

Limits of Cyanex 272 Selectivity for Cobalt Extraction in A Multi-Cationic Industrial Environment: Case Study of Lamikal, Lualaba (DRC)

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Abstract: This study examines the limits of Cyanex 272's absorption capacity in a complex industrial solvent extraction (SX) process for cobalt, applied at the LAMIKAL plants (Lualaba, DRC). The objective is to evaluate the actual performance of Cyanex 272 under multi-metal industrial conditions, where cobalt, copper and manganese coexist. Operating parameters such as pH, extractant concentration, organic/aqueous ratio (O/A) and contact time were optimised. The results show a cobalt extraction yield limited to 31.5%, compared to 98.6% for copper and 97.9% for manganese, revealing a low selectivity of Cyanex 272 towards cobalt in the presence of impurities. Recommendations are made to improve the selectivity of the process in a real industrial context.

Keywords: Solvent Extraction - Cyanex 272 - Cobalt - Copper - Manganese - Selectivity - Extraction yield - Hydrometallurgy - Lamikal - Parameter Optimisation - Ion Competition - Industrial Process.

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I. INTRODUCTION

Solvent extraction (SX) is an essential step in hydrometallurgy, enabling the selective separation of metals in polymetallic solutions (Ritcey, 2006). Cobalt, a strategic metal used in batteries and high-performance alloys, is often associated with copper and manganese, making its purification complex. Cyanex 272, an organophosphoric acid, is known for its selectivity towards cobalt in simple systems (Cole & Feather, 2006). However, its effectiveness decreases in industrial environments where impurities and competitive interactions alter its performance (Flett, 2005). This study aims to identify the critical parameters affecting the

performance of Cyanex 272 in the industrial context of LAMIKAL, in order to optimise the production of a purified cobalt electrolyte suitable for electrolysis.

II. MATERIAL AND METHODS

The tests were carried out on an industrial post-FAM solution from LAMIKAL characterised by average concentrations of Co (7 g/L), Mn (1.75 g/L) and Cu (0.1 g/L). The extractant used was Cyanex 272 dissolved in kerosene. The main parameters studied were: pH (3 to 7), Cyanex 272 concentration (5 to 25% v/v), O/A ratio (0.5 to 2) and contact time (1 to 10 minutes). The metals were analysed by atomic

absorption spectrophotometry (AAS). The tests were conducted in digestion vials under controlled agitation and at room temperature. The extraction yields were calculated using the standard formula:

$$R = [(C_0 - C) / C_0] \times 100 \quad (2.1)$$

➤ Equipment and Analysis Method

Extraction is a process that involves removing a chemical species from the medium in which it is contained. For a chemical species dissolved in a liquid (called a solvent or aqueous phase), another liquid (called an extracting solvent or organic phase) can be used to extract it. This is known as liquid-liquid extraction or solvent extraction. This type of extraction is carried out using a separating funnel in the laboratory.

• The Organic Phase Must Have Four Qualities:

- ✓ the metal to be extracted must be more soluble than in the aqueous phase;
- ✓ it is immiscible with the aqueous phase;
- ✓ it does not react chemically with the metal to be extracted;
- ✓ it poses minimal risk to health and the environment.

• Equipment

The equipment used for the experiment complies with liquid-liquid extraction testing standards (Ritcey, 2006). We therefore used:

- ✓ 250 ml separating funnel;
- ✓ 250 ml flasks;
- ✓ 100 ml and 250 ml beakers;
- ✓ storage flasks;
- ✓ a funnel;
- ✓ the stirrer;
- ✓ pH meter.

• Reagent

The reagent used is:

- ✓ 1N NaOH;
- ✓ Cyanex 272;
- ✓ Petroleum;
- ✓ Lamikal post-FAM solution.

• Protocol

- ✓ Place 100 ml of the aqueous phase in a clean 250 ml beaker;
- ✓ Connect the pH meter and immerse the electrode to measure the initial pH.
- ✓ Fill the dropper with 1N NaOH; this solution is used to adjust the pH.
- ✓ Carefully start the stirrer and set the speed to 360 rpm to stir the aqueous phase while adding the 1N NaOH drop by drop.
- ✓ After adjusting the pH, the cobalt extraction from the aqueous phase can now begin in four steps :
- ✓ The first operation consists of adding the organic phase to the aqueous phase:
- ✓ place the 250 ml separating funnel on a stand so that it remains vertical;
- ✓ check that the tap on the flask is closed;
- ✓ pour the mixture into the separating funnel;
- ✓ seal the separating funnel.
- ✓ The second step is to shake the separating funnel vigorously, ensuring that the shaking time is correct.
- ✓ The third step is to let the mixture settle (decanting), with the flask uncorked, until the organic phase rises to the top.
- ✓ The fourth step is to recover the two phases:
- ✓ place a 100 ml beaker under the tap of the separating funnel to collect the aqueous phase, which is the denser of the two;
- ✓ when the surface separating the liquids is close to the tap, slow down the flow (drop by drop) until the aqueous phase has completely drained;
- ✓ place another 100 ml beaker to collect the organic phase



Fig 1 Presentation of Two Phases (Aqueous and Organic) in A Separating Funnel



Fig 2 Presentation of Two Phases after Agitation (Extraction)

- *Analysis Apparatus*

After extracting the cobalt, we analysed the aqueous phase using this analysis apparatus called: ultraviolet-visible spectrometry 720N is a spectroscopy technique involving photons with wavelengths in the ultraviolet (100 nm - 400 nm), visible (400 nm - 750 nm) or near-infrared (750 nm - 1,400 nm) range.

When exposed to radiation in this wavelength range, molecules, ions or complexes are likely to undergo one or more electronic transitions. This spectroscopy is one of the methods of electronic spectroscopy. The substrates analysed are most often in solution, but can also be in the gas phase and, more rarely, in the solid state.

Transition metal ion solutions are often coloured (i.e. they absorb visible light) because the electrons in metal ions can be excited from one electronic level to another. The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands, and by the degree of oxidation of the metal cation (Skoog et al., 2007).

- *Problem and objective*

The recovery of cobalt from industrial solutions is a major challenge in the field of hydrometallurgy, particularly in terms of the liquid-liquid separation of cobalt from other metals. LAMIKAL's post-FAM solution contains various elements in solution, making the selective separation of cobalt complex. So how can the solvent extraction parameters be optimised to achieve a better cobalt extraction yield with Cynex 272?

- *Sampling*

Sampling is an operation that consists of taking a representative part of a set or batch to determine the characteristics of that set as accurately as possible.

- *Sampling Strategy*

We used the composite sampling strategy, which involves combining several incremental samples taken at different times to form a single representative sample. This is particularly useful when the concentration of an analyte can vary over time, as in an OF flow from a decanter after the FAM circuit. Sampling was carried out after 30 minutes.

- *Sampling location*

The KALUKUNDI Mine, known as LAMIKAL, is a multinational public limited company located in the village of PUMPI, approximately 73 km east of the city of Kolwezi, in Lualaba Province, DRC. Its site covers an area of 27.2 square kilometres.

Ore processing follows a metallurgical process. Ore leaving the mine is stored in the storage area, from where it is transported by truck to a jaw crusher, then by conveyor belt to a semi-autogenous mill. The ore passes through a ball mill to achieve the particle size required for subsequent operations, and the pulp is sent for leaching to be dissolved using a suitable reagent.

During decanting, the overflow forms a high-copper-content solution known as PLS HG, which feeds the solvent extraction (SX) plant;

The underflow passes through a series of counter-current washing stages, at the outlet forming a low-copper-content

solution known as PLS LG, which also feeds the solvent extraction plant. After purification and concentration, the rich electrolyte feeds the electrolysis cells where copper is produced

by electrowinning. The raffinate from the SX circuit is sent to storage ponds, which feed the cobalt circuit.

Table 1 Chemical Characterization of the Sample

Elements	Copper	Cobalt	Iron	Manganese
Concentration	0.07 g/L	6.94 g/L	0.04 g/L	1.75 g/L

➤ Tests Themselves

The tests were carried out on a sample of the post-FAM industrial solution from the LAMIKAL cobalt circuit. We conducted several tests while changing the different parameters to see which parameters would give the best results.

Table 2 Volume Proportions of Extractant and Diluent in Relation to Different Organic Concentrations

Volumes [ml]		% V/V
Petroleum	Cyanex	
50	50	5
850	150	15
750	250	25
650	950	30

From the storage tanks, the iron, aluminium and manganese (FAM) precipitation circuit is fed first. These elements are precipitated by lime milk, then the cobalt-bearing solution is sent to the settling tank where the FAM decanter overflows have two possibilities:

- ✓ The first option is to feed the first-stage cobalt precipitation circuit;
- ✓ The second option is to send our clear solution to an effluent tank. This operation is carried out when the plant encounters problems;
- ✓ The underflow from the decanter also has two possibilities:
- ✓ the first option feeds the filter presses for further solid-liquid separation;
- ✓ The second option is to send the pulp for recirculation to the primary section, which is the FAM section. This operation is carried out in the second and third precipitation tanks (Kyalimu, 2023).
- ✓ The post-FAM solution was sampled at the decanter overflow.

• Sampling Equipment

We used the sampling tap to take samples as follows:

We opened a valve in the decanter flow where we collected and poured the solution into a container that had been thoroughly rinsed with water and the solution. Sampling was carried out calmly without creating turbulence until the container was full.

➤ Characterization of the Sample

Sampling characterisation is a chemical analysis process used to determine the composition, concentration, and chemical and physical properties of the sample.

• Preparation of the Organic Phase

The organic phase consists of two components:

- ✓ Petroleum, which is a diluent;
- ✓ Cyanex 272, which is an extractant.

The volume proportions corresponding to the preparation of the organic phase (1L) are described in the following table. We mixed these organic phase solutions, prepared at different concentrations, with the aqueous phase at different ratios and different pH levels.

• Formula Used

To determine the cobalt extraction yield, we used the following formula:

$$\text{Rdt} [\%] = (C_i - C_f) / C_i * 100 \quad (3.1)$$

Extraction efficiency:

$$E [\%] = D / (D + V_a / V_o) * 100 \quad (3.2)$$

If $V_a = V_o$, we therefore write:

$$E [\%] = D / (D + 1) * 100 \quad (3.3)$$

Acid preparation:

With the fundamental dilution relationship

$$C_{(1)} V_1 = C_2 V_2 \quad (3.4)$$

The methodological approach described in this section provides the experimental foundation necessary for implementing the cobalt extraction process. The choice of equipment, the definition of operating conditions and the rigour in developing the method were respected to ensure optimal selectivity and maximum extraction efficiency. This paves the way for the interpretation of the results obtained and the evaluation of extraction yield in the following chapters.

III. RESULTS AND DISCUSSION

The results show that cobalt extraction yield is highly dependent on operating parameters. Increasing the pH

improves cobalt complexation but also promotes the co-extraction of manganese.

Table 3 Influence of pH on Metal Extraction

TESTS	pH	REFINATE [g/L]			YIELD [%]		
RAFF post FAM		Cu	Co	Mn	Cu	Co	Mn
		0.1	6.94	1.75			
1	4.0	0.09	6.87	1.73	10	1.008	1.142
2	4.5	0.07	6.65	1.72	30	4.178	1.714
3	5.0	0.05	6.32	1.67	50	8.933	4.571
4	5.5	0.03	5.86	1.56	70	15.561	10.857
5	6.0	0.02	5.51	1.48	80	20.605	15.428

The maximum cobalt yield (31.5%) was obtained at pH 6, with a Cyanex 272 concentration of 20% and an O/A ratio of 1. At higher O/A ratios, selectivity decreases significantly. Copper and manganese are preferentially extracted, demonstrating competition between metal ions for the active sites of Cyanex 272. These results confirm the limitations of the process in an industrial environment rich in impurities.

The main objective of our work is to study the optimal conditions for cobalt extraction using the solvent extraction (SX) method, with Cyanex 272 as the extractant, in order to improve extraction yield. The tests were carried out using a cobalt-bearing solution from the cobalt circuit at the Lamikal plants, containing 0.1 g/l Cu, 1.75 g/l Mn, 6.94 g/l Co and a pH of 4.3.

➤ Influence of Certain Parameters on Cobalt Extraction Yield.

• Influence of pH

It is necessary to know the influence of pH on cobalt extraction in the presence of Cyanex 272 in order to optimise the operating conditions of the system. The tests were carried out with a solution whose pH was adjusted to 4.0 by adding a 75 g/l acid solution, under the following conditions:

- ✓ Contact time: 5 min;
- ✓ Agitation: 360 rpm;
- ✓ pH: 4, 4.5, 5.0, 5.5, 6;
- ✓ O/A ratio: 1/1;
- ✓ %V/V: 15%.

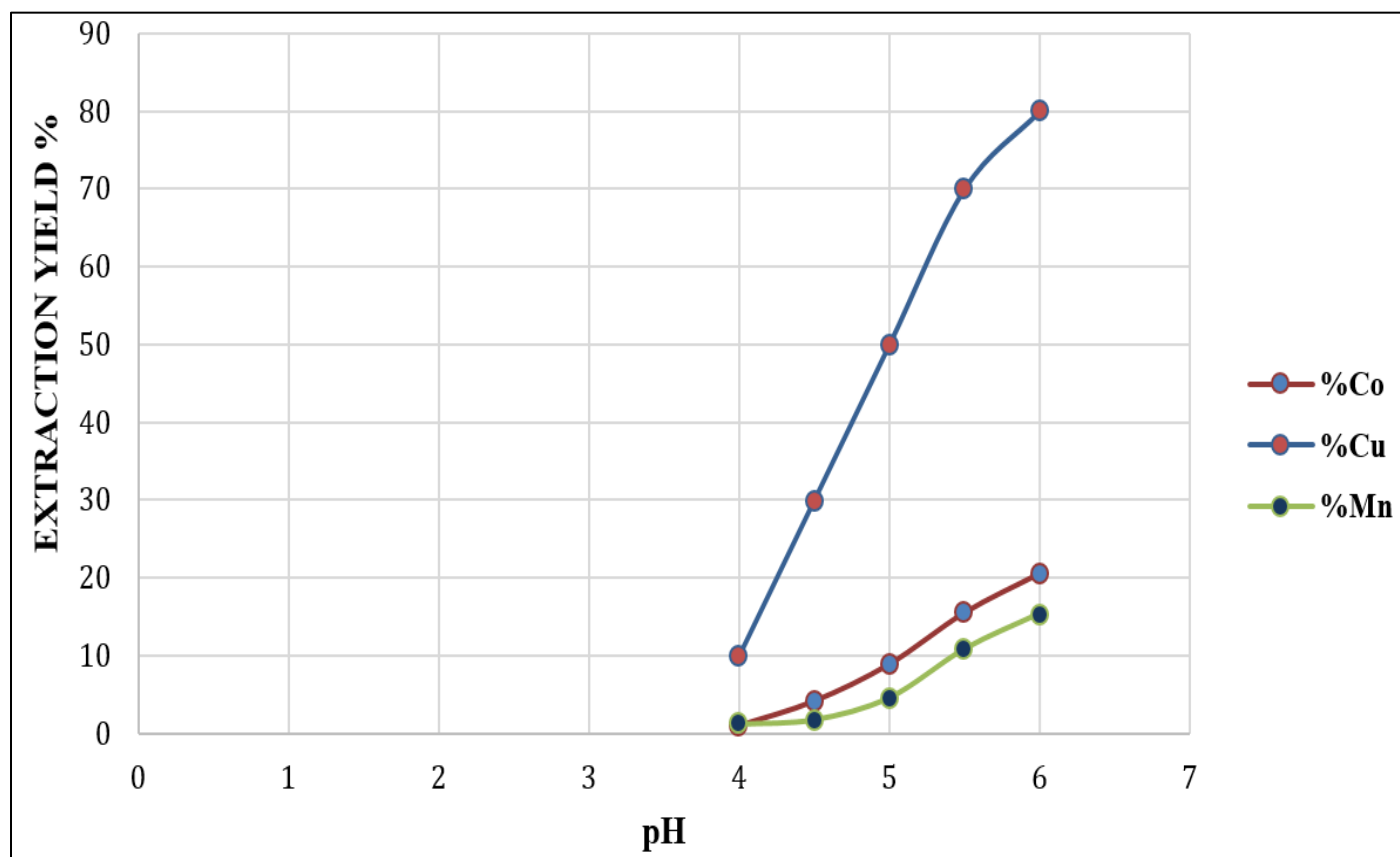


Fig 1 Variation in Metal Extraction Yield as a Function of pH

The results in Table 1 and Fig 1 show that pH significantly affects the extraction yield of metals, including Cu, Co and Mn, in the presence of Cyanex 272.

Analysis of the solutions from the extraction tests reveals that pH is one of the most influential parameters in cobalt extraction, which is consistent with Preston's (1982) work on proton exchange mechanisms. These tests show optimal extraction yields of around 80% Cu, 20% Co and 15% Mn. These results are very significant, highlighting the

effectiveness of the extractant (Cyanex 272) depending on the pH of the solution.

The higher extraction yield of copper, compared to cobalt and manganese, can be proven by the theory that states: Cyanex 272, applied to a cobalt-bearing solution containing other metals, has the ability to extract metals other than cobalt that are present in the solution before cobalt, hence the low extraction yield of cobalt. The phase separation time is one minute.

Table 4 Influence of Extractant Concentration (Cyanex 272) on Metal Extraction Yield

% V/V	Post-FAM raffinate [g/L]			Yields [%]		
Refined post-FAM	Co	Cu	Mn	Co	Cu	Mn
	6.94	0.1	1.75			
5	5.94	0.026	1.55	14.40	73.45	11.22
15	5.33	0.015	1.46	23.15	84.13	16.04
25	5.11	0.003	0.34	26.39	96.02	80.12
35	4.75	0.0013	0.035	31.46	98.61	97.96

• *Influence of Extractant Concentration (Cyanex 272% V/V)*

In line with the vision pursued in this work, in order to achieve the objective, it is undoubtedly fair to say that the extractant concentration will have a major influence on the cobalt extraction yield. The tests were conducted under the following conditions:

- ✓ pH: 6;
- ✓ Agitation: 360 rpm;
- ✓ Time: 5 min;
- ✓ Ratio (O/A): 1;
- ✓ %V/V of Cyanex: 5, 15, 25 and 35.

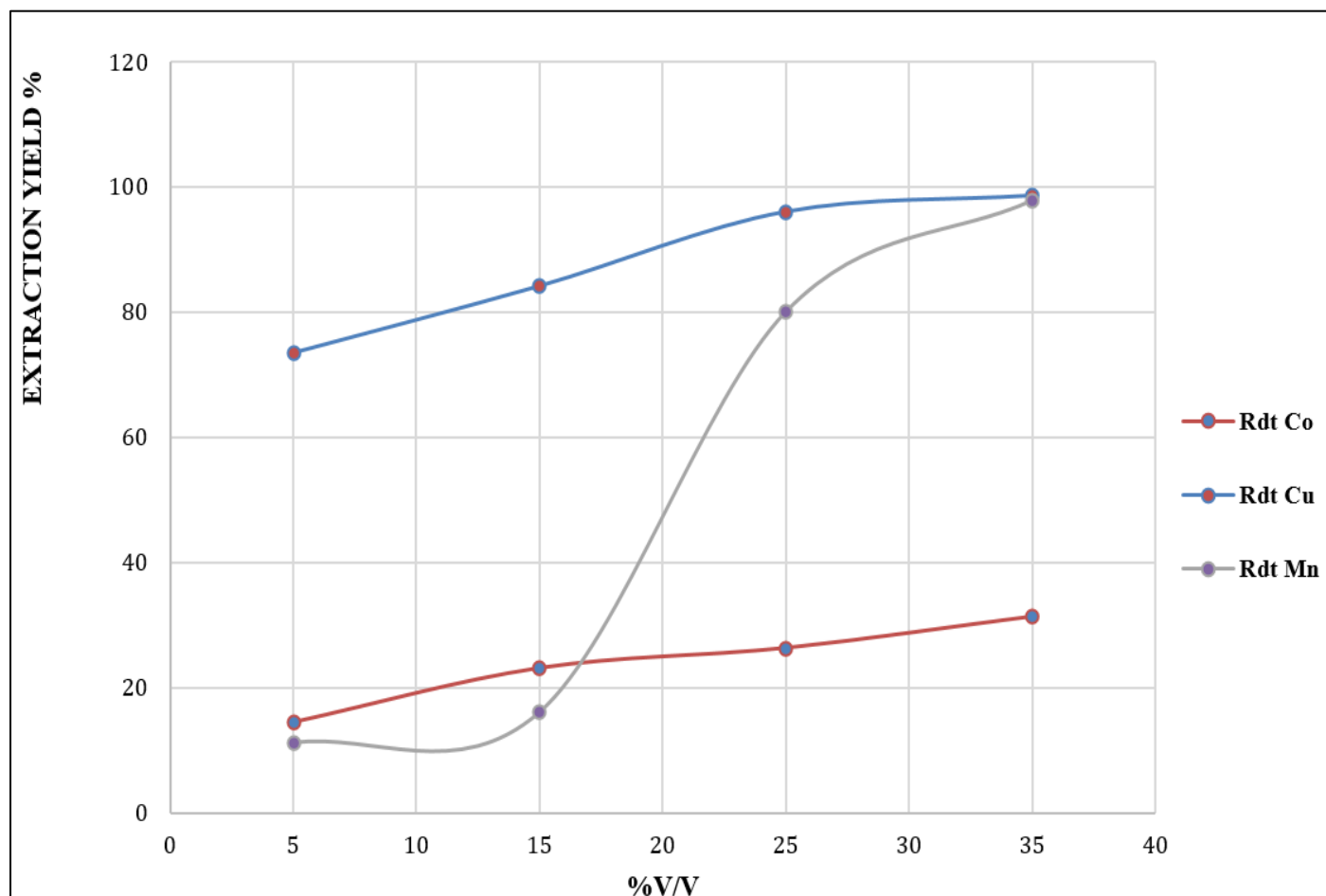


Fig 2 Variation in Metal Extraction Yield as a Function of Cyanex 272 Concentration

The test results clearly show that the extraction yield of cobalt, like that of other metals, varies with the concentration of Cynex 272 (extracting agent). These test results show that the extraction yield of certain metals varies slightly between 5% and 15% and becomes increasingly reliable at higher concentrations.

It is important to note that high organic concentrations require large quantities of extractant (cyanex 272), which becomes increasingly unavoidable for optimal cobalt extraction yield in the case of our study. As a result, the optimal

cobalt extraction yield was found at an extractant concentration of 35%, which gives a yield of 31.4%.

With a volume of 100 ml of organic material, prepared at 35%, requiring 35 ml of extracting agent (cyanex272), for only 31.4% cobalt extraction yield, this becomes problematic for the present work. Based on these results, we can say with certainty that Cyanex 272 becomes increasingly effective at extracting cobalt in the presence of a cobalt solution with 99% purity. The phase separation time is one minute.

Table 5 Influence of the Ratio on Metal Extraction Yield

Ratio (O/A)		Raffinate [g/L]			Yield [%]		
		Co	Cu	Mn			
Refined post FAM		6.94	0.1	1.17	Co	Cu	Mn
1/2	100/200	5.554	0.021	0.087	19,968	78,017	92,531
1/1	100/100	4,884	0.0019	0.0365	29.621	98.073	96,879
2/1	200/100	4,848	0.0007	0.0360	30.135	99.269	96.920

• *Influence of the (O/A) Ratio*

The ratio is a key parameter in solvent extraction, as it directly influences metal recovery in order to achieve optimal extraction efficiency. In order to achieve optimal cobalt extraction efficiency, a moderate variation in the ratio was studied. Operating conditions:

- ✓ pH: 6;
- ✓ Agitation: 360 rpm;
- ✓ Time: 5 min;
- ✓ Ratio (O/A): 1/1, 2/1, 1/2;
- ✓ %V/V: 35%.

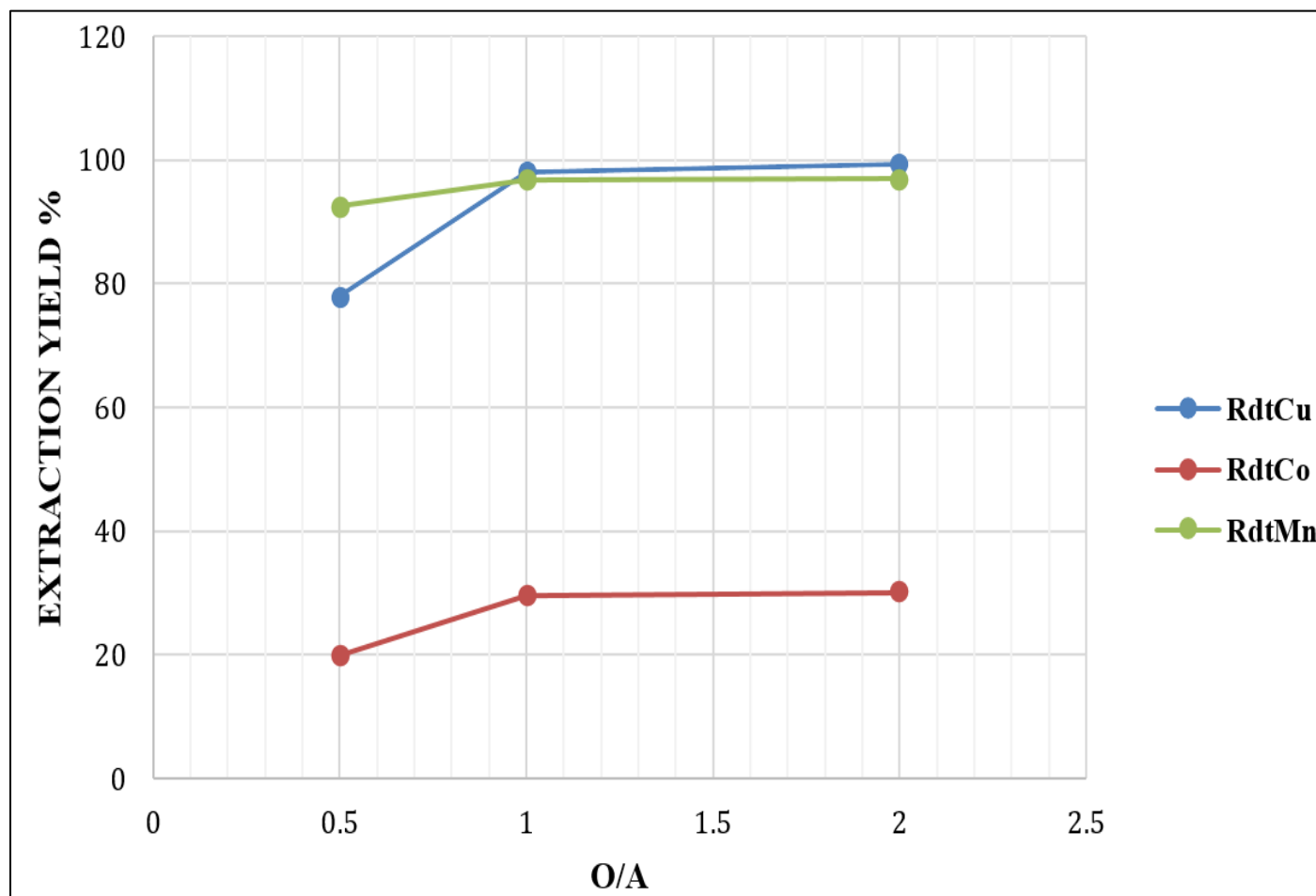


Fig 3 Variation in Metal Extraction Yield as a Function of the O/A Ratio

The test results clearly show that increasing the volume of the organic phase relative to that of the aqueous phase does not significantly improve the extraction yield of cobalt or other metals (Mn and Cu). The phase separation time is 57 seconds.

• Influence of Contact Time

In order to optimise the most influential parameters of cobalt solvent extraction, the contact time between the two phases (organic and aqueous) becomes an essential parameter to study.

Table 6 Influence of Contact Time on Metal Extraction Yield.

Time [min]	Raffinate [g/L]			Yield [%]		
Refined post FAM	Co	Cu	Mn	Co	Cu	Mn
5	4.842	0.002	0.124	30.226	97,822	89,325
10	4,779	0.001	0.044	31,135	98,316	96,218
15	4,954	0.001	0.034	28,614	98,014	97,034
20	5,142	0.009	0.129	25,907	90,351	88.893

The tests were carried out under the following operating conditions:

- ✓ pH: 6;
- ✓ Agitation: 360 rpm;
- ✓ Contact time: 5, 10, 15, 20 min;
- ✓ O/A ratio: 1;
- ✓ %V/V: 35%.

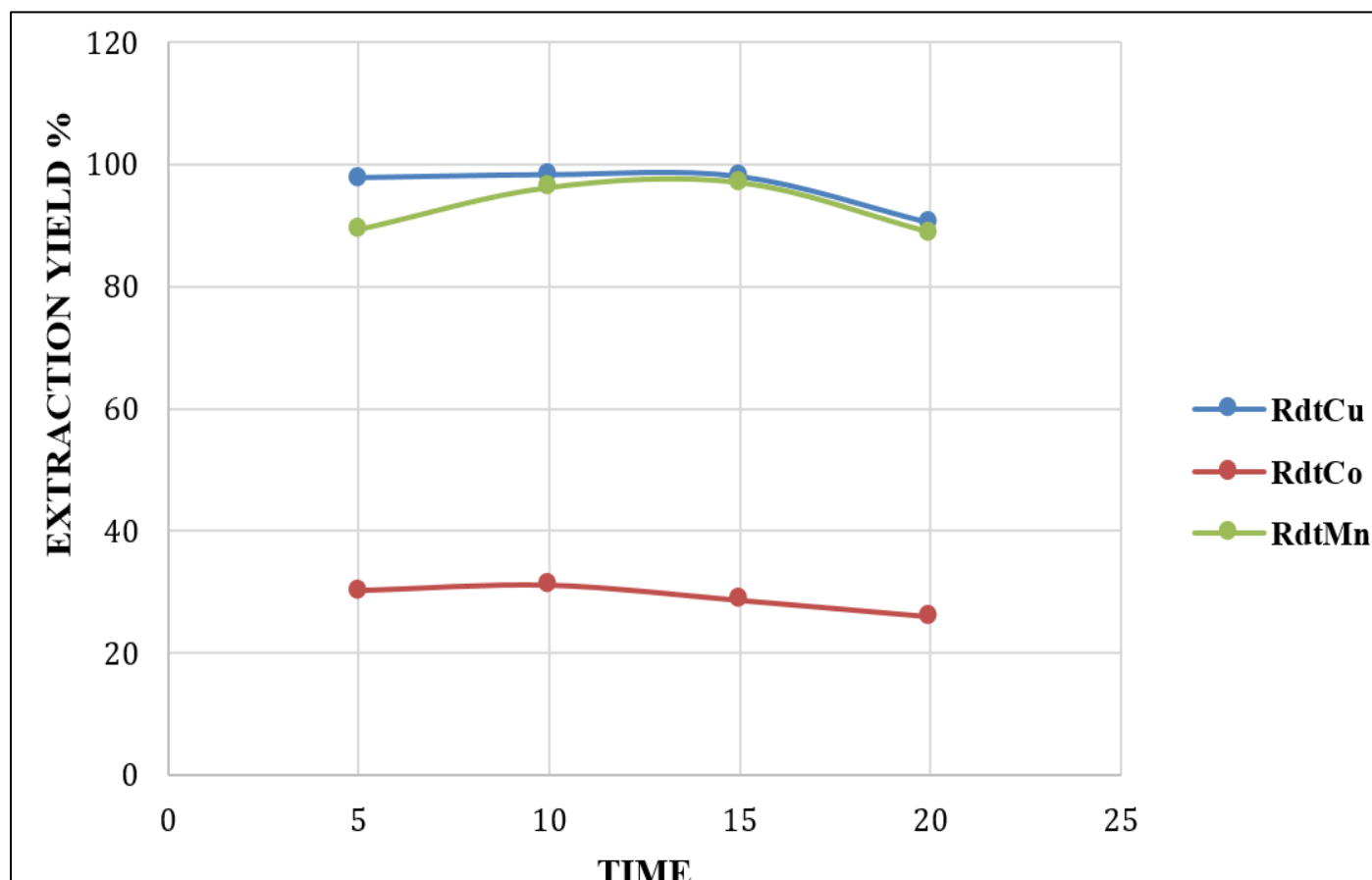


Fig 4 Variation in Metal Extraction Yield As a Function of Contact Time

Analysis of the results of cobalt extraction using Cynex 272 solvent sheds light on the variation in yields as a function of contact time. These results show a high and stable copper yield (98%), indicating the strong affinity of copper with the extractant (Cynex 272), although there is a slight decrease after 20 minutes of agitation. Cobalt yields are very low and decrease over time, from 30.22% to 25.9%, which explains the

inefficiency of Cynex 272 on cobalt in the presence of other metals under certain conditions. Manganese shows a gradual improvement in yield up to 15 minutes (97.03%), before a slight decrease at 20 minutes, suggesting saturation or decomplexation.

We can therefore say that the best extraction time is between 10 and 15 minutes, as this is where efficiency is most balanced. The separation time is 58 seconds.

➤ Partial Conclusion of Results

During the extraction of cobalt with Cyanex 272 at pH values between 4 and 6, analysis of the yields shows that cobalt has relatively low yields, unlike copper and manganese, which are extracted in large quantities.

However, operating parameters such as pH, ratio (aqueous phase/organic phase), contact time and extractant concentration were carefully respected and optimised. This demonstrates that the problem does not stem directly from the operating conditions, but rather from the chemical properties specific to the metals present and the selectivity of the extractant used.

Cyanex 272 is an organophosphorus acid extractant that works through a proton exchange mechanism. Its selectivity is based primarily on the difference in acidity or basicity of the metal ions, as well as on the pH of the solution. However, copper and manganese behave more basically than cobalt with respect to the extractant, which means that they react more easily with the phosphorus groups of Cyanex 272, even at low pH values (their affinity is high). These ions then take priority over the active sites of the extractant, to the detriment of cobalt.

This phenomenon can also be explained by the low intrinsic selectivity of Cyanex 272 in environments where several bivalent metals are present in competition. It is well suited for the separation of pairs such as Co/Ni, but becomes less effective when faced with metals such as copper and manganese, which have a stronger chemical affinity.

➤ Final Discussion s Compared with Existing Studies

Our work confirms that Cyanex 272, although highly selective for Co/Ni in model systems (Ayanda et al., 2013), loses its effectiveness in complex industrial solutions. The observed extraction order (Cu > Mn > Co) corresponds to the sequence established by Preston (1982) for organophosphorus extractants.

The extraction of Co by Cyanex 272 is highly dependent on pH, with a theoretical optimum of 5.3-5.5 (Ayanda et al., 2013), although in our case the maximum yield was observed at pH 6.0 due to competitive interference.

• Article 1 (Ayanda et al., 2013)

- ✓ Review of the use of Cyanex® extractants (particularly Cyanex 272) for Co/Ni separation.
- ✓ Cyanex 272 is the most widely used extractant for Co/Ni separation in sulphate and chloride media due to its stability, physicochemical properties and ability to prevent gypsum crystallisation.
- ✓ The Co/Ni separation factors are: DEHPA (14), PC-88A (280), Cyanex 272 (7000). Cyanex 272 has the best separation factor.
- ✓ Presents industrial process diagrams (Murrin, Bulong, Cawse) using Cyanex 272.

• Article 2 (Evans et al., 2012)

- ✓ Development of an integrated model for cobalt extraction with Cyanex 272.
- ✓ Modelling based on extraction isotherms as a function of pH and temperature.
- ✓ The equilibrium constants (k) for Co, Ni and Mg follow an Arrhenius relationship (except for Ni, which is less temperature-dependent).
- ✓ A Matlab model was constructed to simulate a 3-stage extraction circuit.

➤ Summary of Our Research

- ✓ Our work is an experimental study on the extraction of cobalt from an industrial solution (post-FAM from LAMIKAL) using Cyanex 272.
- ✓ The parameters studied are: pH, extractant concentration (%V/V), ratio (O/A), and contact time.

Table 7 Co/Ni Preferential Selection

Extractant	β^{CoNi}	Optimal pH for Co extraction	20°C	50°C
DEHPA	14	3.6 - 3.8	0.35	0.70
PC-88A	280	5.0	1.21	1.48
Cyanex®272	7000	5.3 - 5.5	1.58	1.94

- ✓ $\beta^{CoNi} = D(II)/Ni(II)$ partition coefficient; separation = $D(Co) / D(Ni)$;
- ✓ $D(M)$ = distribution coefficient of metal (M);
- ✓ Cu and Mn before Co (as indicated in our work: at pH 6, 80% of Cu and 15% of Mn are extracted, compared to 20% for Co).
- ✓ Ayanda's article mentions that Cyanex 272 can extract other cations (such as Cu and Mn) depending on the pH. Indeed, the reported extraction order is: Zn > Cu > Mn > Co > Mg > Ca > Ni

- ✓ $\Delta pH_{50\%Ni-Co} = pH_{50\%Ni} - pH_{50\%Co}$; $pH_{50\%M}$, half the extraction pH of metal ion M, corresponds to the distribution coefficient $D(M) = 1$. This corresponds to the results of our work.

• Key Results

- ✓ pH: Cobalt extraction yield increases with pH, but remains low (max 20.6% at pH 6). Copper and manganese are extracted more efficiently.

- ✓ Cyanex 272 concentration: At 35% V/V, the cobalt yield is 31.46%. However, copper and manganese are extracted at >98%.
- ✓ Ratio (O/A): No significant improvement beyond 1:1 (Co yield ~30%).
- ✓ Contact time: Optimal between 10-15 min (Co yield ~30%), then decreases.

• Interpretation and Comparison

✓ Selectivity of Cyanex 272

The work of (Ayanda et al.): Cyanex 272 is highly selective for Co compared to Ni (separation factor 7000). However, the study shows that Cu and Mn are extracted preferentially over Co. This is because the industrial solution used in our study contains Cu (0.07 g/L) and Mn (1.75 g/L) in addition to Co (6.94 g/L). Cyanex 272 extracts preferentially

✓ Influence of pH

Ayanda's work states that Co extraction by Cyanex 272 is highly dependent on pH. The optimal pH for Co is 5.3-5.5 (Ayanda). In Evans' model, the extent of extraction is modelled by an equation as a function of $[H^+]$.

Our work confirms that Co yield increases with pH (from 1% at pH 4 to 20.6% at pH 6). However, even at pH 6, the yield is low compared to Cu (80%) and Mn (15.4%). This confirms that pH is a key parameter, but the presence of other metals limits Co extraction.

✓ Extractant Concentration

For (Ayanda), an adequate concentration of Cyanex 272 is necessary. In industrial processes, typical concentrations are used. In our work, we found that at 35% V/V, the Co yield is only 31.46%, while Cu and Mn are almost completely extracted. This shows that even at high concentrations, selectivity for Co is poor in the presence of Cu and Mn.

✓ O/A Ratio

In the work of Evans and Ayanda, it is stated that in industrial processes, the O/A ratio is optimised (e.g. 1:1 or other). Evans' model assumes an O/A ratio of 1.

We have proven in our work that a ratio of 1 gives a Co yield of 29.6%. Increasing the ratio (2:1) does not significantly improve the yield (30.1%). This suggests that the ratio is not the limiting parameter.

✓ Temperature

Evans' work states that temperature affects Co (Mg) extraction via the Arrhenius relationship. For Ni, the effect is less significant. We did not take temperature into account in our work.

✓ Modelling

Evans' work developed a predictive model for Co, based on equilibrium constants and mass balances. It can simulate a multi-stage circuit. We did not develop any modelling. The results are purely experimental.

Table 8 Summary of Discrepancies and Recommendations

Parameter	Our work	Articles	Recommendations
Co selectivity	Low (Cu/Mn competition)	High for Co/Ni, but not for untreated Cu/Mn	Pre-treat the solution to remove Cu/Mn (e.g. precipitation).
Co yield	Max 31.46%	>95% in industrial processes	Optimise pre-treatment and use 2 extraction steps.
Optimal pH	6.0 (Co yield = 20.6%)	5.3–5.5	Test at pH 5.5 to improve Co/Ni selectivity.
Temperature	Not studied	Major impact (Arrhenius law)	Study the effect of temperature (35–50°C).

The low selectivity observed for Co in the presence of Cu and Mn confirms the need for pre-treatment steps, as suggested in standard industrial processes (Gupta & Deep, 2002; Zhang et al., 2016).

IV. CONCLUSION AND RECOMMENDATIONS

The study demonstrated that the effectiveness of Cyanex 272 for cobalt extraction is severely limited in LAMIKAL's multi-metal industrial solutions, with results showing that despite rigorous adjustment of operating parameters, the cobalt extraction yield (maximum 31.5% at pH 6, 35% v/v Cyanex 272, O/A ratio 1:1, and 10–15 min contact time) remains significantly lower than that of copper (98.6%) and manganese (97.9%). This limitation can be explained by the low intrinsic selectivity of Cyanex 272 towards cobalt in the presence of copper and manganese, whose ions (Cu^{2+} and Mn^{2+}) have a higher affinity for the phosphorous groups of the extractant.

➤ Conclusion of The Comparison

The work of Evans and Ayanda (especially Ayanda) highlights the high selectivity of Cyanex 272 for Co/Ni, but our work shows that in a real industrial solution (containing Cu, Mn, etc.), the selectivity for Co is compromised by the preferential extraction of Cu and Mn.

We can confirm that pH is a critical parameter, but even at optimal pH, the Co yield remains low (20-30%) in the presence of impurities.

The results of our work suggest that to improve Co extraction, a preliminary step to remove Cu and Mn (e.g. by precipitation) would be necessary, as is done in the industrial processes described by Ayanda (e.g. removal of Fe, Al, Cr before Co extraction). Parametric tests confirmed that:

- ✓ the pH (optimum at 6.0) and the concentration of Cyanex 272 (35% v/v) significantly influence yields;
- ✓ the O/A ratio (>1:1) and contact time (>15 min) do not bring about any notable improvement;

✓ the extraction order observed ($\text{Cu} > \text{Mn} > \text{Co}$) is consistent with the sequence $\text{Zn} > \text{Cu} > \text{Mn} > \text{Co} > \text{Ni}$ reported in the literature for Cyanex 272 (Preston, 1982; Ayanda et al., 2013).

The low yield observed can be explained by ionic competition with copper and manganese, as well as by the sensitivity of the process to pH conditions. To improve industrial performance, it is recommended to test mixtures of extractants (Cyanex 272 + D2EHPA), an approach that has shown promising results in recent studies (Zhang et al., 2016), and to investigate the possibility of selective copper pretreatment following the principles established by Gupta & Deep (2002). Simulate the process on a pilot scale to adjust the O/A ratios (Evans et al., 2012).

These optimisations will increase the purity of electrolytic cobalt and the operational stability of the process. These results highlight the inadequacy of Cyanex 272 alone for the efficient extraction of cobalt from industrial polymetallic solutions.

Despite its limitations, this study contributes to a better understanding of the industrial constraints associated with cobalt purification and paves the way for integrated protocols combining SX and complementary techniques for the sustainable recovery of complex mineral resources.

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