Effect of Impurities: Flocculant and Colloidal Silica

Total suspended solids (TSS) are an important factor in the field operation. The conventional plant scale operation utilises the counter-current decantation process using flocculants for generating the PLS for SX. The TSS can be accelerated by generation of a third phase and crud in the mixing stage [30,31]. In this study, colloidal silica and the flocculant were considered the TSS, commonly used in the Cu acid leaching-solvent extraction process. The crud formation between two phases captured the extractant and eventually dismantled it [30]. Moreover, this crud became a physical impurity and interrupted the phase separation. In the end, this affected the production rate and caused production loss. Therefore, the effect of impurities on the phase separation time was investigated using the flocculant and the colloidal silica.

From the results shown in Figure 9, the addition of the flocculant increases the phase separation time gradually of 10 mg/L and 5 mg/L for Org. 1 and Org. 2, respectively. However, the phase separation time was noticeably increased over 20 mg/L for Org. 1 and 10 mg/L for Org. 2 (Figure 9a). The bubble breaking time for Org. 2 was also significantly increased at over 5 mg/L. On the other hand, no significant effect on Cu extraction was observed at an average of 95%. The effect of the Si in the solution influences the phase separation time similarly to the flocculant addition. At over 50 mg/L of Si, the phase separation time increased steeply (Figure 9b). A combined effect of the flocculant and Si contents was also investigated. However, the phase separation time behaved similarly to the effect of flocculant.

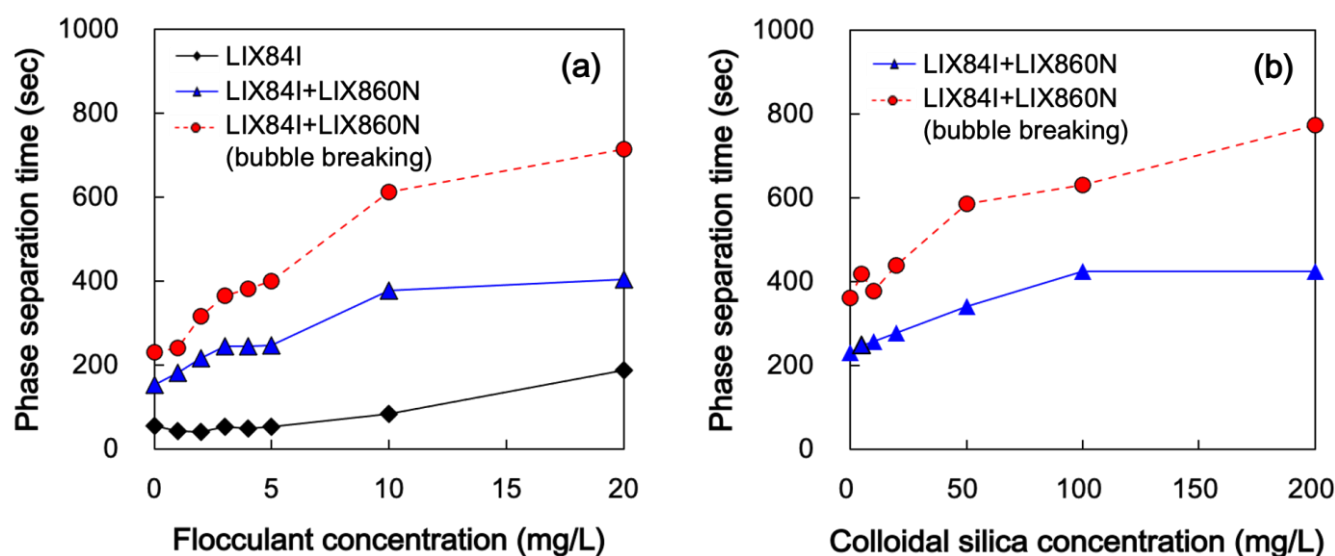


Figure 9. The effect of the impurity on the phase separation time: (a) flocculant addition; (b) colloidal silica addition.

3.7. Phase Separation Behaviour in the Continuous Counter-Current System

After the series of tests, the phase separation behaviour in the continuous counter-current system was investigated using a pilot-scale mix-settler, as illustrated in Figure 10. Two stages of the mix-settler for the extraction test were set up and operated in a total of 62 h under conditions tabulated in Figure 11. Four different batches of the trial were conducted for each parameter. The parameters considered in the scale-up tests were the temperature (at 20, 35 °C, ± 5 °C) and the flocculant level (3, 10 mg/L) in the aqueous solution. The temperature was controlled using a Teflon coated heating element for the PLS filled in a polypropylene bath. For monitoring the phase separation time, an organic and an aqueous sample were taken within a time interval and checked using the apparatus. From the results presented in Figure 12, increasing the temperature affects the phase separation time slightly at each mixer-settler. However, no dramatic changes were observed, as values averaged 107 s at 22 °C and 85 s at 41 °C, respectively. Cu extractions reached over 95% at each mixer-settler.

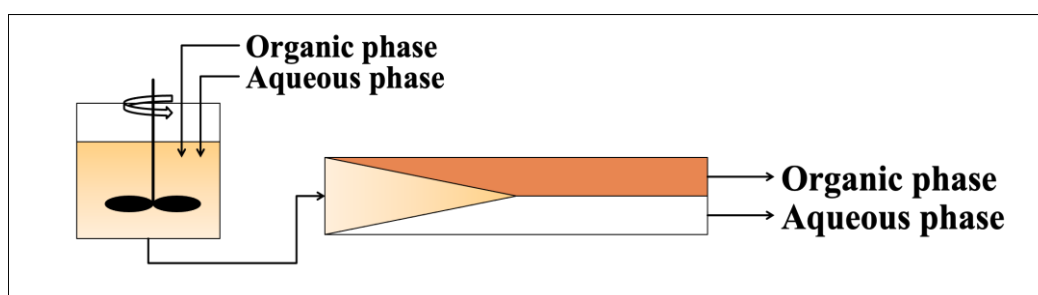


Figure 10. A schematic diagram of the continuous counter-current system.

The phase separation behaviours were affected by many operational parameters from the test results. Many other factors could influence the field operation, including incident, weather, human error, etc. However, the parameters examined in this research could be contributed to the SX field operation by minimising practical trials for optimising the operating conditions.

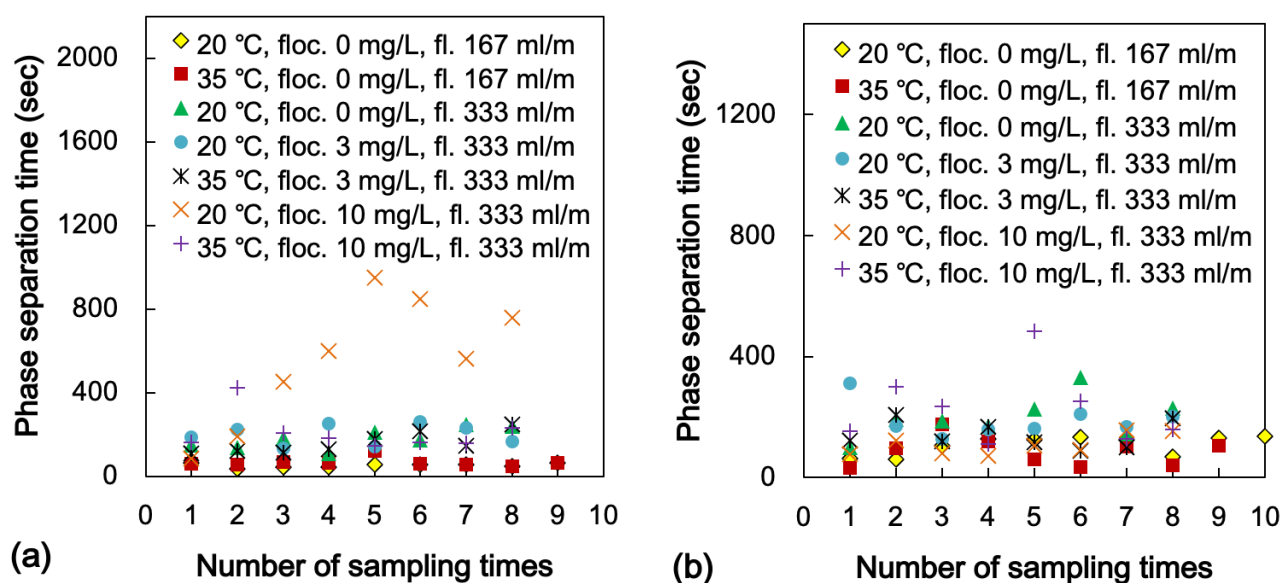


Figure 11. The results of the phase separation time on the continuous counter-current SX system using the pilot scale mixer-settler at different temperature and flowrate: (a) extraction stage 1; (b) extraction stage 2 (floc.: flocculant, fl.: flowrate).

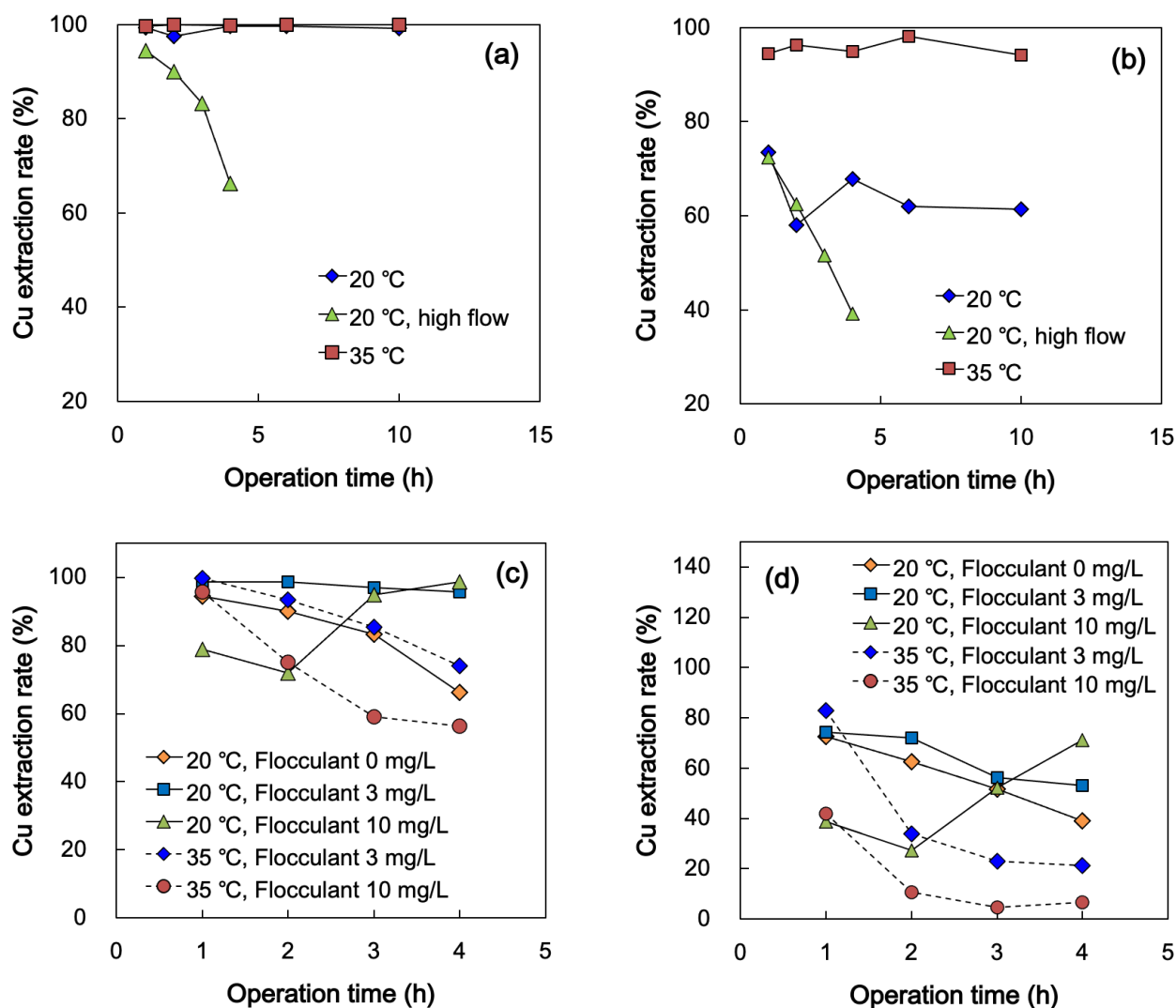


Figure 12. The result of the Cu extraction rate on the continuous counter-current SX system using the pilot scale mixer-settler at different temperature at: (a) extraction stage 1 and (b) 2; and flocculant addition at (c) extraction stage 1 and (d) 2.

4. Conclusions

In summary, the effects of parameters on the phase separation time in the Cu solvent extraction system for considering the plant operation was investigated. From the results, the following has been concluded:

- Typical parameters that influenced the phase separation time were identified and optimized at the temperature $<35\text{ }^{\circ}\text{C}$, the mixing speed $>2000\text{ rpm}$, and the O/A ratio >1.2 ;
- ORP and pH more complicatedly affect the phase separation time as using the ketoxime rich organic (Org. 1) is shown in a decreasing graph when increasing pH from 0.5 to 2.0, while the aldoxime mixed organic (Org. 2) revealed the reverse result. A high ORP ($>900\text{ mV}$) lowers the phase separation time slightly. However, the Cu extraction was significantly affected as a maximum of 40% lower than the optimized condition;
- The effect of the flocculant and silica level in the PLS resulted in extending the phase separation time gradually when the concentration was increased. Particularly, these were physiochemically affected by the organic and accelerated the third phase and the crud generation;
- The phase separation time using the pilot-scale mix-settlers for the continuous counter-current solvent extraction system was investigated. Increasing the temperature in the system effectively lowered the phase separation time and improved the Cu extraction. The flocculant level in the PLS affected the phase separation time dramatically. However, the generation of the crud caused a significant reduction of Cu extraction.

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References

1. Robinson, T.; Sandoval, S.; Cook, P. World copper solvent extraction plants: Practices and design. *JOM* **2003**, *55*, 24–26. [[CrossRef](#)]
2. Kordosky, G.A. Copper solvent extraction: The state of the art. *JOM* **1992**, *44*, 40–45. [[CrossRef](#)]
3. Petersen, J. Heap leaching as a key technology for recovery of values from low-grade ores—A brief overview. *Hydrometallurgy* **2016**, *165*, 206–212. [[CrossRef](#)]
4. Renman, R.; Jiankang, W.; Jinghe, C. Bacterial heap-leaching: Practice in Zijinshan copper mine. *Hydrometallurgy* **2006**, *83*, 77–82. [[CrossRef](#)]
5. Miller, J.D.; Lin, C.; Garcia, C.; Arias, H. Ultimate recovery in heap leaching operations as established from mineral exposure analysis by X-ray microtomography. *Int. J. Miner. Process.* **2003**, *72*, 331–340. [[CrossRef](#)]
6. Rötzer, N.; Schmidt, M. Decreasing Metal Ore Grades—Is the Fear of Resource Depletion Justified? *Resources* **2018**, *7*, 88. [[CrossRef](#)]
7. Naldrett, A.J. World-class Ni-Cu-PGE deposits: Key factors in their genesis. *Miner. Deposita* **1999**, *34*, 227–240. [[CrossRef](#)]
8. Chen, J.; Guo, X.J.; Li, H. Implementation and practice of an integrated process to recover copper from low grade ore at Zijinshan mine. *Hydrometallurgy* **2020**, *195*, 105394. [[CrossRef](#)]
9. Mokmeli, M. Pre-feasibility study in hydrometallurgical treatment of low-grade chalcopyrite ores from Sarcheshmeh copper mine. *Hydrometallurgy* **2019**, *191*, 105215. [[CrossRef](#)]
10. Liu, M.; Wen, J.; Tan, G.; Liu, G.; Wu, B. Experimental studies and pilot plant tests for acid leaching of low-grade copper oxide ores at the Tuwu Copper Mine. *Hydrometallurgy* **2016**, *165*, 227–232.

11. Dreisinger, D.; Cheng, C.; Zhang, W.; Pranolo, Y. Development of the Boleo Process Flow Sheet and the Direct Solvent Extraction (DSX) Circuit for Cobalt and Zinc Recovery. In Proceedings of the 25th International Mineral Processing Congress (IMPC 2010), Brisbane, QLD, Australia, 6–10 September 2010; pp. 309–318.
12. Cheng, C.Y.; Zhu, Z.; Pranolo, Y. *The Development of a New DSX Process for the Separation of Nickel and Cobalt from Iron and Aluminium and Other Impurities*, in ALTA 2011 Ni/Co/Cu; ALTA Metallurgical Services: Perth, WA, Australia, 2011; pp. 240–252.
13. Cheng, C.Y.; Barnard, K.R.; Zhang, W.; Robinson, D.J. Synergistic Solvent Extraction of Nickel and Cobalt: A Review of Recent Developments. *Solvent Extr. Ion Exch.* **2011**, *29*, 719–754. [[CrossRef](#)]
14. Zhu, Z.; Zhang, W.; Cheng, C. A synergistic solvent extraction system for separating copper from iron in high chloride concentration solutions. *Hydrometallurgy* **2012**, *113–114*, 155–159. [[CrossRef](#)]
15. Luo, Y.; Hu, H.; Wang, Y.; Hu, F.; Zhu, S.; Zhang, S.; Zhang, Y.; Li, S.; Wang, J. Phase separation in solvent extraction of copper or nickel from acidic solution using a sulfonic acid (HDNNS) and a carboxylate ester (4PC). *J. Dispers. Sci. Technol.* **2019**, *40*, 819–827. [[CrossRef](#)]
16. Liu, X.R.; Qiu, G.Z.; Hu, Y.H.; Yang, J. Effect of Lix984N content on phase disengagement dynamics in copper-SX. *Trans. Nonferrous Met. Soc. China* **2003**, *13*, 963–967.
17. Kedari, C.S.; Coll, T.; Fortuny, A.; Sastre, A.M. Third Phase Formation in the Solvent Extraction System Ir(IV)—Cyanex 923. *Solvent Extr. Ion Exch.* **2005**, *23*, 545–559. [[CrossRef](#)]
18. Lu, Z.; Dourdain, S.; Pellet-Rostaing, S. Understanding the Effect of the Phase Modifier n-Octanol on Extraction, Aggregation, and Third-Phase Appearance in Solvent Extraction. *Langmuir* **2020**, *36*, 12121–12129. [[CrossRef](#)] [[PubMed](#)]
19. Swami, K.R.; Venkatesan, K.A.; Antony, M.P. Role of Phase Modifiers in Controlling the Third-phase Formation during the Solvent Extraction of Trivalent Actinides. *Solvent Extr. Ion Exch.* **2019**, *37*, 500–517. [[CrossRef](#)]
20. Musadaidzwa, J.M.; Tshiningayamwe, E.I. Skorpion zinc solvent extraction: The upset conditions. *J. South Afr. Inst. Min. Metall.* **2009**, *109*, 691–695.
21. Priest, C.; Hashmi, S.F.; Zhou, J.; Sedev, R.; Ralston, J. Microfluidic Solvent Extraction of Metal Ions from Industrial Grade Leach Solutions: Extraction Performance and Channel Aging. *J. Flow Chem.* **2013**, *3*, 76–80. [[CrossRef](#)]
22. Kriel, F.H.; Holzner, G.; Grant, R.A.; Woollam, S.; Ralston, J.; Priest, C. Microfluidic solvent extraction, stripping, and phase disengagement for high-value platinum chloride solutions. *Chem. Eng. Sci.* **2015**, *138*, 827–833. [[CrossRef](#)]
23. Choi, C.H.; Kim, J.; Nam, J.O.; Kang, S.M.; Jeong, S.G.; Lee, C. Microfluidic Design of Complex Emulsions. *ChemPhysChem* **2014**, *15*, 21–29. [[CrossRef](#)] [[PubMed](#)]
24. Aota, A.; Nonaka, M.; Hibara, A.; Kitamori, T. Countercurrent Laminar Microflow for Highly Efficient Solvent Extraction. *Angew. Chem. Int. Ed.* **2007**, *46*, 878–880. [[CrossRef](#)] [[PubMed](#)]
25. Brugarolas, T.; Tu, F.; Lee, D. Directed assembly of particles using microfluidic droplets and bubbles. *Soft Matter* **2013**, *9*, 9046–9058. [[CrossRef](#)]
26. Bidari, E.; Irannejad, M.; Gharabaghi, M. Solvent extraction recovery and separation of cadmium and copper from sulphate solution. *J. Environ. Chem. Eng.* **2013**, *1*, 1269–1274. [[CrossRef](#)]
27. Aguilar, M.; Cortina, J.L. *Solvent Extraction and Liquid Membranes: Fundamentals and Applications in New Materials*; CRC Press: Boca Raton, FL, USA, 2008.
28. Kordosky, G.A. Copper recovery using leach/solvent extraction/electrowinning technology: Forty years of innovation, 2.2 million tonnes of copper annually. *J. South Afr. Inst. Min. Metall.* **2002**, *102*, 445–450.
29. Sole, K.C.; Feather, A.M. Solvent Extraction of Copper from High-Tenor Pressure Leach Solutions Using New Modified Aldoximes. In Proceedings of the Copper-Cobre 2003: Hydrometallurgy of Copper Book 2, Santiago, Chile, 30 November–3 December 2003; pp. 691–706.
30. Delegard, C.H.; Casella, A.J. *Literature Review: Crud Formation at the Liquid/Liquid Interface of TBP-Based Solvent-Extraction Processes*; Pacific Northwest National Lab. (PNNL): Richland, WA, USA, 2016.
31. Testard, F.; Bauduin, P.; Zemb, T.; Berthon, L. Phase Formation in Liquid/Liquid Extraction: A Colloidal Approach. In *Ion Exchange and Solvent Extraction*; Moyer, B.A., Ed.; CRC Press: Boca Raton, FL, USA, 2009; p. 48.