



Separation and recovery of cobalt and aluminium from spent gas-to-liquid catalysts using CYANEX® 272

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Abstract

In the field of Fischer-Tropsch synthesis catalysts, cobalt, platinum, and aluminium are the primary metal constituents of the conventionally used cobalt catalyst. While platinum recovery remains a focal point in this field, a recent endeavour by a South African company emerged, which aimed to recover cobalt and aluminium from spent Fischer-Tropsch synthesis catalysts for potential use in the agricultural sector. This study aimed to optimally separate cobalt and aluminium from spent Fischer-Tropsch synthesis catalyst for this purpose. It further leverages the OLI® database to predict metal speciation during solvent extraction to aid with experimental planning. Shake-out tests were conducted to determine optimal separation conditions, which were validated using three distinct methods: (i) evaluating the experimental error, (ii) comparing results with similar research, and (iii) validating results against the OLI® database. The investigation revealed the pivotal role of the aqueous pH yielding effective separation at pH 3.13 ($[\text{H}_2\text{SO}_4] = 2.5 \times 10^{-4} \text{ M}$) when using 20 vol.% CYANEX® 272 and 50 mol.% pre-neutralisation. Effective cobalt scrubbing was achieved with 50 g/L Al at pH 2.8, while successful stripping required 1 M H_2SO_4 . Competitive interactions between complexing aluminium and cobalt species were observed when contacting with CYANEX® 272 at a pH < 4. Equipment design analysis for a targeted separation efficiency of 87% dictated the necessity of two mixer stages and a settler measuring $1.5 \text{ m} \times 1.5 \text{ m} \times 6.0 \text{ m}$ (height \times width \times length). This settler would ensure sufficient residence time for gravity separation at a flow rate of $10 \text{ m}^3/\text{h}$.

Keywords

Fischer-Tropsch synthesis, solvent extraction, CYANEX® 272, OLI®, metal speciation

Introduction

In 1922, the Fischer-Tropsch synthesis (FTS), formulated by Franz Fischer and Hans Tropsch, emerged as a pivotal process for the conversion of synthetic gas (syngas), primarily consisting of carbon monoxide (CO) and hydrogen (H_2), into diverse hydrocarbons such as oil, petrol, diesel, and various other chemical compounds. Integral to this transformative reaction is its catalyst. Traditionally, catalysts rooted in ruthenium, nickel, iron, and cobalt have served in the FTS process (Jahangiri et al., 2014). Cobalt-based catalysts stand out as the preferred option within this spectrum due to their cost-effectiveness, heightened activity, selectivity, and extended operational lifespan (Liang et al., 2019). Typically, these cobalt-based catalysts consist of approximately 10 mass% cobalt (Co), < 2 mass% platinum (Pt), with the remaining composition commonly made up of an Al_2O_3 -based supporting material (Jacobs et al., 2002).

Like all catalysts, these components degrade over time. Upon reaching a deactivation threshold (inadequate activity for sustaining the desired productivity), the spent catalyst is replaced with a fresh batch. Presently, Minemet, a company situated in South Africa, specialises in reclaiming the Pt from the depleted catalyst. However, considering the potential agricultural advantages of Co and aluminium (Al) – Co enhances crop yields and mitigates vitamin B12 deficiencies in livestock, while Al alters soil pH, facilitating the growth of plants accustomed to acidic soil conditions (International Plant Nutrition Institute, 2014), it would be beneficial to also recover these metals. Consequently, in this study, the aim was to effectively recover Co and Al from spent FTS catalysts for their agricultural applications. Two final product specifications could be targeted: (i) Al-based (< 100 ppm of Co) or (ii) Co-based (3:1 mass-based ratio of Co to Al), of which the Al-based product was targeted in this study.

Fortunately, many methods have been developed to separate these metals. Within the field of metallurgy, hydrometallurgy focuses on employing processes using aqueous solutions to extract

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or separate metals. Various techniques have been used for the separation of Co and Al, including solvent extraction (SX) (Tsakiridis and Agatzini-Leonardou, 2005), ion exchange (IX) (Botelho et al., 2019), precipitation (Dhiman, Gupta, 2019), selective leaching (Chong et al., 2013), and crystallisation (Ferreira et al., 2009). However, none of these studies have focused on spent FTS catalysts, which contain different metal compositions, thus requiring the development of different optimal separation conditions.

Among these hydrometallurgical techniques, SX has emerged as the preferred method compared with leaching, IX, and crystallisation, due to its remarkable selectivity towards specific metals (Sole, 2008). Furthermore, SX was shown to be effective and feasible for the separation of Co and Al (Tsakiridis, Agatzini-Leonardou, 2005). Hence, in this study, SX was selected as the technique to separate Co and Al. The efficiency of the separation process can be quantified by determining the extraction efficiency (E) and the distribution coefficient (D), as described in Equations 1 and 2, respectively:

$$E(\%) = \frac{m_{i,org}}{m_{i,F}} \times 100; \quad [1]$$

$$D = \frac{m_{Al,org}}{m_{Co,org}}. \quad [2]$$

where E refers to extraction/separation efficiency (%), m refers to the mass of metal i in the organic phase (org) after contact, and in the aqueous feed (F) solution. The optimal separation point must be balanced between maximising the yield and the separation. There are several levers available to optimise and control the extent of separation. These include the choice of extractant and manipulation of the reaction conditions such as pH, temperature, extractant concentration, and pre-neutralisation levels.

Selection of the extractant is a primary consideration in driving mass transfer across the interphase. For Co and Al, acidic extractants, facilitating a cation-exchange mechanism (as shown in Equation 3), have yielded superior selectivity (Makanyire et al., 2016). From these, CYANEX® 272 was chosen due to its widespread availability and competitive separation efficiencies (Tait, 1993).



where M^{n+} refers to a metal ion of n valence, (aq) to the aqueous phase, and (org) to the organic phase.

In terms of the variables affecting the separation efficiency, various studies have highlighted the importance of the aqueous solution pH (Tsakiridis, Agatzini-Leonardou, 2005; Torkaman et al., 2017). Other measurable variables include temperature, extractant concentration, and the extent of pre-neutralisation. Although the effects of these variables have been studied to some extent, the

exploration thereof in this study is crucial due to the current unique feed composition. Furthermore, the effect of additional variables, i.e., the feed metal concentration was evaluated. To further deepen the understanding of variable effects on the separation efficiency, the use of OLI® software was included to identify the metal speciation under various conditions, which has not previously been explored in Al and Co separation studies. These results can be used to aid with experimental planning by means of identifying pH regions where the desired metal species will exist for complexation with CYANEX® 272. The OLI® data can also be used as one layer of validation of the shake-out results.

In summary, the aim for this research was to optimally separate Co and Al from spent FTS catalyst by evaluating variables commonly studied in literature, such as temperature, pH, pre-neutralisation, and additional variables such as feed metal concentration. The study furthermore used the OLI® database to form part of both the experimental planning and to aid with experimental validation. After the optimal conditions for separation were determined, the secondary objective was to develop a conceptual design for a mixer-settler (typically used in SX) with specific focus on sizing the settler, as the need for the design was to obtain a high-level view of footprint required to be able to compare with pertraction technology (outside of the scope of this article).

Materials and methods

Metal speciation

OLI® Studio software (version 11.5.1) was used to determine experimental ranges. According to the complexing mechanism shown in Equation 3, both Al (as Al^{3+}) and Co (as Co^{2+}) should bind with the phosphinic ions present in CYANEX® 272 with active component bis(2,2,4-trimethylpentyl) phosphinic acid. The obtained speciation data of the metal ions at different aqueous pH and temperature conditions were used to guide the pH and temperature range at which the experiments should be conducted. The OLI® databases were leveraged to create three sets of Pourbaix diagrams of Al and Co, as shown in Table 1.

Extraction kinetics

The first experimental step was to quantify the minimum contact time necessary to reach equilibrium. For this, an aqueous phase containing 0.9 g/L Al and 0.1 g/L Co in deionised water (Millipore Milli-Q Plus® Q-pack CPMQ004R1) was contacted for 2 h with a 20 vol.% CYANEX® 272, 5 vol.% tributyl phosphate and the remainder made up of ShellSol 2325. Incremental samples were taken, separated, and analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5110). Additional details on the specifications and suppliers of the aforementioned reagents are provided in Table 2.

Table 1

OLI® Studio Pourbaix diagram set-up conditions

Set	Concentration of aluminium (g/L)	Concentration of cobalt (g/L)	Al:Co ratio (mass)	Temperature (°C)	Pressure (kPa)	pH range
1	0.9	0.1	9:1	25	101.3	1–14
2	0.9	0.1	9:1	40	101.3	1–14
3	0.9	0.1	9:1	55	101.3	1–14

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Table 2

Specifications of reagents used to prepare the synthetic aqueous and organic solutions

Reagent	Purity	Supplier
Cobalt(II) sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$)	> 90%	Anyang General Chemical Co., Ltd
Aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$)	> 90%	Anyang General Chemical Co., Ltd
CYANEX 272	> 85%	Syensqo
ShellSol 2325	–	CHEMQUEST AFRICA
Tributyl phosphate (TBP)	> 98%	Fisher Scientific
Ammonium hydroxide	> 25%	Minema
Sodium hydroxide	> 98%	LABCHEM
Sulfuric acid	> 98%	LABCHEM

Extraction

Contact solution preparation

A synthetic aqueous solution was prepared to obtain the desired 9:1 Al:Co (0.9 g/L Al and 0.1 g/L Co) catalyst composition, based on literature and the analysed pregnant leach solution (PLS). After preparation, the solution was allowed to stand for approximately 2 hours to obtain a homogenous distribution. The concentration of the metals in the solution was confirmed using ICP-OES.

The organic phase consisted of three components, namely the extractant, the diluent, and the modifier, which in this study were 20 vol.% CYANEX® 272, 75 vol.% ShellSol 2325, and 5 vol.% TBP, respectively.

Effect of pre-neutralisation on extraction

To quantify the effect of pre-neutralisation on extraction, the organic and aqueous solutions were contacted at an O:A (organic to aqueous) ratio of 1:1 for 1 h at 40°C using a benchtop shaking incubator (Labotec Orbital Shaking Incubator, 200 rpm) to agitate the mixture. To determine the separation efficiency as a function of the extent of pre-neutralisation, 0.00–0.63 M NH_4OH was added to the standard organic solution (20 vol.% CYANEX® 272, 75 vol.% ShellSol 2325 and 5 vol.% TBP) before contacting with the aqueous phase. The NH_4OH concentration range was based on the guidelines found in the CYANEX® 272 technical datasheet, recommending a maximum of 50% addition of pre-neutralisation with respect to the extractant molar concentration (20 vol.% CYANEX® 272, which is equivalent to 0.61 M CYANEX® 272). After extraction, the mixture was poured into standard separation funnels to settle and separate.

Effect of aqueous feed pH on extraction

To determine the separation efficiency as a function of pH, the pH of the aqueous standard feed solution was adjusted using either H_2SO_4 or NaOH. Two different methods were used: (1) assessing the effect of pH on a solution containing one metal at a time because this is the usual method pursued in similar literature (Tsakiridis, Agatzini-Leonardou, 2005; Torkaman et al., 2017) and will allow for validation of experimental results, and (2) assessing the effect of pH on the standard feed solution containing both metals in a 9:1 mass-based Al:Co ratio (representative of the actual spent FTS solution). The pH values of the solutions were adjusted (with a calibrated Metrohm 744 pH – 6.0258.010 electrode) to

obtain a pH range between ~1 and ~6 representing the effective zone (Tsakiridis, Agatzini-Leonardou, 2005) for both Al and Co extraction. The adjusted solutions were thereafter contacted with the standard organic phase (composition provided in the previous section) at 40°C, pre-neutralised to 50 mol.% CYANEX® 272, shaken at 200 rpm for 1 h, separated, and analysed as described in the aforementioned.

Effect of temperature on extraction

The effect of temperature on the separation efficiency was conducted by contacting the solutions at an O:A ratio of 1:1 at varying temperatures (25–40°C). All organic solutions were preneutralised at 50 mol.% of CYANEX® 272. All aqueous solutions were at a pH of 3.13.

Effect of feed metal concentration on extraction

The effect of feed metal concentration on extraction was determined by varying the metals in the feed from a concentration of 0–1 g/L, using the same reaction conditions as described in the aforementioned. The experiments were conducted by first keeping aluminium constant at 0.9 g/L and varying cobalt concentration whereafter cobalt concentration was kept constant at 0.1 g/L and aluminium concentration was varied.

Extraction isotherms

To obtain the extraction isotherms, the separation efficiency as a function of the feed concentration was calculated, which was varied from 0–10 g/L of Co or Al (as individual metals in solution). In addition to varying the Co and Al concentration in the aqueous solutions, different concentrations of the extractant in the organic phase (10–20 vol.% CYANEX® 272) were used to ensure the mixture contained enough complexation sites to reach true equilibrium (note that TBP was kept constant at 5 vol.% and ShellSol 2325 was adjusted accordingly).

Scrubbing

During the scrubbing test work, the loaded organic phase obtained from the optimised extraction step was contacted with a scrub liquor. Two scrubbing methods were evaluated. According to Tsakiridis and Leonardou (2005), scrubbing with dilute sulfuric acid optimally removes co-extracted Co. Accordingly, in method one, scrub liquors with a pH ranging from 0.7–3.7 (0.1–0.0001 M H_2SO_4) were prepared and contacted with the loaded organic phase.

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In method two, a metal-rich scrubbing liquor containing ~ 50 g/L Al (maximum solubility at room temperature) was prepared at the optimal pH (2.8) and contacted with the loaded organic phase (Botelho et al., 2019; Tsakiridis, Agatzini-Leonardou, 2005). In both cases, the phases were contacted in an O:A ratio of 4:1 for 1 hour at 40°C in a shaking incubator.

Stripping

During the stripping test work, the optimal scrubbed organic phase was mixed with an aqueous strip liquor. A strip liquor was prepared over a concentration range of 0.01–3.0 M H₂SO₄ (Botelho et al., 2019). An O:A ratio of 4:1 was used when contacting the two phases for 1 hour at 40°C in a shaking incubator.

Mathematical design of conventional mixer-settler

From the shake-out tests, the optimal separation conditions were determined, which provided enough information to design an industrial mixer-settler. The objective of the mixer-settler design was to obtain the relative size required to reach the determined equilibrium of the extraction phase for a given throughput. The performance of a mixer-settler is greatly determined by effective contact during mixing and the efficiency of the gravity separation step. Hence, for the simplified mixer-settler design, the two categories were modelled separately: firstly, the stages required for agitation (mixer) and, secondly, the area necessary for complete physical separation during the settling step. The McCabe-Thiele method was used to calculate the number of mixer stages required and the guidelines provided by Rydberg et al. (2004) were followed for the sizing of the settler.

After determining the number of stages, the dimensions (diameter/width) of the tank were varied until a design was obtained that met the five requirements presented in Table 3. According to the rules of thumb pointed out by Rydberg et al. (2004), the following tank dimension assumptions were made: i) height = width and ii) length = 4 × width. The final design geometry was adjusted to include a 20% overdesign factor to account for these assumptions. Once these requirements had been met, the entrainment layer was minimised to allow for complete separation of the two phases.

Results

Metal speciation

Figures 1(a) and (b) provide the Pourbaix diagrams for Al and Co, respectively, in the presence of sulfates.

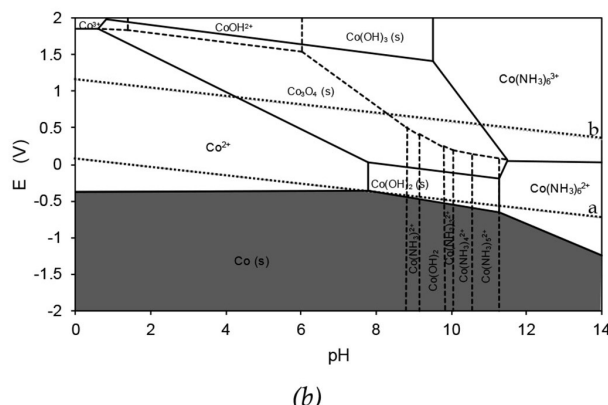
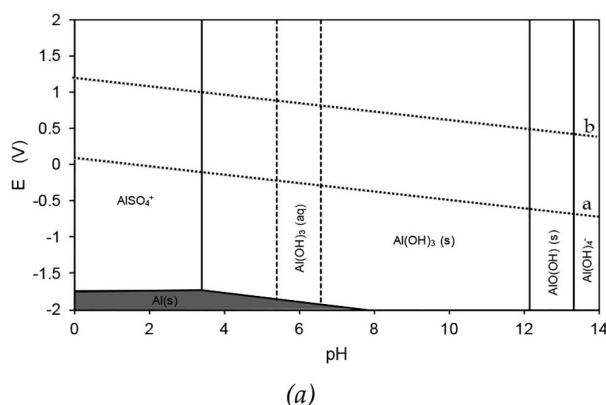


Figure 1—Pourbaix diagrams of (a) 0.9 g/L aluminium and (b) 0.1 g/L cobalt at 25°C, 1 atm in sulfate solutions

Table 3

Requirements for a settler design to ensure gravity separation takes place

Requirement number	Requirement*
1	$Q_c/A_I < v_d$
2	$Q_d/A_I < v_c$
3	$t_d > 2 \text{ min}$
4	$T_{av} > 2 \times T_{minD}$
5	Reynolds (Re) < 5000

* Q_c and Q_d are the overflow rates of the continuous and the dispersed phases (m^3/s), A_I refers to the area of the interface (m^2), v_c and v_d refer to the terminal settling velocity of a droplet in the continuous and dispersed phase, respectively (m/s), t_d refers to the time required to cross the dispersed band (s), T_{av} and T_{minD} are the average residence time of the dispersed phase(s) and the minimum residence time, respectively, as determined by Stokes' law (s)

According to the cation-exchange mechanism provided in Equation 3, typical cations (like Al^{3+} and Co^{2+}) should be the desired metal species that can complex with CYANEX® 272, establishing separation. Pourbaix diagrams were used to obtain the pH ranges for the various species that could occur in such a feed system. Temperatures were varied but no significant change in stable regions was noted. The immunity region (where the pure metal will not dissolve and form ion complexes with the aqueous substance) of Al and Co is illustrated by the dark grey area in Figure 1. The black dashed lines (a and b) indicate the water reduction and oxidation lines, respectively. According to Figure 1(a), the desired species of Al should exist as AlSO_4^+ at pH between 0–3.4, while according to Figure 1(b), Co^{2+} should exist at pH between 0–7.8. The desired complexing species of both Co and Al are expected to be present at low pH values, hence competition between the metals to bind with CYANEX® 272 can be expected at pH between 0–3.8. Neither the Al nor Co desired complexing species are predicted to exist at high pH values (> 7.8), where precipitation would likely occur and therefore experiments above this region are not recommended.

Extraction kinetics

As shown in Figure 2, equilibrium was reached after ~15 min of contact time. This is comparable with literature when using similar conditions (Torkaman et al., 2017). Although 15 minutes were

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adequate under these conditions, all remaining experiments were conducted for 1 hour to ensure that equilibrium was reached when using varying reaction conditions.

Extraction

Effect of preneutralisation on extraction

The effect of preneutralisation on extraction as a function of the NH_4OH concentration is shown in Figure 3. Firstly, without preneutralisation, poor Al extraction (26%) and separation efficiency (15%) were observed. This is to be expected, because in the absence of preneutralisation, i.e., no pH control, H^+ will be exchanged from the extractant to the aqueous phases, resulting in a suboptimal equilibrium pH and a decrease in extraction performance. Preneutralisation with NH_4OH resulted in less variability in pH, resulting in a significant improvement in Al extraction and separation efficiency. According to Figure 3, the optimal point of separation was attained when preneutralising with 0.38 M NH_4OH (~60 mol.% of CYANEX® 272), yielding 98% Al extraction with a separation efficiency of 83%. However, the CYANEX® 272 technical datasheet recommends that no more than 50 mol.% of the extractant should be preneutralised to avoid the risk of sacrificing selectivity, the remainder of the work was conducted at the recommended 50 mol.% (dashed line), which resulted in 87% extraction of aluminium and 17% extraction of cobalt.

Effect of aqueous feed pH on extraction

The dependence of extraction efficiency on pH is shown for the mixed and single metal feeds in Figure 4(a) and Figure 4(b), respectively.

A similar trend in experimental results, as illustrated in Figure 4(a), was observed by Tsakiridis and Leonardou (2005). In both cases, Al was first extracted to the organic phase in a pH range of 1 to 4, before reaching a plateau above pH 4. According to Tsakiridis and Leonardou (2005), 98.7% Al was extracted at pH ~ 2.6, while only 12% Co was extracted at pH 3.15. Accordingly, the optimal separation was between pH 2.5 and 3.5, which also compares with results obtained by Suzuki et al. (2012) who found an optimal extraction pH for Co and Al of 2.8. The difference in the optimal pH values between the data presented in literature and current data (optimum selectivity at pH 3.13), is due to the difference in feed compositions as well as experimental designs. Suzuki et al. (2012) and Tsakiridis and Leonardou (2005) individually determined the

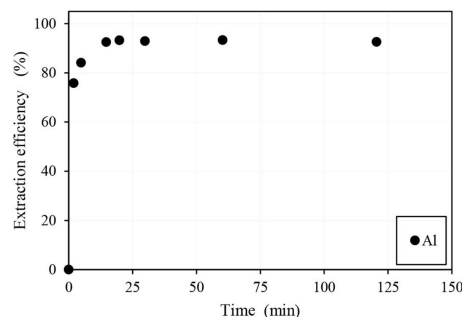


Figure 2—0.9 g/L aluminium solvent extraction kinetics at 40°C and 1 atm with 50 mol.% preneutralisation of 20 vol.% CYANEX® 272, 75 vol.% ShellSol 2325 and 5 vol.% TBP over 2 hours

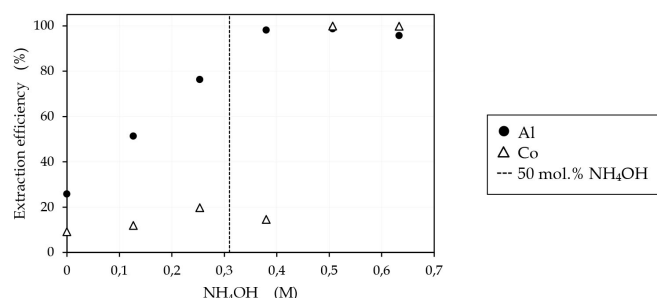


Figure 3—Effect of preneutralisation concentration on 0.1 g/L cobalt and 0.9 g/L aluminium extraction at pH 3.1, 40°C and 1 atm with 50 mol.% preneutralisation of 20 vol.% CYANEX® 272, 75 vol.% ShellSol 2325, and 5 vol.% TBP over 1 hour

pH dependence of extraction of each metal. In Figure 4(b), both the literature and the current data for individual metal extractions are shown, whereby the experimental data obtained differed with a mean absolute error of 4% on both the Al and Co trends.

When a single metal aqueous feed is contacted with an organic phase, no competition amongst metals can be evaluated and therefore cannot truly represent mixture selectivity. When comparing Figure 4(a) and Figure 4(b), the competition of Co and Al ions can be noted, which indicates the internal metal competition for complexation with CYANEX® 272, as predicted from the OLI® database, shown in Figures 1(a) and (b). At pH 2, for example, more than 90% Al was extracted according to Figure 4(b). However, when Al competes with Co, as shown in Figure 4(a), less than 60% of Al was extracted with ~ 30% co-extraction of Co at pH 2. These results confirm the importance of conducting extraction experiments on

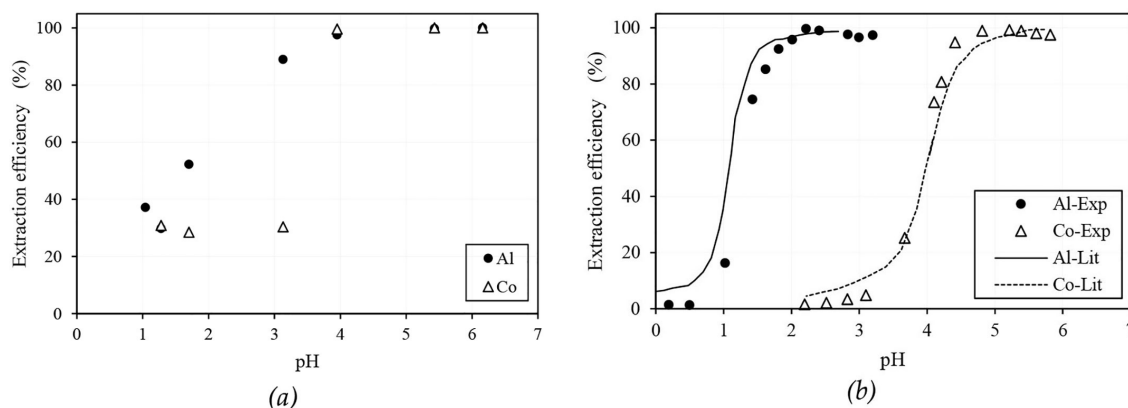


Figure 4—Extraction efficiency dependence on aqueous feed solution pH when the experiment is conducted on (a) the standard feed solution (0.1 g/L cobalt and 0.9 g/L aluminium) and (b) a single metal (0.1 g/L cobalt and separately 0.9 g/L aluminium) in solution: dots = experimental data points and lines = data obtained from literature (Tsakiridis, Agatzini-Leonardou, 2005). Conducted at 40°C and 1 atm with 50 mol.% preneutralisation of 20 vol.% CYANEX® 272, 75 vol.% ShellSol 2325, and 5 vol.% TBP over 1 hour

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representative mixtures to capture underlying metal competition. When combining the stability diagrams generated in Figures 1(a) and (b) with the extraction results presented in Figures 4(a) and (b), it seems that the Al that was extracted in the pH range 0–3.4 might have been in the form of AlSO_4^+ rather than the suggested Al^{3+} form, according to the mechanism shown in Equation 3. It is suggested that additional tests be conducted to further understand the desired metal species that may be required. Furthermore, it is noteworthy to mention that an overall mean absolute experimental error of 5% was obtained.

Effect of temperature on extraction

Figure 5 shows the effect of temperature on the overall extraction efficiency. The temperature only affected the Al extraction within the range of 25°C–40°C, with no significant effect above 40°C. These results compare well with literature findings (Torkaman et al., 2017). Therefore, the temperature of all the experiments was set at 40°C, where optimal separation, with a minimum energy input, is expected.

Effect of feed metal concentration on extraction

The distribution coefficients of Co and Al at varying feed metal concentrations are provided in Figure 6. The data demonstrate that a higher feed metal concentration results in a lower distribution coefficient, which is expected due to factors such as competitive binding (Kislik, 2012). The extraction efficiency is determined by the distribution coefficient of the metal and is therefore also a function of the metal concentration.

Keeping in mind that all the experiments were conducted at pH 3.13 and 50 mol.% preneutralisation, the selectivity changed as the feed metal concentration changed. As a result, in an industry where the feed metal concentration may vary, it is important to adjust the contact pH to ensure optimal conditions.

Extraction isotherms

Figure 7(a) and Figure 7(b) show the extraction isotherms of Al and Co, respectively, varying in concentrations from 0–10 g/L as individual metals in solution, as specified in the Materials and methods section. While the amount of Al extraction increased with increasing CYANEX® 272 concentration, the effect was less significant than the effect observed when extracting Co, as can be observed in Figure 7(b). More Al is transferred to the organic phase when comparing the two metals according to similar concentrations. Unlike Co distribution, Al has a strong drive through the whole concentration range. The extractant is also more selective towards Al, which correlates with the higher distribution coefficient obtained (Figure 6).

Scrubbing

Two scrubbing methods were evaluated: i) dilute sulfuric acid at pH 0.7–3.7 (0.1–0.0001 M H_2SO_4) and ii) an Al-enriched scrubbing liquor (50 g/L) at the optimal pH of 2.8. In both cases, the aim was to scrub off the Co while leaving Al in the organic phase. For the scrubbing, a loaded organic phase (consisting of 0.78 g/L Al and 0.017 g/L of Co) was obtained from extraction at pH 3.13, shaken at 200 rpm, at 40 °C, and preneutralised at 50 mol.% CYANEX® 272 (20 vol.%).

Method 1

The scrubbing efficiency from method one is shown in Figure 8.

From Figure 8, which illustrates the scrubbing efficiency as a function of scrubbing liquor pH, it is apparent that using diluted

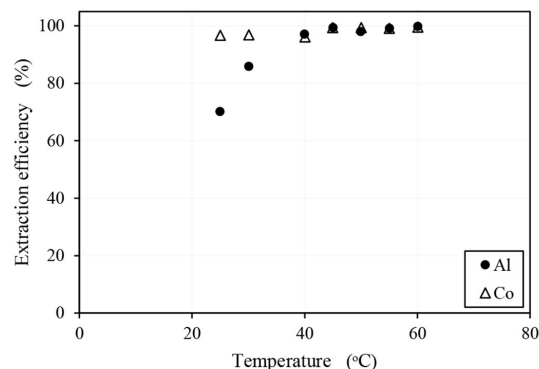


Figure 5—Extraction efficiency dependence on temperature. Conducted at an aqueous solution (containing 0.1 g/L cobalt and 0.9 g/L aluminium) pH 3.13 and 1 atm with 50 mol.% preneutralisation of 20 vol.% CYANEX® 272, 75 vol.% ShellSol 2325, and 5 vol.% TBP over 1 hour

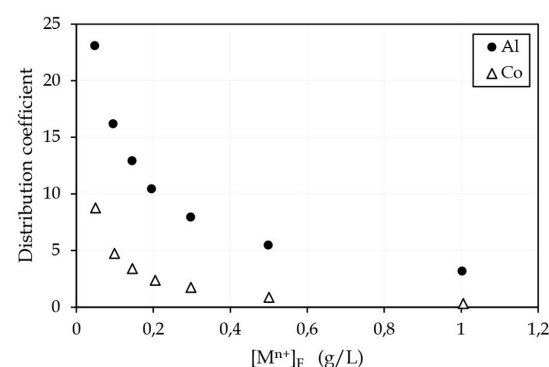


Figure 6—Distribution coefficients of cobalt and aluminium at varying feed metal concentrations. Conducted at an aqueous solution pH 3.13 and 1 atm with 50 mol.% preneutralisation of 20 vol.% CYANEX® 272, 75 vol.% ShellSol 2325, and 5 vol.% TBP over 1 hour

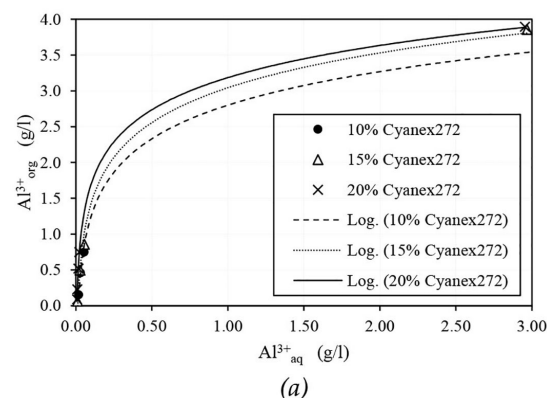


Figure 7—(a) Aluminium and (b) cobalt extraction isotherms with 10–20 vol.% CYANEX® 272. Conducted at 40 °C and 1 atm with 50 mol.% preneutralisation of 10–20 vol.% CYANEX® 272, 75–85 vol.% ShellSol 2325, and 5 vol.% TBP over 1 hour

H_2SO_4 as a scrub liquor was not selective towards Co or Al. Hence method one is not suitable for this application.

Method 2

In this single experiment, 50 g/L Al was added to the scrubbing liquor which was set to pH 2.8. Most (99.7%) of the Co was removed from the loaded organic phase (originally containing 0.017 g/L of Co and 0.78 g/L of Al), resulting in a Co concentration of 0.05 mg/L and an Al concentration of 1.13 g/L due to replacement with Al. At this point, the Co concentration is 44 ppm

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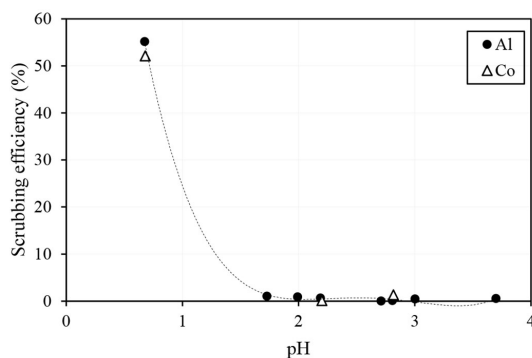


Figure 8—Scrubbing efficiency with H₂SO₄ over a range of pH values. Conducted at 25°C and 1 atm with the loaded organic phase consisting of 0.78 g/L aluminium, 0.017 g/L cobalt in 50 mol.%, preneutralised CYANEX® 272 (20 vol.%), 75 vol.% ShellSol 2325, and 5 vol.% TBP over 1 hour

(with respect to Al concentration) meeting the <100 ppm of Co target set in the Introduction section. Method two was therefore the scrubbing method of choice.

Stripping

To optimise the Al transfer from the organic phase to the aqueous strip liquor, the sulfuric acid concentration was varied from 0.01 M–3.0 M. The resulting stripping efficiency is shown in Figure 9. The point of optimal stripping seems to be at a concentration of 1.0 M sulfuric acid, (which results in an ~80% stripping efficiency of Al and 99.3% stripping efficiency of Co). The final loaded strip solution therefore contains 0.91 g/L of Al and 5.4×10^{-5} g/L of Co resulting in a final strip solution of ~54 ppm Co relative to Al while recovering ~70% of the original Al in the feed solution, thus meeting the initial target of <100 ppm of Co.

Mixer-settler design

The number of stages required to obtain the extraction determined by the shake-out tests was obtained with the McCabe-Thiele method as shown in Figure 10, (which provides a section of the isotherm provided in Figure 7 that is relevant to this application with lower concentrations). Two mixing stages were deemed necessary to attain an extraction efficiency of 87%, as demonstrated in Figure 4(a). Furthermore, the minimum decanter size necessary to ensure efficient gravity separation was determined to be at 1.5 m high, 1.5 m wide, and 6 m in length. The main results of the settler size calculations are presented in Table 4. Only a settler was sized, as this is generally the largest equipment compared (Van Nguyen et al., 2023) to the mixer and the sizing was required to conduct a high-level footprint comparison with pertraction based extraction (outside of the scope of this article).

The overflow rate was less than the settling velocity, ensuring that settling occurred before extraction of a phase at the overflow (applying to both the dispersed and continuous phase). The coalescence time exceeded 2 minutes, ensuring enough time for a molecule to cross the dispersion phase. Finally, the Reynolds number < 5000 ensured that turbulence should not hinder the separation.

Conclusions

The investigation aimed to optimise the separation process for a PLS with an Al:Co ratio of 9:1. Optimal conditions at 40 °C, 1 h contact time, with an aqueous feed solution pH of 3.13 when using CYANEX® 272 as extractant was established. Notably, scrubbing with diluted sulfuric acid lacked efficiency, while using 50 g/L Al at

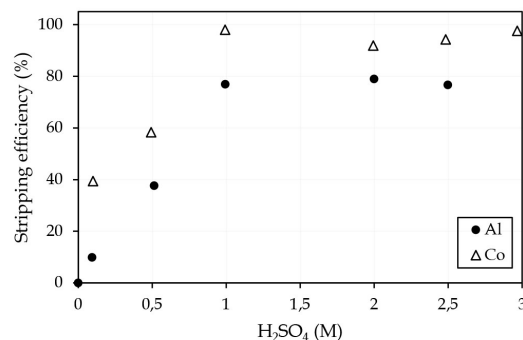


Figure 9—Effect of sulfuric acid concentration on the stripping efficiency of aluminium. Conducted at 25°C and 1 atm on the scrubbed organic containing 1.13 g/L aluminium and 0.05 mg/L Co in 50 mol.% preneutralised CYANEX® 272 (20 vol.%), 75 vol.% ShellSol 2325, and 5 vol.% TBP over 1 hour

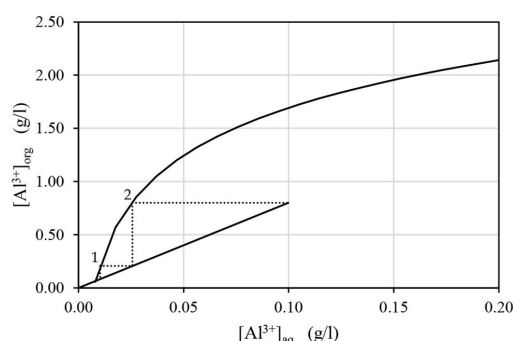


Figure 10—McCabe-Thiele plot determining mixer stages required

Table 4

Mixer-settler design results

Requirement	Result	Units
Requirement 1: $\frac{Q_c}{A_I} < v_d$		
$\frac{Q_c}{A_I}$	0.0003	m/s
v_d	0.001	m/s
Requirement 2: $\frac{Q_D}{A_I} < v_c$		
$\frac{Q_D}{A_I}$	0.0003	m/s
v_c	0.001	m/s
Requirement 3: $t_d > 2 \text{ min}$		
t_d	4	min
Requirement 4: $t_{av} > 2 \times t_{minD}$		
t_{av}	473	s
t_{minD}	103	s
Requirement 5: $Re < 5000$		
Re_D	0.4	-
Re_C	0.3	-

pH 2.8 proved effective. Optimal stripping was attained when using an aqueous solution with 1 M H₂SO₄ and 1 hour contact time. This process obtained 54 ppm Co in the loaded strip liquor, reaching the desired separation target of achieving less than <100 ppm of Co. The predicted coexistence of complexing Al and Co species at

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pH < 4 led to competitive behaviour between the two metals when in contact with CYANEX® 272. This phenomenon was evident in the exchange of metal ions, notably Co, observed at lower pH levels. Moreover, the extraction efficiency proved to be influenced not only by pH and preneutralisation but also by the feed metal concentration. Industries should consider varying the contact pH in response to different feed metal concentrations to optimise overall yield. According to the mixer-settler design study, two mixer stages was required. Additionally, a settler sizing of 1.5 m in height, 1.5 m in width, and 6 m in length was recommended to ensure adequate residence time for gravity separation, catering for a flow rate of 10 m³/h. Moving forward, potential areas for further investigation could include validating the identified Al species in the presence of sulfates, exploring the impact of other potential variables on extraction efficiency, and conducting pilot-scale tests to validate the scalability of the proposed conditions. Additional experimental runs are also recommended to obtain a better representation of the isotherm shapes.

CRediT statement

MK: Investigation, validation, formal analysis, writing - original draft; HMK: Conceptualisation, methodology, writing - review and editing; DvdW: Conceptualisation, methodology, writing - review and editing

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