



Pertraction based separation of cobalt and aluminium from spent catalyst leach solutions

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Preface

Human nature is profoundly good, but in the same breath greedy and selfish. The opportunity to recover or regenerate anything seems like a positive fight-back. This thesis focuses on a newer technology (pertraction) that is safer and has a smaller environmental footprint than conventional technologies (mixer-settlers) to separate cobalt and aluminium. These metals' original intent was to act as a catalyst for Fischer-Tropsch reactions. The thesis will furthermore investigate the variables dictating the separation, determine optimal conditions for the separation to occur and obtain the relevant models to size a mixer-settler extraction phase as well as a pertraction extraction phase. To conclude the thesis, the two technologies will be compared on a preliminary feasibility study level.

Scientific outputs

This work has been orally presented at an international conference of solvent extraction (SXIX – in 2022 Gothenburg, Sweden) and a South African conference (SAIMM – in 2024 Stellenbosch, South Africa). Two articles have been accepted for publication, the content from Chapter 4 in the International Journal of Solvent Extraction and Ion Exchange, while the content of Chapter 3 has been published in the South African Institute for Mining and Metallurgy Journal (DOI: 10.17159/2411-9717/713/2025). A third article, based on Chapter 5, is yet to be submitted to the Journal of Metallurgy.

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It was only later in life that I realised that chemistry is one of my true passions. Being able to change things at a level we can't even see without understanding the reason for the change, was always something that intrigued me. Therefore, I would specifically like to acknowledge Lettie Fischer for being a science teacher at heart, a teacher whose spirit could light up the room and who directly influenced my love for science.

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Abstract

Fischer-Tropsch (FT) spent catalysts contain three primary metals: platinum, aluminium, and cobalt. While platinum recovery is well-established, aluminium and cobalt remain largely unutilised. This study explores the feasibility of separating and recovering aluminium and cobalt from spent FT catalyst leach solutions for potential agricultural applications (specifically focusing on aluminium). Two separation technologies were evaluated and compared: (i) conventional mixer-settlers and (ii) pertraction.

Initial shake-out mixer-settler experiments were conducted to determine optimal reaction conditions, followed by regression modelling to assess the influence of extraction variables. An industrial-scale mixer-settler system was also designed for the extraction step. Subsequently, benchtop pertraction experiments were performed under the optimal conditions identified from shake-out tests to evaluate the separation capability and obtain overall mass transfer coefficients. A dynamic model was developed to simulate benchtop membrane performance and provide insights into industrial scale pertraction implementation. Finally, a preliminary feasibility study compared both technologies from a Greenfield investment perspective.

The shake-out tests identified optimal conditions, achieving 87% aluminium extraction with 17% cobalt co-extraction at 50 mol.% pre-neutralisation, pH 3.13, and 40°C. A scrubbing step with an aluminium-rich solution at pH 2.8 removed >99% of cobalt, followed by stripping with 1 M H₂SO₄, recovering over 94% of aluminium. The final product contained 54 ppm cobalt, meeting the <100 ppm product specification. An industrial-scale mixer-settler design based on McCabe-Thiele analysis required two mixer stages and a 16.7 m³ settling tank to ensure effective phase separation.

Linear regression models failed to capture the complexity of the relationship between extraction efficiency and the targeted variables, necessitating the use of artificial neural networks. Among Levenberg-Marquardt, Scaled Conjugate Gradient, and Bayesian Regularisation algorithms, the latter demonstrated acceptable accuracy, with $R^2 = 0.99$ and a mean absolute error of 3.5%. The modelling results indicated that feed pH, composition, and pre-neutralisation equally influenced extraction efficiency, highlighting the need for control loops in industrial applications to maintain optimal performance.

Benchtop pertraction experiments confirmed the technology's capability to separate aluminium and cobalt. The experimental mass transfer coefficients for aluminium and cobalt were determined as 5.6×10^{-5} m/s and 7.4×10^{-6} m/s, respectively. The validated dynamic model predicted these coefficients with ~4% error and was used to assess four industrial-scale membrane options. The Liqui-Cel 14x40 (X40) membrane emerged as the best choice, offering a low pressure drop (~8 bar), minimal membrane requirements (13 modules in series), high overall aluminium recovery (85%), an optimal

production rate at a 16 m³/h minimum flow rate. The extraction phase of the PX technology required only ~0.6 m³ compared to the 16.7 m³ required for the mixer-settlers (due to the compact size of a membrane module while providing a very high surface contact area).

From a Greenfield investment standpoint, the choice between pertraction and mixer-settlers depends on process needs and constraints. Pertraction is preferred when space is limited, solvent losses must be minimised, high selectivity is required, or modularity and sustainability (location dependent and customer driven) are prioritised, while mixer-settlers offer proven reliability, easier troubleshooting, and are more suitable for high-throughput processes where footprint and solvent inventory are less of a concern.

Key words: Selective recovery, cobalt, aluminium, spent catalyst, solvent extraction, pertraction, mass transfer kinetics, artificial neural networks

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List of symbols

Symbol	Unit	Description
Solvent extraction		
EE	%	Extraction efficiency
$x_{i,feed}$	g/L	Concentration of metal i in the feed
c_{ext}	g/L	Concentration of metal i in the extract
$x_{i,raf}$	g/L	Concentration of metal i in the raffinate
c_{raff}	g/L	Concentration of metal i in the raffinate
$m_{i,org}$	g	Mass of metal i in the organic phase
$m_{i,aq}$	g	Mass of metal i in the aqueous phase
V_{aq}	m ³	Volume of aqueous phase
V_{org}	m ³	Volume of organic phase
Q_c	m ³ /s	Overflow rate of the continuous phase
Q_d	m ³ /s	Overflow rate of the dispersed phase
A_I	m ²	Area of the interface
v_c	m/s	Terminal settling velocity of a droplet in the continuous phase
v_d	m/s	Terminal settling velocity of a droplet in the dispersed phase
t_d	s	Time required to cross the dispersion band
T_{av}	s	Average residence time of the dispersed phase
T_{minD}	s	Minimum residence time
Re	-	Reynolds number
M^{n+}	-	Metal (M) with n valence
Linear and non-linear regression		
N_h	-	Number of hidden neurons
n_{in}	-	Number of input variables (dimensions)
n_{out}	-	Number of output variables (dimensions)
RMSE	-	Root mean square error
MAE	-	Mean absolute error
e	-	Error
p	-	Predicted value
a	-	Actual value
I	%	Relative importance
w	-	Neural network weights
m	-	Number of hidden neurons
H	-	Coefficients A-E
n	-	Number of samples / output neurons
k	-	Number of input neurons
D	-	Distribution coefficient
y	%	Experimental extraction efficiency data
$\hat{y}$	%	Predicted extraction efficiency data
x	-	Input variables
CF	-	Cost function
γ	-	Strength of penalty term
A-D	-	Coefficients
E	-	Bias

Symbol	Unit	Description
Mass transfer		
V_{mod}	m^3	Volume of the membrane module(s)
V_{Batch}	m^3	Volume of the initial batch
k_{var}	m/s	Calculated varying mass transfer coefficient
V_{aq}	m^3	Volume of aqueous
V_{org}	m^3	Volume of organic
V_{pores}	m^3	Volume of pores
$k_{exp,ov}$	m/s	Experimentally determined overall mass transfer coefficient
A	m^2	Cross sectional area of membrane shell
m	$\%/s$	Slope required to calculate the mass transfer coefficient
Q	m^3/s	Flow rate
J	$kg\ m^{-2}\ s^{-1}$	Flux – movement of solute per unit area
F	-	Driving force function
K_{var}	m/s	Predicted overall mass transfer coefficient
K_m	m/s	Membrane pore mass transfer coefficient
K_{tube}	m/s	Membrane fibre side mass transfer coefficient
K_{shell}	m/s	Membrane shell side mass transfer coefficient
$d_{f,in}$	m	Diameter of the fibre inner
$d_{f,out}$	m	Outer diameter of the fibre
d_{mod}	m	Diameter of the module
ϵ	-	Membrane porosity
τ	-	Membrane tortuosity
δ_m	m	Membrane wall thickness
μ	$Pa\cdot s$	Dynamic viscosity
L	m	Length of membrane
ρ	kg/m^3	Fluid density
Sh	-	Sherwood number
Re	-	Reynolds number
$\bar{u}$	m/s	Fluid velocity
ϕ	-	Packing density
Sc	-	Schmidt number
β	-	Non-dimensional randomness factor
ν	m^2/s	Kinematic viscosity
z	m	Distance through the membrane
C_s	g/L	Concentration of solute
ΔP	Pa/m	Pressure drop
f	-	Darcy-Weisbach friction factor

1 Introduction

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1.1 Background

In 1922, Franz Fischer and Hans Tropsch developed a process to convert synthetic gas (syngas), consisting mainly of CO and H₂, into different hydrocarbons to produce products such as oil, petrol, diesel and a variety of other chemicals [1]. The syngas can be derived from natural gas, coal or (more recently) biomass [2]. This conversion became known as the Fischer-Tropsch Synthesis (FTS). While alternative energy sources are being developed, the increase in population remains a driver for the rising demand for fuel and chemical products to which the FTS supply contributes [3].

An essential component of the FTS reaction is its catalyst. Commonly, ruthenium-based, nickel-based (Ni), iron-based and cobalt-based catalysts have been used [1], [2], [4], [5]. Due to their reasonable cost, high activity, product slate, selectivity and longer lifetime, cobalt-based catalysts are currently the common choice [3], [6]. Generally, these cobalt-based catalysts consist of ~10 wt.% Co, <~2 wt.% Pt, with the remainder made up of support, which is usually Al₂O₃-based [3].

Due to a loss of catalytic activity, catalysts deteriorate over time, known as catalyst deactivation [7]. This deactivation can result from a combination of poisoning, fouling or ageing [8]. Once the catalyst activity becomes too low to maintain the desired productivity, a new catalyst batch is introduced. Currently, companies such as Minemet recover the platinum component from the spent catalyst, while the residual cobalt and aluminium tend to be discarded. However, due to possible agricultural benefits and uses, there is a need to recover the residual cobalt and aluminium.

Apart from its current use in various products ranging from alloys to art supplies, cobalt is used in agriculture to both increase crop yields and decrease vitamin B₁₂ deficiencies in livestock [9], [10]. In addition to aluminium's wide use in construction, such as aerospace or beverage containers (due to its high strength-to-weight ratio), aluminium can be used to alter the pH of the soil and consequently allow acidic soil plants to flourish [11], [12].

Since the cobalt and aluminium must be separated for most applications, the purpose of this study was to investigate the recovery and separation of cobalt and aluminium from spent FTS catalysts. Two routes were considered for this purpose: mixer-settlers (conventional solvent extraction (SX) technology), commonly used for hydrometallurgical separations and pertraction (PX), a relatively new technology, which uses SX-based separation principles but enforces the separation in a different equipment design [13]. The main difference between mixer-settlers and PX is that the PX technology contains a physical separator (membrane) between the organic and aqueous phases, providing numerous advantages over the mixer-settler technology, such as a known contact area, safer operations and reduced plant footprint [14].

While the mixer-settler separation of cobalt and aluminium has been studied by researchers like Tsakiridis and Leonardou [15] and Torkaman et al [16], both the application and source material differed in this study. The first step was therefore to determine the optimal conditions for the mixer-settler separation of cobalt and aluminium from the spent FTS catalyst. This entailed exploring how feed pH, pre-neutralisation and feed composition influence the separation efficiency, using both linear and non-linear regression techniques. A high-level sizing of the main equipment (mixer-settler) was also conducted to compare the conventional technology's footprint with that of the alternative PX technology. Since mixer-settler and PX facilities consist of the same repeating technology blocks (i.e. extraction, scrubbing and stripping), the sizing was only done on the extraction stage, with the findings assumed to apply to the scrubbing and stripping stages.

Literature on PX facilities is limited, with no information found on the separation of cobalt and aluminium using PX. Hence, to be able to compare a mixer-settler and PX, the first step in the PX research section was to establish experimentally whether PX could separate cobalt and aluminium. Secondly, an industrial PX facility's footprint would have to be designed. In-depth sizing and mathematical modelling procedures are well established for the mixer-settler technology, but not for the PX technology. Therefore, with the aid of existing mass transfer rules, liquid-liquid separation principles and coding programmes like Python, a fit-for-purpose mass transfer equation should be developed to estimate the size of an industrial facility.

The mass transfer equation would not only be a function of factors such as the membrane characteristics and fluid properties, but it would also depend on the flow regime and driving force to transfer from one liquid to another. Of these factors, the membrane characteristics and fluid properties are constant values that are relatively easy to obtain from the technical datasheets. However, the flow regime and the drive to transfer are expected to vary as a function of the distance through the membrane and the metal concentrations respectively. To quantify the metals' drive to transfer, the distribution coefficient was used while the Sherwood number provided a method to classify the flow regime.

For PX, different methods of quantifying the distribution coefficient were explored to provide a better understanding of the relationship between the distribution coefficient and the remaining metal ions in the aqueous phase. Additionally, since PX is a relatively novel technology, a tailored Sherwood approximation would have to be developed to capture the resistance to metal transfer specific to PX applications. Properly quantifying both the distribution coefficient function and the Sherwood equation was critical to mathematically determine the overall mass transfer coefficient at each point in the membrane. In addition, the varying mass transfer coefficient of a membrane module had to be mathematically determined based on the equipment and fluid characteristics for the sizing calculations for industrial scale membranes.

To verify the hypothesis that the PX technology offers advantages, such as requiring less space, over the traditional SX technology, both technologies were assessed in terms of sizing and key business-related factors. These factors include construction complexity, technology robustness, and their suitability as a future-proof Greenfields facility investment. The findings would contribute to a high-level pre-feasibility study.

1.2 Problem statement

The primary research question of this study was to compare the PX-based separation of cobalt and aluminium (from spent FTS catalysts) to conventional mixer-settler technology.

1.2.1 Research questions

1. What is the effect of the pre-neutralisation of Cyanex272 on the separation efficiency of SX?
2. What are the optimal conditions used to separate cobalt and aluminium with SX?
3. How sensitive is the mixer-settler separation efficiency to the operating variables?
4. Can PX be implemented for this separation?
5. How do Greenfields conventional mixer-settlers compare to PX?

1.3 Aim and objectives

This study aimed to determine the preferred technology for new Greenfields facilities by comparing the suitability of both mixer-settler and PX technologies for the recovery and separation of cobalt and aluminium from a synthetic solution representing the spent FTS catalyst solution after platinum removal. The objectives were:

Objective 1: To optimise SX experimental conditions and size an extraction phase mixer-settler

- a) Determine the optimal organic phase composition in SX.
- b) Establish overall SX optimal conditions for separation.
- c) Size the extraction phase mixer-settler required for the separation.

Objective 2: Apply linear and non-linear modelling techniques to SX experimental results

- a) Quantify the variables affecting the extraction efficiency of aluminium and cobalt in SX applications with the use of linear and non-linear modelling.

Objective 3: Determine if the PX technology is capable of separating cobalt and aluminium and size an industrial extraction PX phase

- a) Determine the mass transfer kinetics for the PX separation.
- b) Size the membrane required for the PX extraction step.

Objective 4: Compare the two technologies

- a) Compare the mixer-settler and PX technology with a quantitative pre-feasibility study.

1.4 Thesis overview

After the introductory chapter (Chapter 1) provided the background, scope, aim and objectives and thesis overview, a comprehensive literature review is presented in Chapter 2. It provides an in-depth overview of relevant terminologies and phenomena, including Fischer-Tropsch synthesis, catalyst theory, the applications of cobalt and aluminium and metal separation techniques. In line with the aim of this study, attention was also given to SX and PX, with detailed discussions on conventional SX equipment and PX systems.

Following the literature review, the thesis is structured into three content chapters, each presented in article format starting with a brief introduction outlining its purpose, followed by a description of the methodology applied and the results obtained before concluding with a summary of the key findings and references pertaining to that chapter. The thesis was structured in article format to present each of the three content chapters as self-contained studies. Given the mathematical nature of the work, this format allows for a clearer discussion of the methods and results, making it easier for the reader to follow the logic and progression of each. Table 1.1 offers an overview of the content chapters along with the corresponding objectives as outlined in Section 1.3.

Table 1.1. Thesis outline of content chapters and the corresponding objectives

Chapter number	Content chapter	Objective
3	Separation and recovery of cobalt and aluminium from spent gas-to-liquid catalyst using Cyanex272.	1
4	Modelling the selective recovery efficiency of cobalt and aluminium with linear and non-linear regression techniques.	2
5	Adapting the Sherwood number for mass transfer modelling in pertraction-based separation of cobalt and aluminium from spent catalyst leach solutions	3
6.1.4	Comparison of industry scale mixer-settlers and pertraction facilities as new Greenfields investment options	4

Finally, the evaluation, conclusion and general recommendations are presented in Chapter 6, critically assessing whether the work presented in this thesis addresses the initial aim and objectives. Apart from summarising the results, the conclusion also discusses their implications for the field. Finally, recommendations are presented, offering suggestions for future studies that can enhance the understanding of the mixer-settler and PX based separation and recovery of cobalt and aluminium from a spent FTS catalyst.

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2 Literature study

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2.1 Introduction

This chapter stands to inform the reader on important concepts that appear in the succeeding chapters. Figure 2.1 provides the general philosophy behind the literature study, indicating the main ideas to be discussed. Section 2.2 first focuses on the use of an FTS reaction and explains the need for a catalyst. The theory and composition of the specific catalyst used in this study is explained in Section 2.3. Next, the uses of cobalt (Co) and aluminium (Al) are expanded on (Section 2.4). Numerous techniques have been used to separate these two metals. The literature-based findings on these techniques are explained in Section 2.5. The conventional SX technique and PX technique are discussed in Section 2.6 and Section 2.7 respectively, as it is the focus point of this thesis and deserves greater attention.

Specifically considering SX, the separation principle and main variables affecting the separation efficiency are discussed. Thereafter, forming part of Section 2.6, conventional SX equipment is explained as it applies to the sizing that follows in Chapter 3. To conclude this chapter, Section 2.8 touches on terminology related to feasibility studies that will be employed when comparing the two technologies.

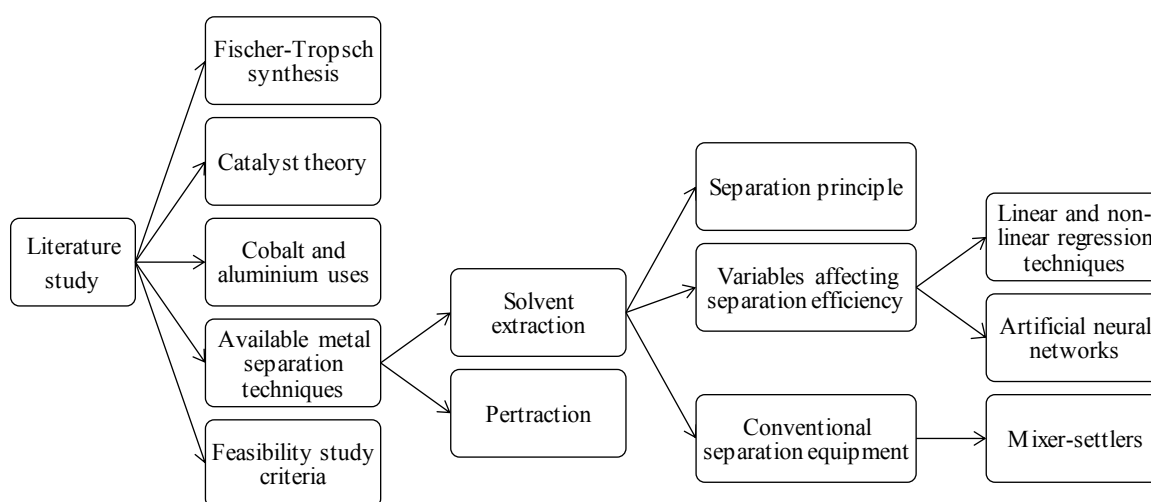


Figure 2.1. Literature review outline

2.2 Fischer-Tropsch synthesis

In 1922, Franz Fischer and Hans Tropsch developed a means to convert synthetic gas (syngas) into different hydrocarbons with the use of a heterogeneous catalysed reaction called the FTS [1]. The different hydrocarbons can be converted into products such as oil, petrol, diesel and a branch of chemicals. The work offered hope to countries that do not have oil reserves as a natural resource as they could now produce fuel-related products and not only rely on imports. South Africa started using this

technology in the 1950s to produce fuels from coal. This helped relieve the pressure on the country because of the sanctions imposed at that time.

The FTS mechanism can be described as three major steps, i.e., adsorption, chain initiation and chain termination. Initiating the chain FTS typically requires a heterogeneous catalyst. The most used catalysts for FTS include ruthenium-based, nickel-based, iron-based and cobalt-based catalysts [1], [2], [3], [4]. Ruthenium-based catalysts are highly active and very selective for FTS, but the downfall lies in their scarcity and unsuitability for commercial use. Nickel-based catalysts have a high hydrogenation activity and are therefore undesired due to high selectivity with respect to methane production. The disadvantage of iron-based catalysts is their characteristic of being active during the water gas shift reaction, consequently producing more CO_2 , but it can be a desired catalyst depending on the chosen product slate [2]. The cobalt-based catalyst has reasonable cost, high activity, selectivity superior to iron, while also producing lower CO_2 emissions [5]. The cobalt-based catalyst further displays a longer lifetime and higher CO conversion in comparison with iron-based catalysts [6]. Cobalt-based (Co-based) catalysts are consequently the most widely used catalysts for gas-to-liquids processes.

2.3 Catalyst theory

Conventionally, a heterogeneous catalyst consists of three components: an active phase component, the promoter and the support on which the active and promoting components are dispersed. The active phase of the FTS catalyst used here refers to the Co metal mentioned earlier [1]. The reduction of the active phase is necessary when a catalyst needs an activation state that the active phase does not have in its natural form [7]. Effective reduction of the active phase therefore plays a key role in the overall performance of the catalyst. This can be achieved by adding small amounts of promoters, which in effect significantly improves the reducibility of Co. The promoters will improve both the activity and the selectivity of the catalyst by altering the electronic character of the active phase. In general, certain transition metals, i.e., copper, palladium, platinum and ruthenium are used as promoters of Co-based FT catalysts [1].

Typical composition of the FTS Co catalyst is ~10 wt.% Co, <~2 wt.% Pt (platinum) and the remainder consists of support [6]. The morphology, porosity and resistance to attrition are all crucial factors in the support of the catalyst. The support consequently also plays a great role in the stability of the catalyst. Aluminium oxide (Al_2O_3), silicon dioxide, titanium dioxide and zirconium dioxide are typically used in FTS due to their high surface areas and good mechanical strength [1].

Due to the loss of catalytic activity, catalysts deteriorate over time, which is known as catalyst deactivation [4]. This deactivation can result from a combination of poisoning, fouling or ageing. Once the catalyst activity becomes too low to maintain the desired productivity, a new catalyst batch is

introduced. However, due to the value of Pt, to ensure that the FTS process is sustainable and economically feasible, the focus has been on the recovery of Pt [8]. However, the recovery of the remaining metals, Co and Al, also need to be prioritised to ensure that circularity in the metal lifecycle is pursued, not only from an environmental perspective, but also from a catalyst viability perspective. Both Co and Al have numerous uses as presented below.

2.4 Uses of cobalt and aluminium

The popularity of Al is mainly due to its wide variety of uses since it has a lucrative high strength to low weight characteristic. It is commonly used in beverage containers, aerospace, windows, doors and other construction materials [9]. On the other hand, Co uses stretch from health and nutrition to the alloy industry. Approximately 50% of the yearly cobalt use is allocated to alloy production in industry [10]. These alloys have been used in the production of jet engines, gas turbine engines, compasses, microphones, batteries and cutting tools.

Aside from the numerous uses of Co and Al mentioned above, this paper focuses specifically on its use in the agricultural industry. Co is needed in agriculture due to its role in the nitrogen fixation step in plants and the synthesis of vitamin B12 in animals [11]. The most obvious markers in crops indicating a Co deficiency are the yellowing and stunting of crops. These symptoms were first noted in peanuts. The addition of 8 ppm Co dissolved in water led to an increase of 34% in overall peanut growth. The success of growth was attributed to an increase in nitrogen fixation [11]. Co deficiency symptoms in livestock are related to vitamin B12 deficiency symptoms. Vitamin B12 is necessary for a healthy metabolism, good energy and the production of red blood cells. Common symptoms displayed by most livestock include a reduction in appetite, scaly ears and anaemia. Co can be administered to livestock either by means of crop, crop fertiliser, or supplements [12].

Aside from the possible use of Al in tractor components, it is also very important to acidic plant life, despite the contrasting views on the uses of Al in soil. It has recently been discovered that Al stimulates root growth, leading to stronger plants since a greater area exists to take up water and nutrients to supply to the plant [13].

Consequently, in this study, the aim was to effectively recover Co and Al from spent FTS catalysts for agricultural applications. Two final product specifications could be targeted – as requested by Minemet (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.

2.5 Separation techniques

There is a drive to recover Co and Al. However, recovery specifically for use in agriculture implies separation to a certain purity, as specified in Section 2.4. Fortunately, numerous techniques have been developed to date to separate metals. The branch of science dedicated to the properties of metals, their production and their purification is known as metallurgy. The process of recovering the metals (usually from ore) can be divided into three steps, i.e., mineral processing, physical separation and pyrometallurgy or hydrometallurgy. Mineral processing refers to the crushing/grinding of the ore. Hereafter, physical separation and concentration that takes place. Physical separation techniques include gravity separation or magnetic separation [14].

Once the metal ores have been subjected to physical separation methods, further purification or extraction of the desired metals is done during the pyrometallurgy or hydrometallurgy steps. Both these categories of techniques are very successful [15]. Hydrometallurgy uses an aqueous solution to extract metals, whereas pyrometallurgy uses high temperatures. One major drawback of pyrometallurgical techniques is their reliance on high temperatures, leading to significant energy consumption. In regions with high electricity costs, hydrometallurgy therefore emerges as a more attractive alternative [15].

Hydrometallurgical techniques include leaching, precipitation, ion exchange, crystallisation, SX and more recently, PX. Leaching is defined as the process of transferring targeted species from a solid to an aqueous phase [16]. Precipitation is the process of forming a solid in a solution and thereafter separating the liquid and solid phases [17]. SX is the exchange of a metal between two immiscible liquids based on a difference in solubility [18]. Mixer-settlers are the conventional technology used to enforce the SX separation principle today. Mixer-settlers forces maximum contact by mixing the two phases. During the mixing, it is aimed to achieve optimal droplet sizes to maximise contact area for the mass transfer. Thereafter, a settler is required to separate the two phases on a gravitational, density separation principle. Finally, PX, also called membrane-based SX, is where a membrane is introduced to avoid the need for mixing the two immiscible liquids [19].

Numerous studies to separate Al and/or Co with these techniques were conducted in the past with varying success. In 2008, Li-ion batteries consisting of Al and LiCoO_2 as cathodes were separated from copper (main component within anode) with the use of a leaching and crystallisation mechanism [20]. To clarify, crystallisation differs only from precipitation based on the product. Crystals form (meaning well-structured 3D solids) during crystallisation, whereas more amorphous solids form with precipitation [21]. The leaching of the cathode with sodium hydroxide (NaOH) proved to be very selective with respect to Al. It was found to be very sensitive to the NaOH concentration while practically being unaffected by temperature changes, which is uncommon in the leaching environment.

Further leaching of LiCo_2 led to a recovery of 97% of Co [20]. The main drawback of leaching is the generation of acidic waste, which poses significant environmental concerns [22].

Precipitation has been used for decades. Dating back to the early 1940s, Al has been separated from Co with the use of precipitation [23]. It has also been reported that leaching and precipitation have been combined. During this process, leaching proved to be a better option for the separation of Al, and the Co is precipitated out thereafter. The efficiency of the Co separation was reported as an astounding 100% [24]. However, the recovery of the hydroxide precipitation results in a very low purity of the recovered metals. This raises the need for post-treatment to obtain the desired purity [24].

SX is the preferred separation technique compared to leaching and precipitation due to its excellent selectivity with respect to numerous metals [25]. Specifically considering Co and Al separation, studies have proven that SX is an efficient and viable option [26], [27]. SX is therefore used in this study as a technique to separate Co and Al. Since similar studies have been conducted, this paper's experiments on SX can be validated. However, since PX poses numerous advantages over mixer-settlers, its capability is also investigated in this study. SX and PX are thoroughly discussed below.

2.6 Solvent extraction

SX was initially mainly a technique used to separate metals of very similar chemical characteristics. However, the Manhattan Project during the Second World War led to the industrialisation of SX as it was used to separate the isotopes used in nuclear weapons. Now, SX is used across numerous industries, such as the pharmaceutical industry, agriculture, and in the refining of precious metals [25]. The use of SX is now known for its excellent selectivity with certain metals while using stable extractants [25]. The generalised SX process is presented in Figure 2.2. To understand the jargon used in the remainder of the thesis, some terminology related to SX is discussed below.

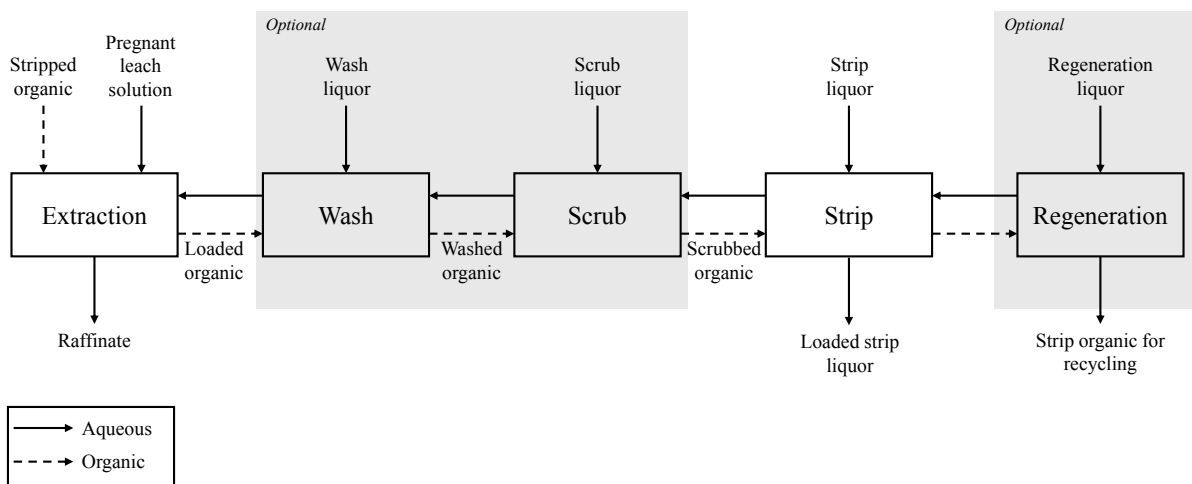


Figure 2.2. Block flow diagram of a generalised SX process [25]

2.6.1 Separation principle

The aqueous feed solution contains a mixture of metals, one of which is the desired metal. In hydrometallurgical applications, this is generally referred to as the pregnant leach solution (PLS) or the feed. Depending on the capabilities of a plant, the organic phase can be cleaned (stripped of any impurities) at the end of the process and recycled to the beginning to re-use. It is therefore known as the stripped organic phase. The organic phase is also known as the extractant, usually consisting of the extractant itself, a modifier and a diluent.

When the two immiscible liquids make contact, the desired metal species are transferred to the organic phase, hereafter known as the loaded organic phase or extract. The raffinate refers to the aqueous phase exiting the extraction circuit, which is now to an extent depleted of the desired metal [25].

In the strip circuit, the aqueous strip liquor is brought into contact with the loaded organic phase to strip the organic phase of the desired metal. Hence, the desired metal once again relocates to the aqueous phase. The organic phase exiting the strip circuit is hereafter referred to as the stripped organic phase, while the concentrated aqueous phase is referred to as the loaded strip liquor. In some instances, the aqueous phase may remain entrained in the organic phase during the extraction circuit, which will result in less-than-optimal separation. To improve this situation, a wash circuit can be incorporated [28]. The aqueous wash liquor is added to the loaded organic phase. This allows the removal of unwanted aqueous molecules entrained in the organic phase [25].

In an ideal world, the desired metal will completely and solely be extracted by the extraction circuit. However, in numerous cases, additional metals are co-extracted with the desired metal. To remove unwanted co-extractants, the scrubbing circuit can be implemented. An aqueous scrub liquor is introduced and contacts the loaded organic phase. This produces a scrubbed organic phase, mainly consisting of the desired metal by removing the co-extracted metals to the aqueous phase. The scrub circuit is not necessary for all extractions, for instance during separation with high selectivity with respect to a desired metal [25]. Note, however, that washing and scrubbing are used interchangeably in literature and may be perceived as having a different purpose in other papers. The definition of each given above will be used as trivial in this thesis. However, overall, the term scrubbing is preferred above washing based on IUPAC recommendations [29]. Finally, the regeneration circuit is sometimes incorporated to recycle the organic phase for re-use in the process and therefore reduces operating cost [25].

The performance of this technique is quantified as the separation efficiency as shown in Equation (2-1). When designing a SX plant, the aim is to achieve optimal separation efficiency. One of the techniques used to maximise the separation efficiency is operating on a counter-current basis (referring to the flow

of aqueous and organic streams) as shown in Figure 2.2 [30]. Counter-current operation ensures maximum concentration gradients, which acts as a drive for the mass transfer to occur over the contact surface.

$$EE = \frac{x_{i,feed} - x_{i,raf}}{x_{i,feed}} \times 100 \quad (2-1)$$

Where EE refers to extraction efficiency (%), $x_{i,feed}$ and $x_{i,raf}$ refers to the concentration (g/L) of metal component i in the feed and the raffinate respectively.

However, the separation efficiency is governed by the distribution coefficient. It is a measure of how the metal distributed itself between the organic and the aqueous phases [31]. Therefore, it also quantifies the drive for a metal to transfer from one phase to another. This drive to separate can further be dependent on numerous factors specific to the metals in need of separation.

Specifically related to Co and Al separation, a collection of literature results indicates that the main factors affecting this separation efficiency are (i) the type of organic phase used, (ii) the extent of pre-neutralisation carried out on the organic phase, and (iii) the feed pH [26], [27], [32].

2.6.2 Variables affecting the separation efficiency

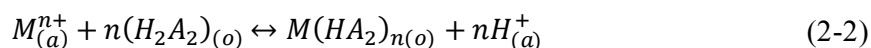
The main variables are mentioned above. Since the main metal ion separation occurs during the extraction step, most of the emphasis is on this step. However, the scrubbing and stripping steps remain important as they determine the purity of the product and the recovery attainable. These steps are discussed after the extraction variables have been explained.

2.6.2.1 Extraction

As mentioned in the previous section, the organic phase is one of the most important factors, along with aqueous pH, and will set the maximum limit for separation efficiency, assuming reaction conditions are optimal. The organic solution introduces a difference in solubility to the desired metal from what the aqueous phase can offer. This sets the capacity of how much metal will relocate to the organic phase during extraction. It is therefore understood that this choice is crucial. Fortunately, decades of research have gone into the extraction of metallic ions using organic solvents. The main extraction mechanisms include acidic extractants, solvating extractants and basic extractants. Makanyire et al provide the mechanisms of each [18]. They follow below.

a) *Acidic extractants*

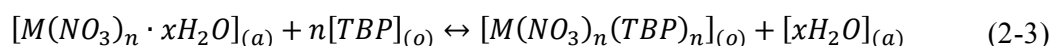
An acidic extractant uses a cation exchange mechanism as shown in Equation (2-2). A hydrogen ion from the extractant is displaced by the desired metal ion. Conventionally used acidic extractants include phosphoric, phosphonic and carboxylic acids. These extractants exist in a dimeric form expressed as H_2A_2 once dissolved in organic solvents [18].



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

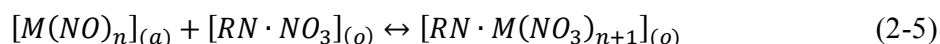
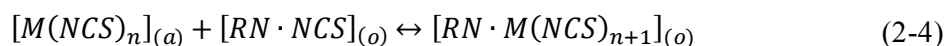
b) *Solvating extractants*

The solvating extractants remove the water molecule from a hydrated metallic ion to a certain extent. This removal increases the metal's solubility into the organic phase. One of the most well-known solvating extractants is tri-butyl-phosphate (TBP). The mechanism is presented in Equation (2-3) [18].



c) *Basic extractants*

As a contrast to acidic extractants, the basic extractants obtain the separation of metallic ions using anionic complexes with anion exchange. Usually, long chain amines are used as basic extractants [18]. The mechanisms indicated in equations (2-4) to (2-6) show the primary steps of salt formation.



Regarding Co SX, acidic extractants are commonly used due to their proven selectivity in the Co-Ni separation field. Further research conducted by Van der Voorde et al reported that the phosphinic acids obtain the greatest extraction efficiency [33]. A summary of the conventionally used acidic extractants is presented in Table 2.1 [32].

Table 2.1. Conventionally used acidic extractants for cobalt separation [32]

Extractant type	Extractant names
Alkyl phosphoric acids	D2EHPA ($C_{16}H_{35}O_4P$)
Alkyl phosphonic acids	PC-88A / Ionquest 801 ($C_{16}H_{35}O_4P$)
Alkyl phosphinic acids	Cyanex272 ($(C_8H_{17})_2P(O)OH$) Cyanex302 ($(C_8H_{17})_2P(S)OH$) Cyanex301 ($(C_8H_{17})_2P(S)SH$)

Early in the 1990s, Tait published a comparison between Cyanex301 (dithiophosphinic acid), Cyanex302 (monothiophosphinic acid) and Cyanex272 (dialkyl phosphinic acid) in the separation of Co

and Ni. The findings showed that the separation efficiency of these extractants is Cyanex301 > Cyanex302 > Cyanex272, due to the number of sulfur donor atoms available. However, the same phenomenon that causes Cyanex301 to be the most effective has an inverse effect on the pH at 50% of extraction: $pH_{0.5} = 1.3, 4.0$ and 5.3 for Cyanex301, Cyanex302 and Cyanex272 respectively. The very low pH of Cyanex301 would require an extremely strong acid in the stripping phase and is therefore disregarded due to the effect it would have on the membranes used in PX [34]. Furthermore, Cyanex301 and Cyanex302 also proved to be quite unstable [35]. The choice is then narrowed down to either Cyanex302 or Cyanex272.

Research into Co-Ni separation can guide the selection of the right organic phase. Co-Al separation, on the other hand, is vaguer due to the scarcity of research done on this topic. Tsakiridis and Agatzini-Leonardou published their findings on the separation of Al from Co in the presence of Ni and magnesium from sulfate solutions in 2005. The organic phase of choice was Cyanex272, diluted in Exxsol D-80 (dearomatized aliphatic hydrocarbon solvent) with TBP [26].

According to Tait, both Cyanex302 and Cyanex272 should be viable options for Co extraction [34]. However, a crucial component missing from Tait's research is the presence of Al. Tsakiridis and Agatzini-Leonardou's research fortunately includes Al, and the behaviour of Cyanex272 towards Al can be assessed [26]. Cyanex272 was therefore chosen as the extractant since it was able to extract 99.5% Al together with TBP and Exxsol D-80.

After the extractant is chosen, the first objective of any reaction is to ensure that the reaction reaches equilibrium. With SX, the equilibrium is reached if enough contact time is allowed. Both Torkaman et al and Olivier and Dorfling showed that a contact time of 10 minutes ensures equilibrium for temperatures ranging between ambient and 50°C for their use of volume [27], [32].

Assuming equilibrium is reached, Co-Al separation is very strongly dependent on the feed pH due to Co and Al speciation in the aqueous phase as seen in Figure 2.3. Due to this strong dependence, pH control throughout the experimental process is usually advised when using the extractant in its natural form [26]. However, as an alternative, pre-neutralisation can be done on the extractant to mitigate the need to control pH throughout the reaction.

Pre-neutralisation is known as a process where the ionisable proton in the solvent is replaced [19]. For Co separations, either an ammonium (NH_4) salt or a sodium (Na) salt can be used to pre-neutralise the Cyanex272. The reaction occurs because a cation exchange takes place. After neutralising the organic phase, either NH_4^+ or Na^+ is exchanged, rather than H^+ . This phenomenon causes a significant reduction in the pH drop as a function of extraction. Consequently, when the reaction occurs, much less variability

in pH occurs [32]. The pre-neutralisation step then removes the need for pH control. This is a big advantage since pH control can be quite expensive to implement at a commercial scale facility.

In addition to pH and pre-neutralisation, the temperature of the reaction was also considered. Temperature has a negligible effect on the separation efficiency of Co-Al separation when using Cyanex272 [27].

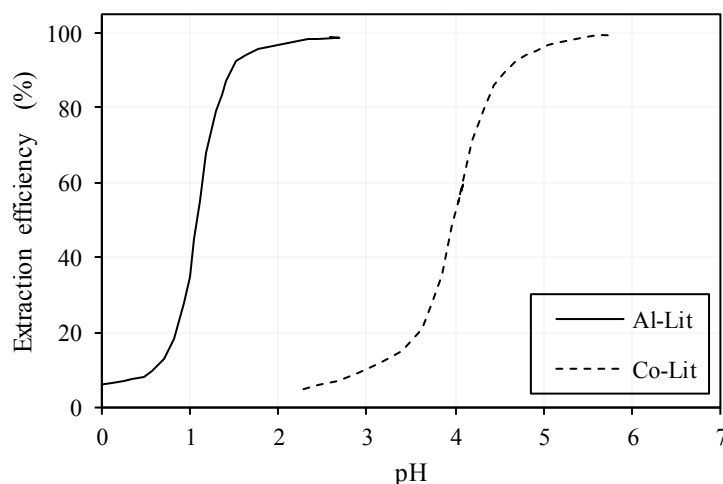


Figure 2.3. Extraction using Cyanex272 in Exxsol D-80 with 5% TBP at 40°C adapted from Tsakiridis and Leonardou [26]

2.6.2.2 Scrubbing

Studies found that an aqueous solution containing the desired metal contacted to the loaded organic phase has success in removing co-extracted metals, subsequently purifying the loaded organic phase [32], [36]. Specifically considering acidic extractants like Cyanex272, the lower the pH at which a metal extracts, the higher its chemical affinity would be for the extractant. By again presenting the extractant with the opportunity to accommodate the desired metal instead of the co-extracted metal, the metals exchange places, which results in an increase in purity [32].

However, this method of scrubbing can be expensive, since a large portion of this metal will not be recovered and sold. Another method proven to be successful with Co-Al separation is scrubbing with acidified water (or diluted sulphuric acid). The pH again is a crucial variable since it changes the selectivity of the extractant with respect to the metal ions [26]. A pH of 2.8 proved to be optimal to scrub off co-extracted Co from the loaded organic phase [26]. However, this method might be specific to the type of extractant used and the liquid conditions.

2.6.2.3 Stripping

Stripping is the second to last or the last stage of SX. After the separation and purification, the only remaining step is to recover the metal from the organic phase and displace it to an aqueous phase since it is much more usable in this form. The general stripping process uses an acid such as sulphuric acid (H_2SO_4) and brings it into contact with the scrubbed organic phase to recover as much metal as possible. Literature indicates that 2 M H_2SO_4 in the stripping of Al delivered as high as 99.7% recovery specifically for the use of Cyanex272 [26].

2.6.3 Techniques used to quantify the effect variables have on the separation efficiency

The variables affecting separation efficiency were reviewed and discussed in the previous section. Next, it is important to quantify the effect that each of these variables has on the separation efficiency. The result would provide information on how sensitive a process is to certain conditions, which would help minimise on process losses.

Mono-variant experiments can be conducted to quantify the individual dependence of separation efficiency on reaction conditions such as temperature, pH, extractant pre-neutralisation, etc. However, the interactions between the variables are not quantifiable. This creates the need for a design of experiments (DOE). DOE, however, has some drawbacks, such as the complexity level and the number of experimental runs that must be completed to reach statistical significance [37].

If experimental funding or time is limited, an alternative can be to quantify the significance of the independent variables. One of the simplest and most well-known techniques is linear regression [38]. Linear regression techniques can quantify the assumed linear relationship between independent variables and the dependent variable. Multiple linear regression techniques exist to date. Since multiple input variables are used, the ordinary multiple linear regression model is a good starting point as it is the most straightforward method [38]. Ridge regression has the added advantages of preventing overfitting and accounting for multicollinearity that might be present. On top of these advantages, the Lasso regression includes variable selection to increase prediction accuracy [39]. Both the Ridge and Lasso introduces a penalty term into the costing function, which aims to exclude less important predictors.

2.6.3.1 Ordinary Linear Regression model

The ordinary linear regression (OLR) model uses the method of least squares to minimise the residuals as shown in Equation (2-7). The separation efficiency is being modelled as a linear equation presented in Equation (2-8). The square of the error between the modelled separation efficiency ($\hat{y}$) and the actual separation efficiency (y) is minimised to obtain coefficients A-E where E represents a bias [38], [39]. Furthermore CF refers to the cost function and x refers to the input variables.

$$CF_{ordinary} = (y - \hat{y})^2 \quad (2-7)$$

$$\hat{y} = Ax_1 + Bx_2 + Cx_3 + Dx_4 + E \quad (2-8)$$

2.6.3.2 Ridge Regression model

The Ridge regression uses the cost function provided in Equation (2-9) where H refers to the sum of coefficients A-E as presented in Equation (2-8) and λ refers to the strength of the penalty term [39].

$$CF_{ridge} = (y - \hat{y})^2 + \lambda \sum_{i=0}^n H_j^2 \quad (2-9)$$

2.6.3.3 Lasso Regression model

The Lasso regression uses the cost function provided in Equation (2-10) [39].

$$CF_{lasso} = (y - \hat{y})^2 + \lambda \sum_{i=0}^n |H_j| \quad (2-10)$$

Since linear regression will fall short when the system inherently contains non-linear relationships, artificial neural networks (ANNs) can also be put to test to model the dependent variable as a function of the independent variables to account for possible non-linear behaviour [40]. In general, ANNs also need large datasets, but some cost function algorithms can largely overcome this. ANNs can act as a quantifier beyond the mono-variant experimental results' capabilities. This technique has not been used before with Co-Al separation to learn the behaviour of the experimental results and quantify the effect variables have on the separation efficiency.

2.6.3.4 Artificial neural networks

In layman's terms, an ANN is a technique used to recognise patterns or quantify the dependence an expected output will have on inputs. ANNs are inspired by the mechanisms where biological neural networks can process numerous input data (smell, taste, touch, etc.) and determine the outcome. They are used specifically due to their tailored capability to recognise patterns in data where other linear fitting curves fall short and do not model the expected output accurately [40]. This technique was used to quantify the effect of individual variables and combinatory changes in the variable on the expected extraction efficiency.

The simplified network topology is shown in Figure 2.4. An ANN topology can be classified as a multi-input-multi-output (MIMO), multi-input-single-output (MISO), single-input-multi-output (SIMO) or single-input-single-output (SISO) ANN. When the ANN predicts an output value for the first time, the known input values are provided and weighted individually with random weights in the input layer. These weighted input values are summed and sent through an activation function (usually sigmoidal),

which works on probability principles in the hidden layer. Conventional networks have additional neurons (nodes) that introduce additional weighting in the hidden layer before it is sent to the activation function. Finally, the output from the sigmoidal function is transformed into the correct format and presented in output layer.

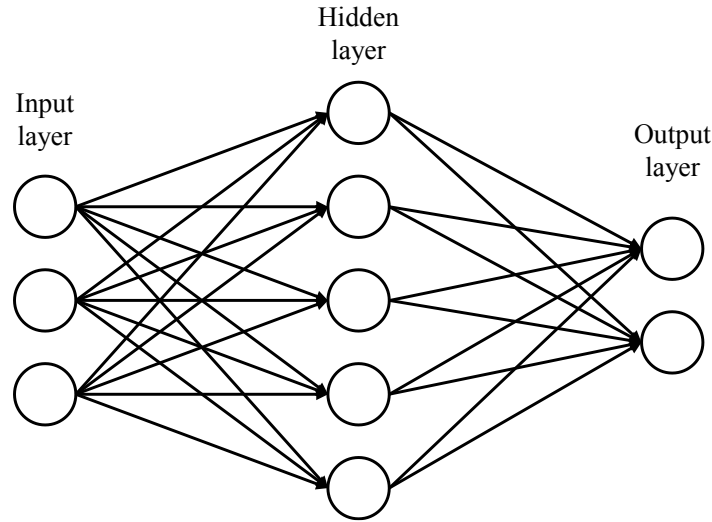


Figure 2.4. Simplified structure of an artificial neural network

The number of hidden neurons (N_h) used in an ANN is very important. A set number cannot be given since there are too many factors to consider, one of which is the behaviour of the data. The optimal number of hidden neurons must be determined for each unique case. However, some rules of thumb can be used as a starting point based on the number of input variables (n_{in}) and predicted variables (n_{out}) [41]. A few examples are given in equations (2-11) to (2-14) [42]. The input and output neurons do not refer to the number of data points in the sample space but are rather an indication of the number of dimensions that are modelled.

$$N_h = n_{in} + n_{out} - 0.5 \quad (2-11)$$

$$n_{out} < N_h < n_{in} \quad (2-12)$$

$$N_h = \frac{2}{3} n_{in} + n_{out} \quad (2-13)$$

$$N_h < n_{in} \quad (2-14)$$

This process is known as a feed-forward step (once-through from input to output). After the network has made its prediction based on the set of input values, a costing function is used to minimise the error between the predicted values and the actual output values. To minimise this error, the costing function changes the weights originally guessed. These weights must be changed strategically to minimise the computational time and power needed to obtain an ANN that can accurately predict. To achieve this strategic change in weights, numerous algorithms have been developed.

Some of the well-known algorithms include the Levenberg-Marquardt (LM), Scaled Conjugate Gradient (SCG) and Bayesian Regulation (BR) algorithms. Bahrami et al compared more than 20 different algorithms and concluded that LM, SCG and BR are most suitable when using small datasets [43]. Although the LM algorithm generally converges fast and in a stable manner it tends to be a bit slower than the Gauss-Newton algorithm, but it can converge for problems with more complex error surfaces [44]. The LM, SCG or BR costing functions can therefore be used in this study.

Each offers distinct advantages and trade-offs. LM is widely valued for its fast and stable convergence, particularly when handling nonlinear models with complex error surfaces. However, it can be computationally intensive, especially for large networks or datasets, due to the storage and inversion of Jacobian matrices. In contrast, SCG is a memory-efficient algorithm that avoids the computational cost of matrix inversion, making it faster for larger networks, but it may converge more slowly or less precisely than LM in certain cases. BR, on the other hand, introduces a regularization term into the cost function, which helps prevent overfitting—a key advantage when working with small or noisy datasets. The trade-off is that BR may result in longer training times, as it optimizes a more complex objective function. Overall, the choice of algorithm depends on the specific requirements of the problem, including data size, model complexity, and the need for generalization.

Another factor worth mentioning is how the error between the predicted value and the actual output value is calculated.

The errors associated with the ANN are an indication of its performance. However, the type of error that is calculated is very important. It is conventional to use either the mean squared error (MSE) or the root mean squared error (RMSE) with regression analyses. The RMSE is a good choice to interpret the errors, since it is in the same units as the data and is representative of the size of a typical error. Another good choice of error measurement is the mean absolute error (MAE) since it has similar attributes as the RMSE but is easier to understand. This paper uses the coefficient of determination (R), together with the MAE and RMSE to quantify the performance of the neural networks. The equations for these errors (e_i) are given in Equation (2-15) and (2-16) [45].

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (e_i)^2} \quad (2-15)$$

$$MAE = \frac{1}{n} \sum_{i=1}^n |e_i| \quad (2-16)$$

Where $e_i = p_i - a_i$ with p_i and a_i referring to the predicted and actual value in a dataset with n samples.

Lastly, to be able to quantify the dependence of the extraction efficiencies with respect to the input variables, an algorithm was used as developed by Garson and modified by Goh in the 1990s [46]. The weights obtained from the optimal neural network is used to determine the relative importance of each variable contributing to the extraction efficiency. The applicable equation is presented in Equation (2-17).

$$I_j = \frac{\sum_{m=1}^{N_h} \left(\left(\frac{|w_{jm}^{ih}|}{\sum_{k=1}^{N_i} |w_{km}^{ih}|} \right) |w_{mn}^{ho}| \right)}{\sum_{k=1}^{N_i} \left[\sum_{m=1}^{N_h} \left(\left(\frac{|w_{jm}^{ih}|}{\sum_{k=1}^{N_i} |w_{km}^{ih}|} \right) |w_{mn}^{ho}| \right) \right]} \quad (2-17)$$

Where w indicates connection weights and i, h and o refer to the input, the hidden and the output layer respectively. Furthermore k, m and n refer to the input, hidden and output neurons respectively.

2.6.4 Metal speciation analysis

The predictive model obtained from either linear or non-linear regression techniques helps to understand the sensitivity of the separation efficiency with respect to the variables. What the model, in this application, cannot capture though, is the understanding of the metal speciation. The use of the OLI[®] databases can provide clarity on why and how the metals distribute between the two immiscible phases as conditions vary. The linear and non-linear modelling techniques are employed in this thesis specifically to evaluate the sensitivity of the experimental results with respect to specific variables, whereas the metal speciation analysis provides a view of the natural ionic compounds forming under different conditions (as exposed to during the experimental series) in accordance to the discussion in Section 2.6.2.1.

2.6.5 Conventional SX plant equipment

SX plants are designed to extract a component of interest and separate it from its original solution. As mentioned earlier, SX is a separation technique based on liquid-liquid extraction, more specifically, two immiscible liquids that make contact and differ in solubility for the components of interest. The desired component, in this case Al, can therefore spontaneously relocate to the liquid offering a greater solubility. The extent of the separation is quantified by the distribution coefficient as explained in Section 2.6.1.

To realise this separation, the conventional equipment used in an SX plant is known as mixer-settlers. A representation of a mixer-settler is provided in Figure 2.5. This is the equipment that establishes a liquid-liquid contact and is therefore accountable for the separation that takes place. Mixer-settlers are used in numerous applications, including the purification of metals, recovering carboxylic acids, the

extraction of aromatics, etc. [47], [48]. Mixer-settlers have been in the industry for decades now. Papers dating back to the early 1970s already describe the reliability of this equipment [49]. Mixer-settlers together with the well-known distillation columns make up the largest portion of the separation technology used to date [48].

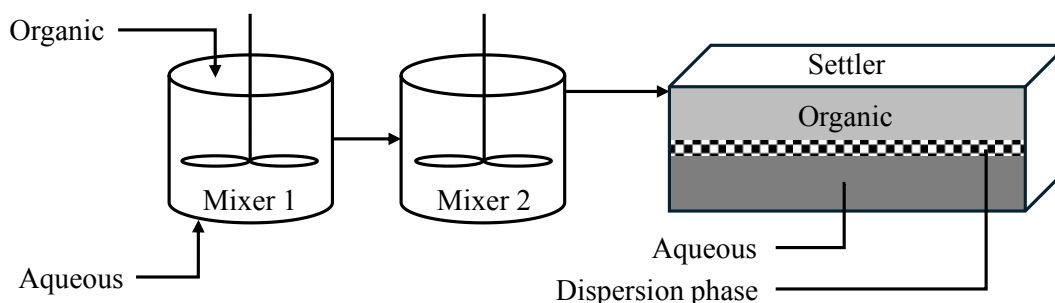


Figure 2.5. Schematic representation of a mixer-settler as adapted from Bjornstad et al [50]

A mixer-settler first establishes a large contact area between the two immiscible liquids by agitating the mixture [51]. This agitation is one of the most common operations known. However, it presents numerous challenges for computer simulations [47]. The agitation is usually introduced with an impeller mounted on a shaft governed by a gearbox that helps it rotate at a desired speed [47]. The agitation step is extremely important since it drives the chemical separation by creating droplets to maximise surface contact area. Following the mixing section is the settling/decanter section that ensures physical separation of the two immiscible liquids based on their response to gravitational forces [47].

During the settling stage, typically two layers form, each representing the original immiscible liquids (organic and aqueous phases). However, it is not uncommon for a third phase to be present. This phase is typically referred to as the dispersion band and can be caused by too harsh agitation, leading to a mixture reluctant to physically separate [47]. This occurrence is one of the major drawbacks of mixer-settlers. It results in greater settling size requirements (increasing capital cost) and further causes higher entrainment levels [47]. Another drawback of mixer-settlers lies in the agitation step. The agitation causes an unknown contact area, which can lead to instabilities in operation [52]. Furthermore, disregarding the additional need for space if a dispersion band is present, mixer-settlers in general have large specific and long settling time requirements. On top of that, the settling tanks are usually filled with solvents with flammable characteristics, which poses a safety concern.

Nonetheless, this equipment has been used for a long time and with that comes experience. Main factors affecting the design of a mixer-settler include the chemistry of the system, the kinetics and thermodynamics of the ion exchange reaction and temperature [53]. Much work has gone into the optimisation of conventional mixer-settlers. Sulzer, a leading company in fluid engineering, posted some

information on mixer-settlers configured in the form of a column (ECMS- Kühni mixer-settler-column). This column can provide stage-wise operation while minimising the footprint of the facility [48].

2.7 Pertraction

In simple terms, two immiscible fluids (similar to SX) are brought into contact. This technique has been patented by van der Westhuizen et al [55]. With SX, the agitation step drives molecular contact and optimises the possibility for mass transfer. When using a membrane, the pores provide opportunity for contact. A representation of a hollow fibre membrane is provided in Figure 2.6.

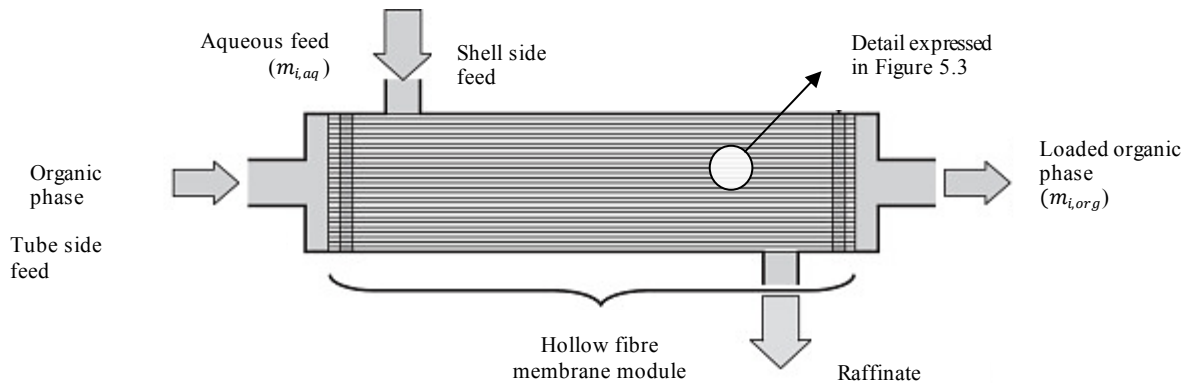


Figure 2.6. Simplified representation of a parallel flow membrane as adapted from [54]

The metal distributes itself across the aqueous and organic phases based on its relative solubility in each phase under the given chemical conditions. This distribution is quantified by the distribution coefficient, D_i , of metal i (Equation (2-18), where m_i refers to metal i dissolved in the organic (*org*) or aqueous (*aq*) solution). Since the distribution coefficient measures the amount of metal that is expected to reside in each phase after contact, it is also a measure of the drive behind the ion exchange or mass transfer that occurs at the contact area.

$$D_i = \frac{m_{i,org}}{m_{i,aq}} \quad (2-18)$$

When designing a PX facility, it is very important to quantify the mass transfer coefficient. To predict the separation efficiency in a membrane module, accurate mass transfer kinetics becomes critical. For the metal ion or solute to relocate from the aqueous phase to the organic phase, it must overcome three hurdles. The ion first must travel through its aqueous bulk molecules to reach the surface of a pore. Secondly, it must cross the membrane pore barrier to the organic phase, and finally, it has to travel from the pore through the organic molecules to reach the bulk. The concentration gradient between the fluid bulk and the pore and the distribution coefficient are the driving forces. This phenomenon explains why counter-current flow should result in better separation efficiencies for the same time of contact allowed, since the concentration gradients with this configuration are maximised and equilibrium is disturbed.

Since PX is still a new technology, the research on this is scarce. Mans et al specifically published their findings on PX-based separation of Co and Ni [19]. The PX technology contains some disadvantages, such as (i) that the membranes are susceptible to fouling, (ii) channelling or maldistribution of fluid may occur when not operating as per advised conditions, and (iii) additional operating cost might be incurred due to membrane replacement. Keeping these disadvantages in mind, the design of a PX process should focus on minimising the drawbacks and maximising the advantages that the technology has to offer.

Their findings further indicate the ability of the PX plant to deliver a Ni purity of 99.99% in the raffinate [19]. Mans et al also mention that PX contains numerous advantages compared to the use of SX, such as (i) that no mixing occurs, eliminating the need for a separation period in the process, (ii) safer operation due to the absence of open solvent baths, (iii) more compact design, (iv) known contact area, and (v) a decrease in the metal-lock up experienced (specifically relevant to the PGM industry).

2.8 Feasibility study

The purpose of a feasibility study is to determine how viable, practical, or realistic ideas are. A couple of things must be considered to determine the feasibility of implementing a PX plant that will separate Al and Co. This includes the cost of physically installing the equipment necessary to complete the task, the impact on the environment, the operating cost, the foreseeable profit to be made, etc. A feasibility study is crucial to ensure proper consideration before the implementation of any project.

The KLM technology group, a group of technical consultants that provides engineering solutions, published a document indicating the recommended practice for feasibility studies [56]. They explain that the Engineering Standard requires different stages for a feasibility study, i.e., the opportunity study, then a pre-feasibility study, and finally a detailed feasibility study. Each of these stages has conventional and required factors to take into consideration. The opportunity study refers to the identification of opportunities. The pre-feasibility study refers to the analyses of project alternatives and preliminary technology selection. Finally, the detailed feasibility study refers to the final technology selection and investment decisions.

The feasibility study in this thesis aims to provide a preliminary comparison between the proposed PX plant and conventionally known equipment. Only a pre-feasibility study is necessary to achieve this aim. The pre-feasibility study and detailed feasibility study have similar objectives but the details and level of accuracy differ. The factors that should be taken into consideration for either are listed below [55]. Each factor is briefly explained.

1. Scope of the project
2. Marketing concept
3. Raw materials and supply

4. Location, site and environment
5. Engineering and technology
6. Organisation and overhead cost
7. Human resources (labour cost)
8. Project implementation

Scope of the project: The scope of the project refers to a detailed outline of the project. This describes the resources, timeline, etc. [57].

Marketing concept: The marketing concept focuses on the needs and wants of the customer. The five known marketing concepts include production concept, product concept, selling concept, marketing concept and societal marketing concept [58]. The production concept refers to the fact that customers will favour a more affordable product. The product concept refers to the product that offers the most quality and innovative features. The selling concept speaks to the idea that customers are more intrigued by the willingness of a company to go large-scale. The marketing concept is aimed at the delivery to the market, to be trustworthy and stable. Finally, the societal marketing concept refers to the fact that the product should be able to improve society's well-being. For the mixer-settler concept and the PX concept, the customer is the same (Minemet) and the required product purity is also the same. These five concepts will be considered individually, keeping in mind that the customer and product quality are a constant for both.

Raw materials and supply: The raw materials for both conceptual designs include: (i) aqueous feed solution (PLS), (ii) ammonium hydroxide, (iii) sulfuric acid, and (iv) sodium hydroxide. However, Minemet leaches out platinum and the remainder containing cobalt and aluminium is then used as the feed stream to either the mixer-settler or the PX plant.

Location, site and environment: This factor is fairly intuitive. The effect each concept has on the environment should be compared and taken into account. Location refers to an inland facility vs. close to a port in case of exports, while the site refers to how far removed it is from any towns, which will influence the cost of construction.

Engineering and technology: The engineering and technology factor takes into account the sustainability, innovation and complexity of the plant.

Organisation/overhead cost and human resources: Factors six and seven can be grouped as operational cost or the running cost of the plant (OPEX – operational expense). This can include equipment maintenance, labour, electricity, etc.

Project implementation: The final factor is also referred to as CAPEX (capital expense). This refers to the actual cost of implementing the plant, i.e., design, manufacturing, shipping, installation, etc.

When a plant is designed and it is not deemed profitable, it will not be implemented. The expenses have to be weighed against the income to determine its profitability. Expenses can be characterised as either capital expenses or operating expenses (CAPEX or OPEX as mentioned) [59]. These expenses should be weighed against the possible income that the plant will likely obtain. This lies outside of the scope of this study.

Based on the literature reviewed in this chapter, it can be hypothesised that the PX technology has the potential to outperform conventional mixer-settler systems under comparable operating conditions. The key differentiator is that PX does not require a dedicated mixing step, thereby avoiding the associated operational complexity, residence time requirements and additional plot space needed for phase separation in these systems. This inherent simplification could result in a smaller facility footprint, lower operational risk, and improved safety. This hypothesis forms the basis for the experimental design and analytical evaluations presented in the following chapters, which aim to test the comparative performance of PX and mixer-settlers.

2.9 Chapter conclusion

Given the wide array of Co and Al uses, specifically in agriculture, the separation of these metals can be justified. Various techniques to separate these metals currently exist. These techniques include leaching, precipitation, SX and PX. Leaching poses environmental concerns due to its acidic waste produced. Precipitation is an old technique that is very well understood, but it does present challenges with reaching the desired purity.

SX is a popular technique due to its proven selectivity while using stable extractants. To obtain optimal separation conditions with SX, specifically for Co-Al separation, Cyanex272 was found to be the best candidate for the organic phase due to its proven selectivity and stability in the Co-Ni industry. It is a preferred choice since the behaviour of Al and Co in the presence of Cyanex272 is known. Furthermore, since this reaction is highly pH sensitive, pre-neutralisation is a good choice to avoid pH control. Scrubbing with a diluted acid seems adequate to remove co-extracted metals, but this may only be relevant to a particular case. This method should be compared to the conventional method of scrubbing.

Mono-variant experiments should be conducted to quantify how the variables affect the separation efficiency of SX. The results of these experiments can then be used to construct linear and non-linear models with the use of linear regression techniques such as the ordinary linear regression model, the ridge regression model, and the lasso regression model. To allow for the possibility of non-linear relationships among the variables, artificial neural networks should also be used to construct models.

The Levenberg-Marquardt, Scaled Conjugate Gradient and Bayesian Regulation algorithms can all be put to test. The linear and non-linear models' performance should be then compared to select the best performing model based on the coefficient of determination, the MAE and the RMSE. The OLI's database should also be used to analyse the metal speciation under different conditions.

The conventional SX equipment in use is mixer-settlers that consist of an agitation stage and a settling stage to allow phases to separate again. PX uses the same principle of separation as mixer-settlers. It poses numerous advantages over mixer-settlers as mentioned in Section 2.7. To be able to determine which technology is superior, a pre-feasibility study should be conducted to compare both technologies.

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3 Separation and recovery of cobalt and aluminium from spent gas-to-liquid catalysts using Cyanex272 with solvent extraction techniques

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3.1 Introduction

This chapter focusses on determining optimal conditions for the separation and recovery of a feed stream containing 0.9 g/L Al and 0.1 g/L Co (addressing objective 1 (tasks a and b) as outlined in Section 1.3) with solvent extraction, using shake-out or batch tests. This will be done by evaluating variables commonly studied in literature, such as pre-neutralisation, temperature, pH and additional variables such as feed metal concentration. The chapter also relies on the use of the OLI database for both the experimental planning and to aid with experimental validation. Once the optimal conditions for separation have been determined, the secondary objective was to develop a high-level conceptual sizing for a mixer-settler (addressing objective 1 (task c) as outlined in Section 1.3).

The purpose of this step was to obtain a view of the footprint that is required to conduct the separation and therefore, specific focus was placed on the settler sizing (as it is the largest portion of the mixer-settler unit). The high-level sizing will be used later in the study (Chapter 6) to compare the mixer-settler technology with PX technology. Since a comparison between mixer-settlers and PX is desired, a full-scale facility design was therefore not required and not conducted. As a result, only the extraction stage will be sized. The following section will discuss the methodology followed to obtain the above-mentioned goals.

3.2 Method

3.2.1 Metal speciation

OLI Studio software (version 11.5.1) was used to determine experimental ranges for the SX batch shake-out tests. According to the complexing mechanism shown in Equation (2-2), Section 2.6.2.1, both Al (as Al^{3+}) and Co (as Co^{2+}) should bind with the phosphinic ions present in Cyanex 272. The speciation data obtained for 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 two sets of Pourbaix diagrams of Al and Co, as shown in Table 3.1. The two variables, temperature and pressure, were specifically selected based on literature guidance (Section 2.6.3) identifying them as key factors that typically influence separation efficiency.

Table 3.1. OLI® Studio Pourbaix diagram setup 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

3.2.2 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 with a Cyanex272-containing organic phase for 2 h. 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 above-mentioned reagents are provided in Table 3.2 (MSDSs can be obtained in Appendix A).

Table 3.2. 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
Cyanex272	> 85%	Syensqo
ShellSol 2325	-	CHEMQUEST AFRICA
Tributyl phosphate	> 98%	Fisher Scientific
Ammonium hydroxide	> 25%	Minema
Sodium hydroxide	> 98%	LABCHEM
Sulfuric acid	> 98%	LABCHEM

3.2.3 Extraction

3.2.3.1 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 as explained in Section 2.3 as the analysed pregnant leach solution (PLS)). After preparation, the solution was allowed to stand for approximately 2 h 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, the extractant, the diluent, and the modifier, which in this study were Cyanex272, ShellSol 2325, and TBP, respectively.

3.2.3.2 Effect of pre-neutralisation on extraction

To quantify the effect of pre-neutralisation on extraction, the organic and aqueous solutions 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 before adding it to the aqueous phase. The NH_4OH concentration range was based on the guidelines found in the Cyanex272 technical datasheet [1], recommending a maximum of 50% addition of pre-neutralisation with respect to the extractant molar concentration (20 vol.% Cyanex272, which is

equivalent to 0.61 M_{Cyanex272}). After extraction, the mixture was poured into standard separation funnels to settle and separate.

3.2.3.3 *Effect of aqueous feed pH on extraction*

To determine separation efficiency as a function of pH, the pH of the aqueous standard feed solution was adjusted using either H₂SO₄ 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 [2], [3] that allows 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 Metrohm 744 pH – 6.0258.010 electrode)¹ to obtain a pH range between ~1 and ~6 representing the effective zone for both Al and Co extraction [2]. The adjusted solutions were thereafter contacted with the organic phase at 40°C, pre-neutralised to 50 mol.% Cyanex272, shaken at 200 rpm for 1 h, separated, and analysed as described in sections 3.2.3.1 and 3.2.3.2.

3.2.3.4 *Effect of temperature on extraction*

The effect of temperature on the separation efficiency was determined by contacting the solutions at an O:A ratio of 1:1 at varying temperatures (25–40°C). All organic solutions were pre-neutralised at 50 mol.% of Cyanex272. All aqueous solutions were at a pH of 3.13.

3.2.3.5 *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 above. The experiments were conducted by first keeping Al constant at 0.9 g/L and varying Co concentration whereafter Co concentration was kept constant at 0.1 g/L and Al concentration was varied.

3.2.3.6 *Extraction isotherms*

The extraction isotherms were determined by calculating the separation efficiency as a function of the feed concentration, 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.% Cyanex272) were used to ensure the mixture contained

¹ Before each series of sample analysis, the pH meter was calibrated using pH 4.01 and 7.01 buffer solutions (Hanna instruments). The calibration was repeated if the calibration line was below 95%, using freshly prepared KCl electrolyte.

enough complexation sites to reach true equilibrium (note that TBP was kept constant at 5 vol.% and ShellSol 2325 was adjusted accordingly).

3.2.4 Scrubbing

During the scrubbing stage, a scrub liquor was added to the loaded organic phase obtained from the optimised extraction step. Two scrubbing methods were evaluated. According to Tsakiridis and Leonardou (2005), scrubbing with dilute sulfuric acid optimally removes co-extracted Co [4]. Accordingly, in method one, scrub liquors with a pH ranging from 0.7–3.7 (0.1–0.0001 M H₂SO₄) were prepared and added to the loaded organic phase. 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 added to the loaded organic phase [3], [4]. In both cases, the phases were contacted in an O:A ratio of 1:1 for 1 h at 40°C in a shaking incubator.

3.2.5 Stripping

During the stripping stage, 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 [2]. An O:A ratio of 1:4 was used when mixing the two phases for 1 h at 40°C in a shaking incubator.

3.2.6 Mathematical sizing of a 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 determine the relative size required to reach the equilibrium of the extraction phase for a given throughput. The performance of a mixer-settler is greatly influenced by the effective contact during mixing and the efficiency of the gravity separation step. 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 [5] were followed for the sizing of the settler (the guidelines are provided in Appendix B). After determining the number of stages, the dimensions (diameter/width)² of the tank were varied until a design was identified that met the five requirements presented in Table 3.3.

² According to the rule of thumb pointed out by Rydberg et al [5], 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.

Table 3.3. 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	$Reynolds (Re) < 5000$

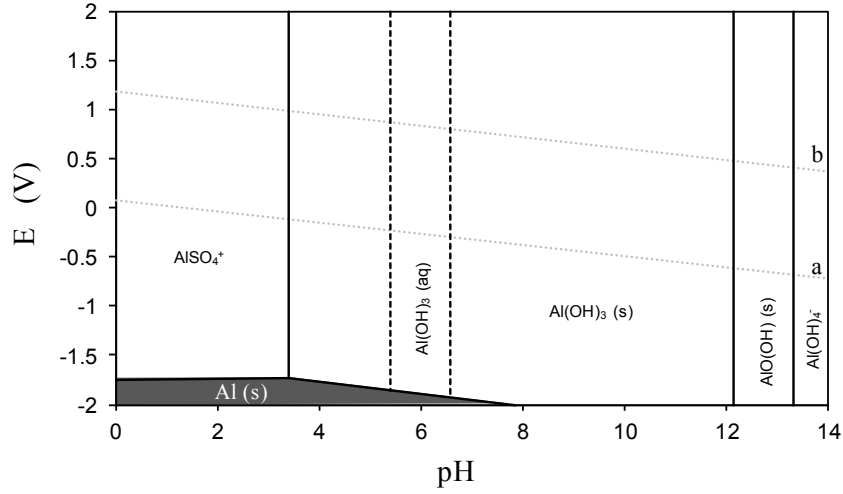
Q_c and Q_d are the overflow rates of the continuous and the dispersed phases (m^3/s), A_I refers to the area of the interface (m^2), v_c and v_d refer to the terminal settling velocity of a droplet in the continuous and dispersed phase, respectively (m/s), t_d refers to the time required to cross the 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's law (s).

3.3 Results

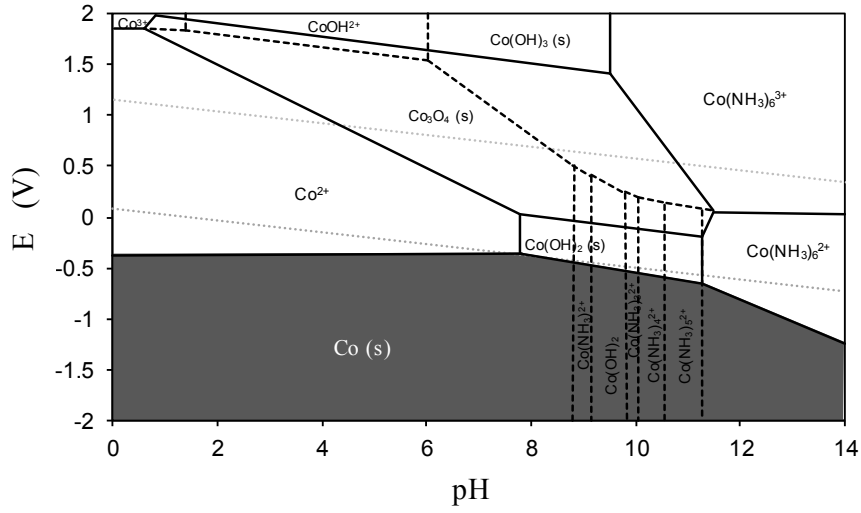
3.3.1 Metal speciation

Figure 3.1 (i) and (ii) provide the Pourbaix diagrams for Al and Co, respectively, in the presence of sulfates as obtained from the OLI modelling.

According to the cation-exchange mechanism provided in Equation (2-2), typical cations (like Al^{3+} and Co^{2+}) should be the desired metal species that can complexate with Cyanex272, 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 3.1. The grey dashed lines (a and b) indicate the water reduction and oxidation lines, respectively. According to Figure 3.1 (i), the desired species of Al should exist as AlSO_4^+ between pH 0–3.4, while according to Figure 3.1 (ii), Co^{2+} should exist between pH 0–7.8. The desired complexing species of both Co and Al are expected to be present at low pH values, so competition between the metals to bind with Cyanex272 can be expected between pH 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. Experiments above this region are therefore not recommended.



(i)



(ii)

Figure 3.1. Pourbaix diagrams of (i) aluminium and (ii) cobalt at 25°C in a sulfate solution

3.3.2 Extraction kinetics

As shown in Figure 3.2, equilibrium was reached after ~15 min of contact time. This is comparable with literature when using similar conditions [4]. Although 15 min was adequate under these conditions, all remaining experiments were conducted for 1 h to ensure that equilibrium was reached when using varying reaction conditions.

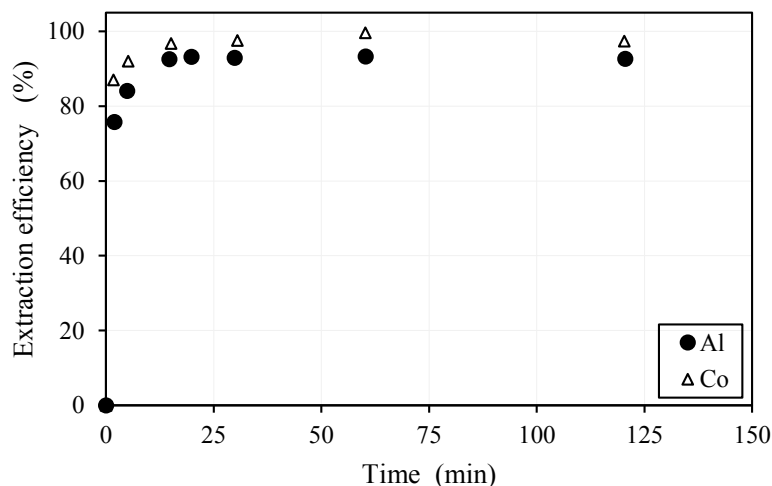


Figure 3.2. Aluminium and cobalt ion-exchange kinetics over 2 h; individual experimental results plotted with aluminium experiments conducted at a pH of 3.1 and cobalt conducted at a pH of 5

3.3.3 Extraction

3.3.3.1 Effect of pre-neutralisation on extraction

The effect of pre-neutralisation on extraction as a function of the NH_4OH concentration is shown in Figure 3.3. Firstly, without pre-neutralisation, poor Al extraction (26%) and separation efficiency (15%) were observed. This is to be expected, because in the absence of pre-neutralisation, i.e., no pH control, H^+ is exchanged from the extractant to the aqueous phases, resulting in a suboptimal equilibrium pH and a decrease in extraction performance (as explained in Section 2.6.2). Pre-neutralisation with NH_4OH resulted in less variability in pH, resulting in a significant improvement in Al extraction and separation efficiency.

According to Figure 3.3, the optimal point of separation was attained when pre-neutralisation with 0.38 M NH_4OH (~60 mol.% of Cyanex272), yielding 98% Al extraction with a separation efficiency of 83%. However, the Cyanex272 technical datasheet recommends that no more than 50 mol.% of the extractant should be pre-neutralised 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 Al and 17% extraction of Co.

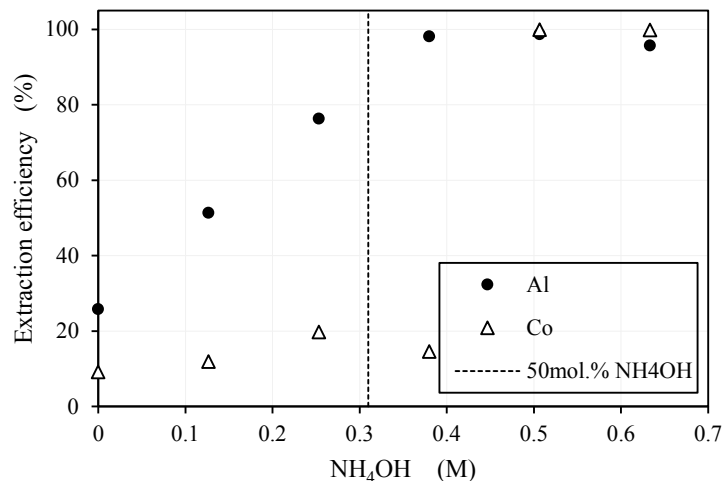


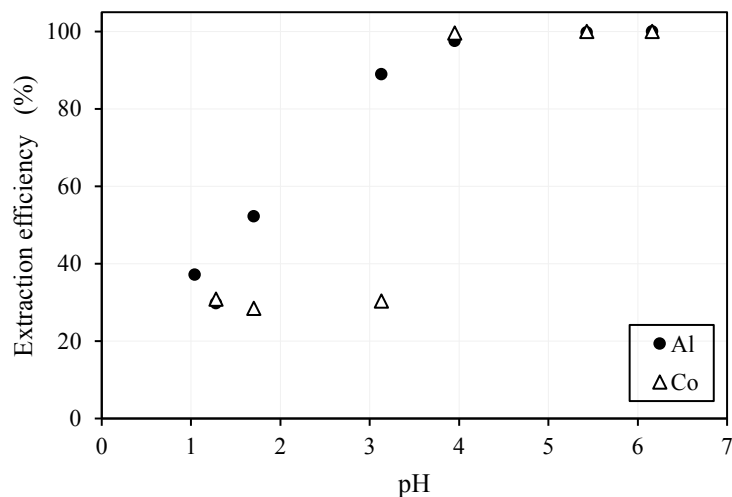
Figure 3.3. Effect of pre-neutralisation concentration on cobalt and aluminium extraction at pH 3.1

3.3.3.2 Effect of aqueous feed pH on extraction

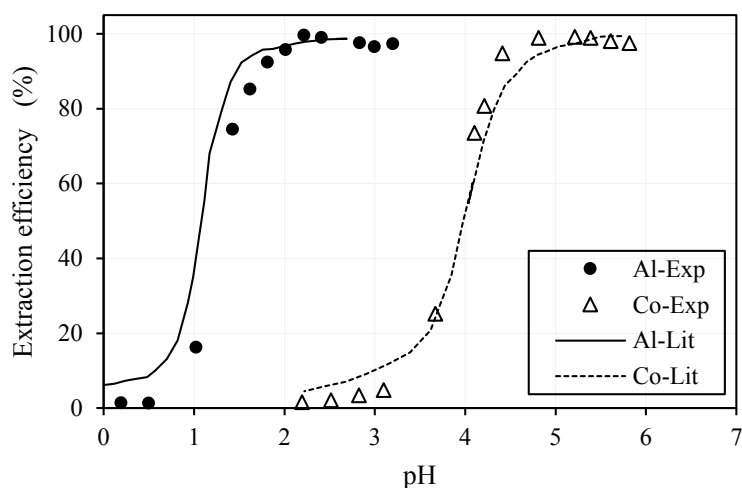
The dependence of extraction efficiency on pH is shown for the mixed and single metal feeds in Figure 3.4 (i) and (ii), respectively.

A similar trend in experimental results (Figure 3.4 (i)) was observed by Tsakiridis and Leonardou [4]. 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 [4], 98.7% Al was extracted at pH ~ 2.6, while only 12% Co was extracted at pH 3.15 leading to an optimal separation between pH 2.5 and 3.5, which also compares with results obtained by Suzuki et al [6], 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 and experimental designs. Both Suzuki et al [6] and Tsakiridis and Leonardou [4] individually determined the pH dependence of extraction for each metal. In Figure 3.4(ii), both literature and the current data for individual metal extractions are shown. The experimental data differed with a mean absolute error of 4% from both the Al and Co trends.



(i)



(ii)

Figure 3.4. Extraction efficiency dependence on aqueous feed solution pH when the experiment is conducted with (i) the standard feed solution (Al:Co = 9:1 mass-based) and (ii) a single metal in solution (dots represent experimental data points and lines represent data obtained from literature [4])

When a single metal aqueous feed is added to an organic phase, the competition amongst metals cannot be evaluated and the action can therefore not truly represent mixture selectivity. When comparing Figure 3.4 (i) and (ii), the competition of Co and Al ions can be noted, which indicates the internal metal competition for complexation with Cyanex272, as predicted from the OLI database, shown in Figure 3.1 (i) and (ii). At pH 2, for example, more than 90% Al was extracted according to Figure 3.4 (ii). However, when Al competes with Co (Figure 3.4 (i)), 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 representative mixtures to capture underlying metal competition.

When combining the stability diagrams generated in Figure 3.1 (i) and (ii) with the extraction results presented in Figure 3.4 (i) and (ii), 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 (2-2). It is suggested that additional tests be conducted to further understand the desired metal species. Furthermore, it is noteworthy to mention that an overall mean absolute experimental error of 5% was obtained.

3.3.3.3 Effect of temperature on extraction

Figure 3.5 shows the effect of temperature on the overall extraction efficiency. The temperature only affected the Al extraction within the range of 25–40°C, with no significant effect above 40°C. These results compare well with literature findings [3]. Therefore, the temperature of all the experiments was set at 40°C, where optimal separation, with a minimum energy input, is expected.

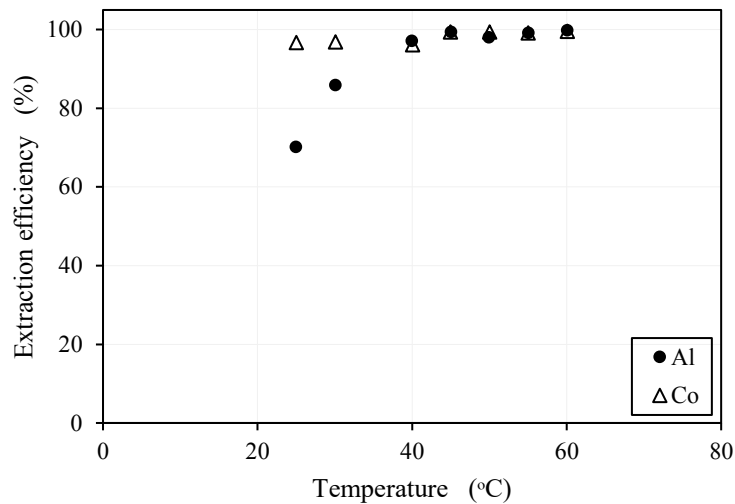


Figure 3.5. Extraction efficiency dependence on temperature

3.3.3.4 Effect of feed metal concentration on extraction

The distribution coefficients of Co and Al at varying feed metal concentrations are provided in Figure 3.6. 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 [7]. The extraction efficiency is determined by the distribution coefficient of the metal and is therefore also a function of the metal concentration.

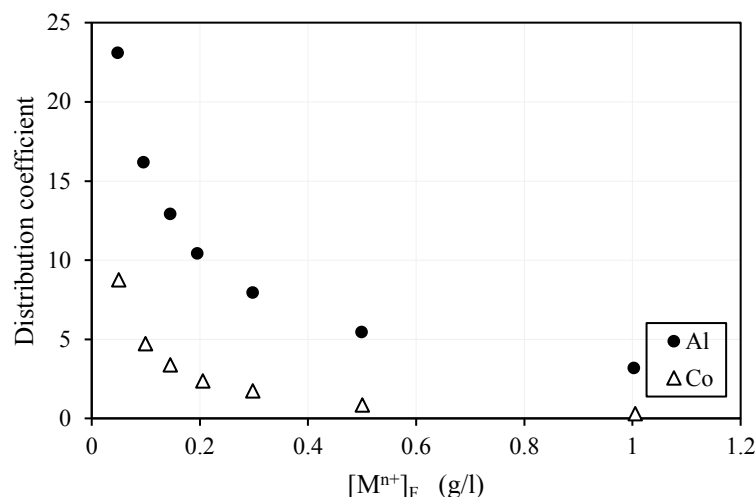


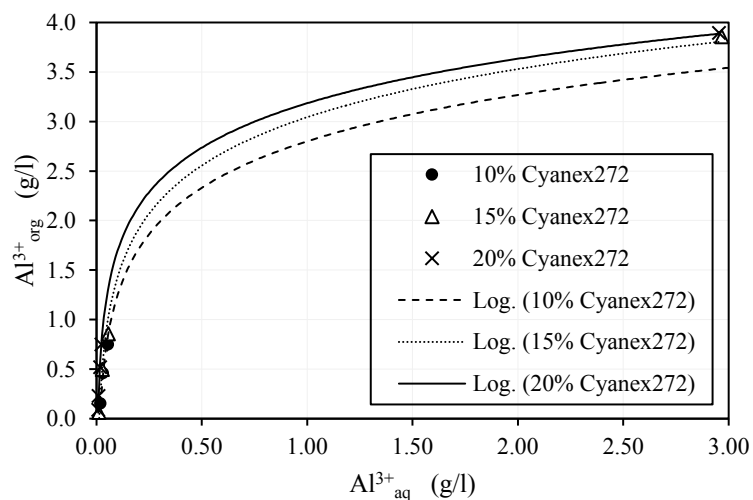
Figure 3.6. Distribution coefficients of cobalt and aluminium at varying feed metal concentrations

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

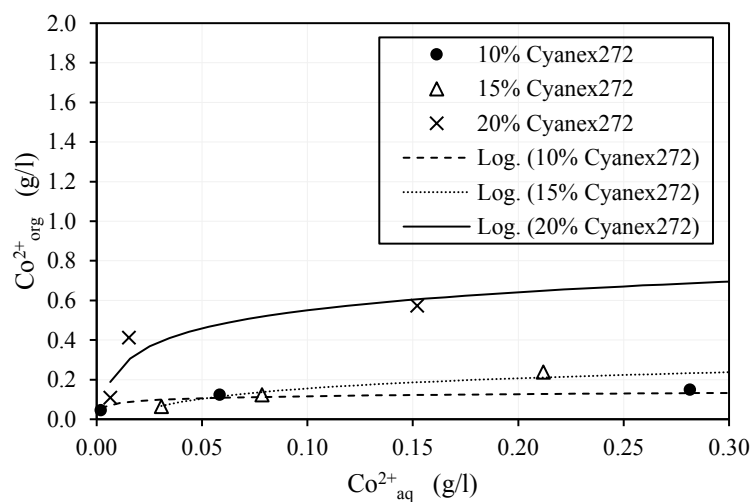
3.3.3.5 Extraction isotherms

Figure 3.7 (i) and (ii) show the extraction isotherms of Al and Co, respectively. While the amount of Al extraction increased with increasing Cyanex272 concentration, the effect was less significant than the effect observed when extracting Co (Figure 3.7(ii)). More Al is transferred to the organic phase when comparing the two metals in similar concentrations.

Unlike Co distribution, Al has a strong transfer drive that was independent of the concentration. The extractant is also more selective for Al, which correlates with the higher distribution coefficient obtained (Figure 3.6).



(i)



(ii)

Figure 3.7. (i) Aluminium and (ii) cobalt extraction isotherms with 10-20 vol.% Cyanex272

3.3.4 Scrubbing

Two scrubbing methods were evaluated: (i) diluted 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 was obtained from extraction at pH 3.13, shaken at 200 rpm and 40°C, and pre-neutralised at 50 mol.% Cyanex272 (20 vol.%).

3.3.4.1 Method 1

The scrubbing efficiency of Method 1 is shown in Figure 3.8.

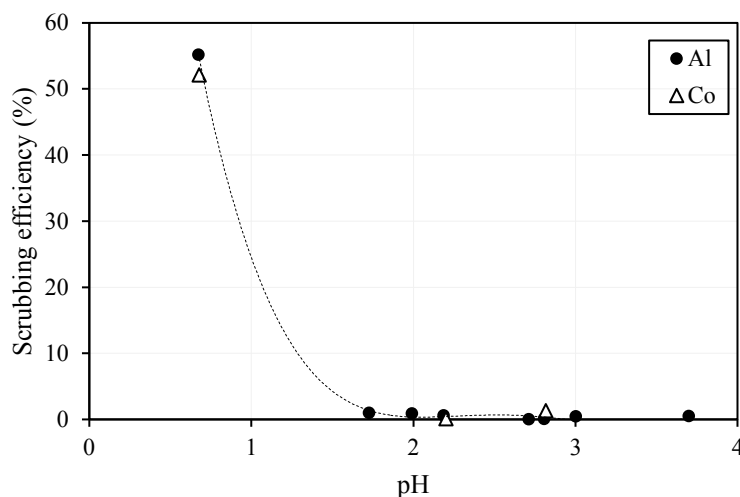


Figure 3.8. Scrubbing efficiency with H_2SO_4 as a function of pH

Figure 3.8 shows the scrubbing efficiency as a function of scrubbing liquor pH. It is apparent that using diluted H_2SO_4 as a scrub liquor was not selective with respect to either Co or Al. Method 1 is therefore not suitable for this application.

3.3.4.2 Method 2

In this single experiment, 50 g/L Al was added to the scrubbing liquor which was set to pH 2.8 [4], [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 (with respect to Al concentration) meeting the <100 ppm of Co target set in the Section 2.4. Method 2 was therefore identified as the scrubbing method of choice.

3.3.5 Stripping

To optimise the Al transfer from the organic phase to the aqueous strip liquor, the sulfuric acid concentration was varied from 0.01–3.0 M [2], [3], [4], [9]. The resulting stripping efficiency is shown in Figure 3.9. The point of optimal stripping seems to be at a concentration of 1.0 M sulfuric acid (which result 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 meeting the initial target of <100 ppm of Co.

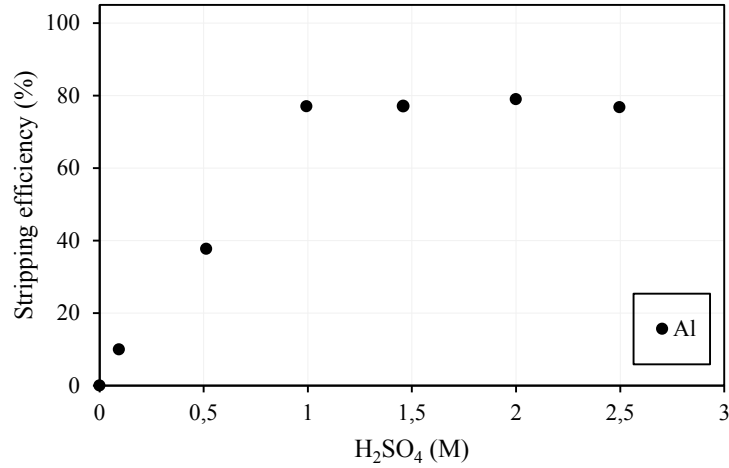


Figure 3.9. Effect of sulfuric acid concentration on the stripping efficiency of aluminium

3.3.6 Mixer-settler sizing

The number of stages required to obtain the extraction determined by the shake-out tests was determined using the McCabe-Thiele method as shown in Figure 3.10. Two mixing stages were deemed necessary to attain an extraction efficiency of 87%, as demonstrated in Figure 3.4 (i). Furthermore, the minimum decanter size necessary to ensure efficient gravity separation was determined to be 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 3.4. Since the settler usually makes up ~80% of the mixer-settler volume, the total footprint of the mixer-settler is estimated to be 16.7 m³ for the extraction phase.

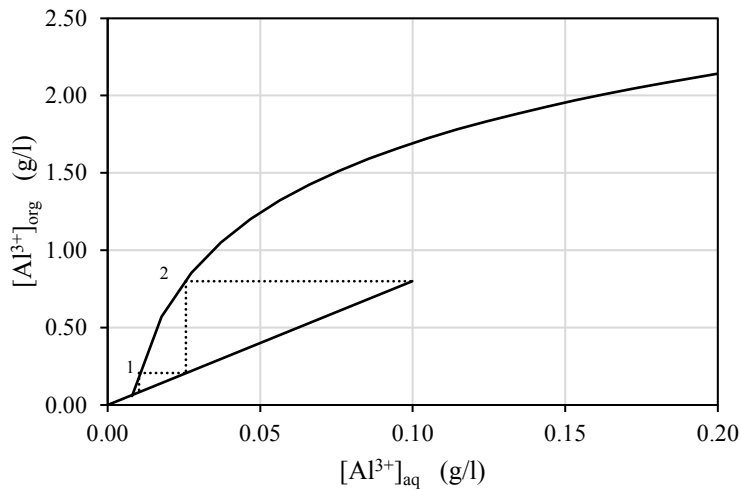


Figure 3.10. McCabe-Thiele plot determining mixer stages required

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 min, ensuring enough time for a molecule to cross the dispersion phase. Finally, the Reynolds number < 5000 ensured that turbulence should not hinder the separation.

Table 3.4. Mixer-settler design results

Requirement	Result	Units
Requirement 1: $\frac{Q_c}{A_I} < v_d$		
Q_c/A_I	0.0003	m/s
v_d	0.001	m/s
Requirement 2: $\frac{Q_D}{A_I} < v_c$		
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	-

3.4 Chapter conclusion

The investigation aimed to optimise the separation process for a PLS with an Al:Co ratio of 9:1. Optimal conditions were determined to be 40°C, 1 h contact time, with an aqueous feed solution pH of 3.13 when using Cyanex272 as extractant. Notably, scrubbing with diluted sulfuric acid lacked efficiency, while using 50 g/L Al at pH 2.8 proved effective. Optimal stripping was attained when using an aqueous solution with 1 M H_2SO_4 and >15 min 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 $\text{pH} < 4$ led to competitive behaviour between the two metals when in contact with Cyanex272. 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 pre-neutralisation but also by the feed metal concentration. 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 (equivalent mixer-settler sized at $\sim 16.7 \text{ m}^3$) was recommended to ensure adequate residence time for gravity separation, catering for a flow rate of $10 \text{ m}^3/\text{h}$. 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.

3.5 References

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4 Linear and non-linear modelling of the selective recovery efficiency of cobalt and aluminium from spent Fischer-Tropsch catalyst

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4.1 Introduction

The focus of this chapter is to use both linear and non-linear regression techniques, including ANNs to quantify the dependencies of the operating variables from Chapter 3 on extraction efficiency. While multiple techniques exist to analyse variable dependencies, as highlighted in Section 2.6.3, this study employs regression-based methods to assess the significance of independent variables while also considering their interactions.

Mono-variant experiments provide a fundamental understanding of how individual variables influence separation efficiency. However, these experiments fail to capture interactions between variables, necessitating the use of statistical modelling approaches. Linear regression methods, such as OLR and Ridge regression, offer a straightforward way to quantify variable significance while addressing issues like overfitting and multicollinearity. Additionally, Lasso regression enhances prediction accuracy by incorporating variable selection.

Since linear regression techniques assume a linear relationship between variables, their effectiveness is limited when the system exhibits inherent non-linearity. To address this, ANNs can be employed to model the relationship between the dependent and independent variables, capturing potential non-linear effects. Despite their typical requirement for large datasets, certain optimisation algorithms mitigate this limitation, making ANNs a viable approach for this study. Notably, ANNs have not yet been applied to Co-Al separation (resulting in few references as seen in Section 4.5), presenting an opportunity to explore their potential in quantifying variable effects and improving process optimisation.

4.2 Method

4.2.1 Experimental results and variable identification

Mono-variant experiments were conducted in Chapter 3, where each of the four variables (extent of pre-neutralisation, pH, concentration of Al and Co in the feed) were altered individually while keeping the others constant. After analysing the product concentrations (data is obtained from Section 3.3), the extraction efficiency was calculated. The experimental results were obtained from Chapter 3 using the experimental layout and conditions described therein. These results formed the boundaries for the sample space used for the regression analyses. The three commonly used linear regression techniques, as discussed in Section 2.6.3 (OLR, Ridge and Lasso), were compared by modelling the separation efficiency as a function of the four independent variables. Similarly, the ability of the three applicable ANN algorithms (Levenberg-Marquardt – LM, Scaled conjugate gradient – SCG and Bayesian regulation – BR) to model the separation efficiency, was determined. Subsequently, the optimal linear regression model was compared to the optimal ANN algorithm. In the final evaluation, the optimal ANN

model weights were used to determine the ranking of the dependency of the variables using the algorithm developed by Garson and modified by Goh [1].

4.2.2 Linear regression models

Three steps were taken for each of the linear regression models. In the first step, the correlation and directionality of the data were analysed and since all three models use the same data set, this step was only conducted once. The Pearson methodology was used to determine the correlation of the variables, while the directionality in the data was determined visually [2].

Secondly, the models were developed and thirdly, the models were evaluated to determine their validity and usefulness. The models were validated, and their performance was compared by determining the R^2 , mean absolute error (MAE) and root mean square error (RMSE) values, as discussed in Section 2.6.3 (Equation (2-15) and (2-16)).

The data obtained from Section 3.3 were presented as scatter plots to visually identify any possible dependencies. Correlation coefficients were then calculated and compared with the directionality observed from the scatter plots.

Subsequently, the three linear regression models (OLR, Ridge and Lasso) were determined using equations (2-7) to (2-10) as described in Section 2.6.3, where the coefficients and the bias (A-E) were determined by minimising the cost function, which is a combined consideration of the MSE and the coefficient of determination.

4.2.3 Non-linear models

All the ANNs were developed using MATLAB (R2020a). Like the linear regression models, the non-linear models were first built and then validated. During the development of each network, the optimal topology had to be obtained before validation could be done. This was attained by deciding on the MIMO/MISO (multi-input-multi-output, multi-input-single-output) outline, the optimal number of hidden neurons and the type of algorithm. All these decisions were evaluated in terms of the R^2 , RMSE and MAE.

For the LM algorithm the MIMO, which was used to predict both the Co and the Al extraction efficiency, and the MISO topology were first compared by employing the LM cost function algorithm while varying the number of hidden neurons between 3 and 7 (as determined with the rules of thumb provided in equations (2-11) to (2-14)). The optimal topology was determined by assessing the performance factors of the LM algorithm.

The dataset was split into 70% training, 15% testing and 15% validation. Model performance was evaluated on the test set and consistency between validation and test accuracy indicated that the model generalised well to unseen data. Based on these results the best topology was used for the other two models (SCG and BR algorithms) again using 3 to 7 hidden neurons. Subsequently, the performance indicators of the LM, SCG and BR were compared to determine an overall best ANN. Finally, the non-linear correlation was determined, using the weights of the optimal ANN in the Garson modified by Goh algorithm (see Section 2.6.3), to determine the relative importance of each variable [1].

4.3 Results

4.3.1 Linear regression models

4.3.1.1 Data correlation and directionality

Scatter plots showing the effect of pH, feed metal concentration and the extent of pre-neutralisation on the extraction efficiency of Al are shown in Figure 4.1 (i) to (iii), respectively providing information on the data directionality.

According to the results, initially both the pH and the concentration of NH_4OH (pre-neutralisation) had a positive linear effect on extraction efficiency before reaching a plateau (all Al extracted = 100% extraction efficiency) above a pH of 4 and NH_4OH concentration of 60 mol%. This confirms findings by Tsakiridis and Agatzini-Leonardou [3].

Since the plateau (Figure 4.1 (i)) was due to the complete extraction of Al to the organic phase above a pH of 4, the region of pH 4-7 cannot be interpreted as affecting the extraction efficiency. However, the initial linear effect of the pH (pH = 1 – 4), can theoretically be equated to $[M^{n+}]_{aq} \propto -k \log[H^+]$.

The same trend observed with pH (initial increase before reaching a plateau), was evident for pre-neutralisation (Figure 4.1 (ii)), which is understandable considering the intent of pre-neutralisation, i.e. to limit the exchange of $[H^+]$ to protect the contact area from the pH environment by replacing it with $[\text{NH}_3^+]$ ions (as explained in Section 2.6.2). The effect of the feed metal concentration shown in Figure 4.1 (iii) had a non-linear negative effect on the extraction efficiency [4].

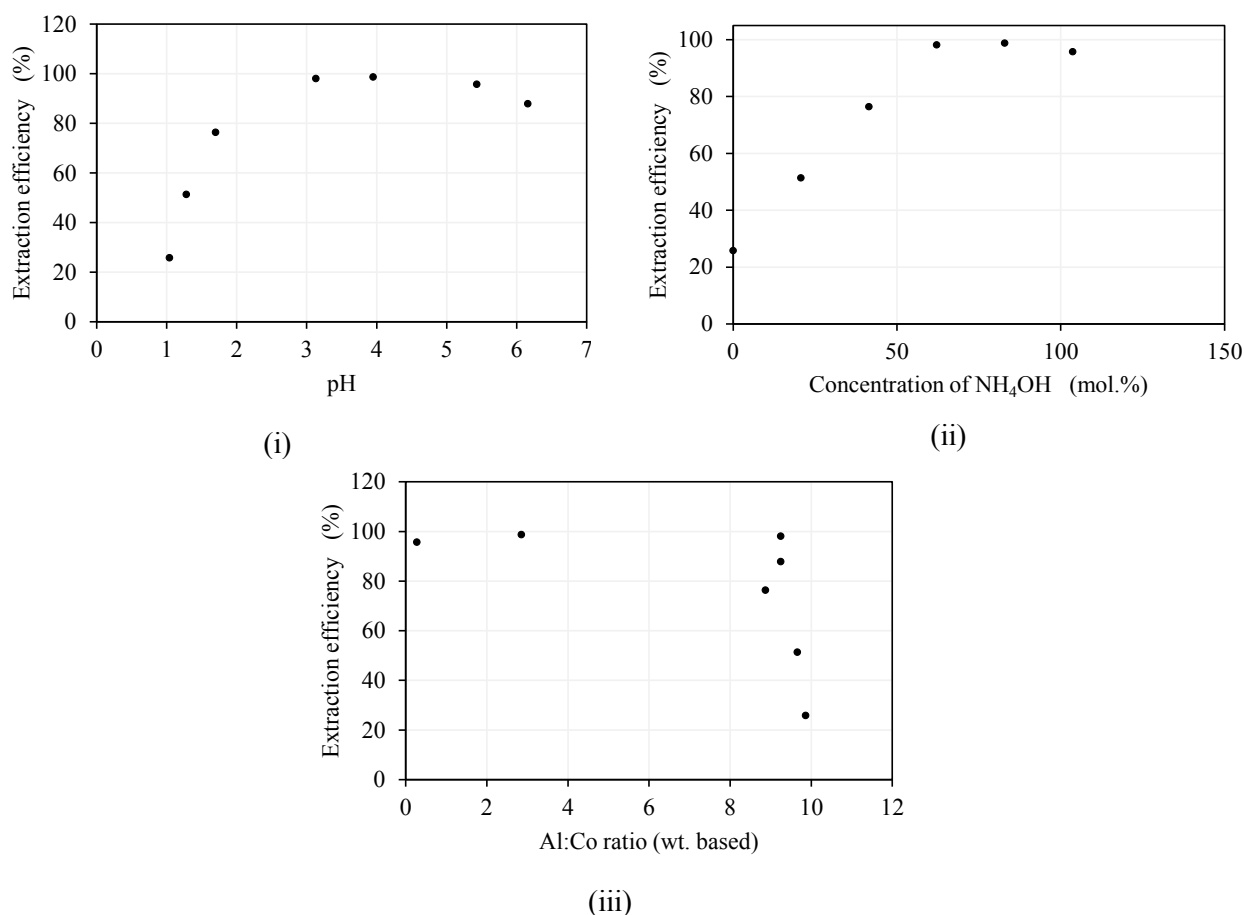


Figure 4.1. Scatter plots of the extraction efficiency of aluminium as a function of (i) pH, (ii) pre-neutralisation (NH_4OH concentration) and (iii) feed metal concentration ratio

The correlation coefficients for the three variable ranges (pH = 1.7-6.16, pre-neutralisation NH_4OH concentration = 0-104% mol/mol Cyanex272 and feed metal concentration = 0-0.1 g/l and 0-0.9 g/l for Co and Al respectively) were calculated as presented in Table 4.1. According to the results, pH had the most significant effect on the separation efficiency, which again corresponds with the findings of Tsakiridis and Agatzini-Leonardou [3], while the impact of the pre-neutralisation and the two feed concentrations were similar (≈ 0.4). Furthermore, the positive correlation coefficients of the pH and pre-neutralisation (concentration of NH_4OH) agree with the positive relationship visually identified in the scatter plots (Figure 4.1 (i) and (ii)). The same is also true for the negative correlation coefficients of Al and Co concentration, confirming the negative correlation observed in Figure 4.1 (iii).

Table 4.1. Correlation coefficients of variables pH, feed metal concentrations and extent of pre-neutralisation on the extraction efficiency of aluminium

Independent variable	Correlation coefficient (R)
pH	0.75
Pre-neutralisation	0.43
[Al] _{feed}	-0.40
[Co] _{feed}	-0.37

The results confirm that all the variables had a substantial impact on the separation efficiency which verified the need to include the initial feed metal concentrations as an important variable when determining the extraction efficiency of Al from a Co and Al mixture. Since that hypothesis was validated, all four variables were included in both the linear and non-linear models.

4.3.1.2 Ordinary, Ridge and Lasso regression

Figure 4.2 shows a comparison of the modelled extraction efficiencies vs the target value (experimental) as a function of the number of sample points for the three linear models. While the tendencies broadly correlate, the models did not accurately predict the target value, which is confirmed when considering the large error values ($R^2 \leq 0.8$, RMSE > 80 and MAE > 10) provided in Table 4.2.

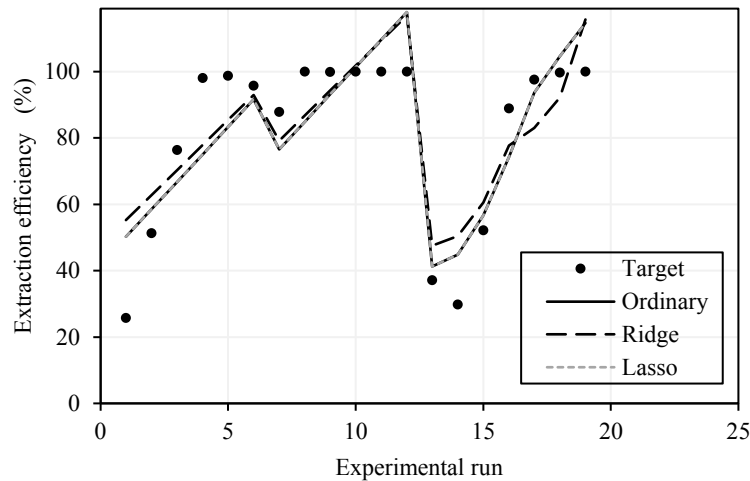


Figure 4.2. Comparison of linear regression model capabilities in relation to the target values obtained experimentally

From Table 4.2, it is evident that the penalty term $\lambda \rightarrow 0$. Since this indicates little to no multicollinearity, it implies that all three models should have similar predictions as was confirmed by the similar tendencies obtained with the three models shown in Figure 4.2 (refer to Section 2.6.3, equations 2.9 and 2.10 for discussion related to λ and the coefficients A-E).

Table 4.2. Validation and corresponding coefficients of the linear regression models

	Ordinary	Ridge	Lasso
R^2	0.76	0.74	0.76
RMSE	84.2	186.2	194.4
MAE	10.9	12.0	11.0
Coefficients			
A	13.4	12.5	13.1
B	0.4	0.4	0.4
C	-24.4	-1.5	-19.5
D	558.9	376.4	434.1
E	-22.3	-17.6	-14.2
λ	-	-9.6E-04	3.0E-07

When comparing the three linear models, the ordinary linear regression technique has the best performance parameters (lowest RMSE and MAE) among the three models. The R^2 values however indicate that even the best linear regression models (Ordinary and Lasso) were only able to capture and model 80% of the relationships. This could suggest that the data does contain some non-linearity, which could possibly be captured using ANNs.

The MAEs for all three models were large (considering that an acceptable error is usually in the range of 4-8% given that a confidence of 95% was achieved), with the smallest mean error (11%) obtained for the Ordinary model. Similarly, the smallest RMSE was 84% (Ordinary), which confirms the existence of several points where the model's predictions were inaccurate.

4.3.2 Non-linear regression models

4.3.2.1 Levenberg-Marquardt (LM) algorithm

As discussed in Section 2.6.3.4, the first step for the development of the non-linear models, was comparing both MIMO and MISO topologies, which in this study was done using the LM algorithm. The modelled extraction efficiencies of the MIMO and MISO models vs the target value when using 3 to 7 hidden neurons, as guided by the rules of thumb discussed in Section 4.2.3, in the LM algorithm are given in Figure 4.3 and Figure 4.4 respectively.

Visually, both models seemed similar, showing a significantly improved correlation with the target extraction efficiencies when compared to the correlation provided by the linear models (Figure 4.2).

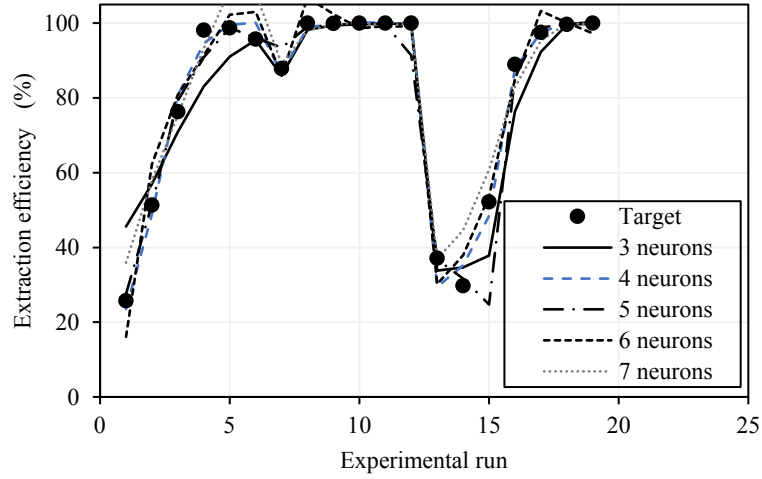


Figure 4.3. MIMO topology prediction with the use of the LM algorithm

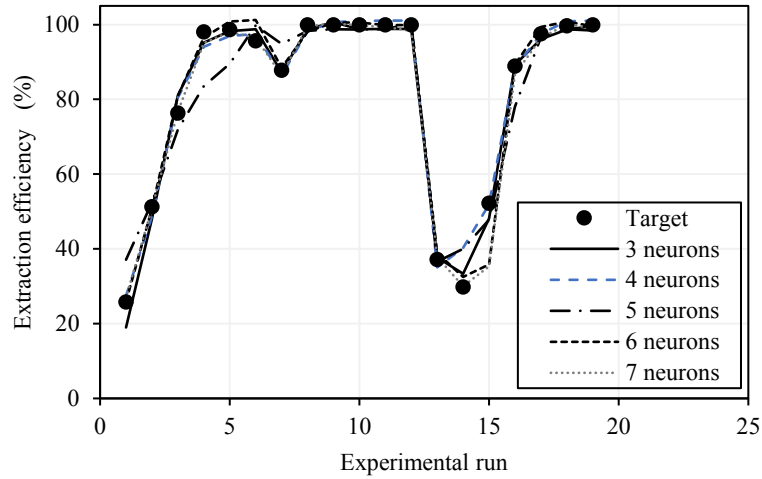


Figure 4.4. MISO topology prediction with the use of the LM algorithm

The performance factors of the models with different hidden neuron selections are provided in Table 4.3 for both the MIMO and MISO topologies. Considering all three values, four hidden neurons seem optimal (highest R^2 and lowest MAE and RMSE values) in predicting the MIMO model, while three hidden neurons seem optimal when predicting the MISO model. Although there was no clear tendency, it seems that for both MIMO and MISO model, five hidden neurons resulted in the worst fit when considering both R^2 and RMSE.

The performance indicators further showed that the MISO topology was more accurate in predicting the extraction efficiency than the MIMO topology considering that the R^2 on average was larger while the MAE and the RMSE were smaller for the MISO topologies than for the MIMO topologies, implying higher accuracy and predictability. This was expected since the MISO network uses the same amount

of known information than the MIMO model but is required to predict only one dependent variable and not two. Based on these results, the MISO topology was used for the SCG and BR algorithms. It is noted that all topographies delivered high R^2 values. Since it is not uncommon for neural networks to overfit when applied to small datasets, the following were considered: (i) careful selection of the number of hidden neurons in accordance to the guidance provided in literature (as discussed in Section 2.6.3.4) and (ii) reliance on MATLAB's built-in early stopping mechanism, which is enabled by default to help prevent overfitting.

Table 4.3. Validation of models and comparison of a range of hidden neuron results using the LM algorithm and the MIMO or MISO topology

Hidden neurons	R^2	RMSE	MAE
MIMO			
3	0.96	7.86	5.23
4	0.99	2.99	2.06
5	0.97	7.04	3.31
6	0.98	5.51	4.54
7	0.98	6.37	4.31
MISO			
3	0.99	2.68	2.03
4	0.99	3.03	2.04
5	0.97	6.34	4.56
6	0.99	4.28	2.26
7	0.99	4.04	1.75

4.3.2.2 Scaled Conjugate Gradient (SCG) algorithm

The results when modelling the extraction efficiencies using the SCG model are provided in Figure 4.5, while the calculated performance parameters are given in Table 4.4. It is clear from both the figure and the table that the SCG is alike and as suitable as the LM algorithm in predicting the target extraction efficiencies. The performance factors in Table 4.4 indicate that the use of six hidden neurons seems optimal (highest R^2 and lowest MAE and RMSE) for the SCG model.

Similar to the LM model, this non-linear model provides a significant improvement over the linear models presented in Figure 4.2, despite some observed deviations from the experimental data, for example at sample point 18 when using three or four neurons. This visual inaccuracy is however reflected in both cases in the higher RMSE obtained, which however was still significantly lower than the best RMSE (84.2) obtained for a linear model.

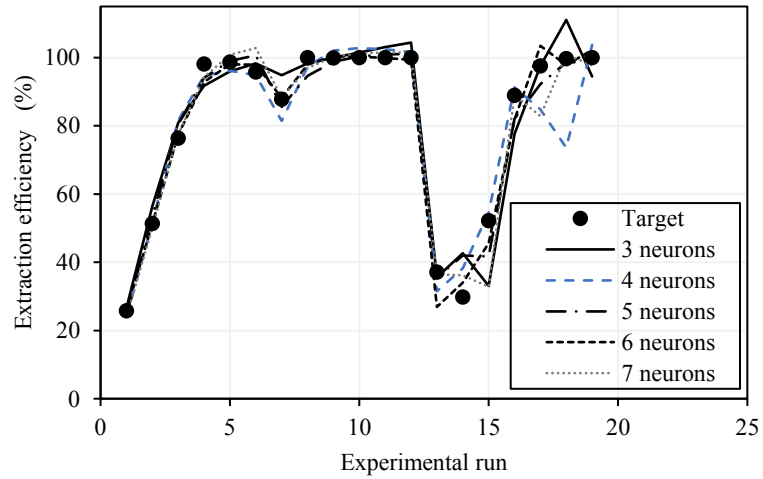


Figure 4.5. MISO topology prediction with the use of the SCG algorithm

Table 4.4. Validation of models and comparison of a range of hidden neuron results with the use of the SCG algorithm

Hidden neurons	R ²	MAE	RMSE
3	0.99	5.34	7.26
4	0.99	4.92	7.58
5	0.99	3.50	4.81
6	0.99	2.72	3.98
7	0.96	3.69	6.19

4.3.2.3 Bayesian Regulation (BR) algorithm

The results when modelling the extraction efficiencies using the BR model are provided in Figure 4.6, while the calculated performance parameters are given in Table 4.5.

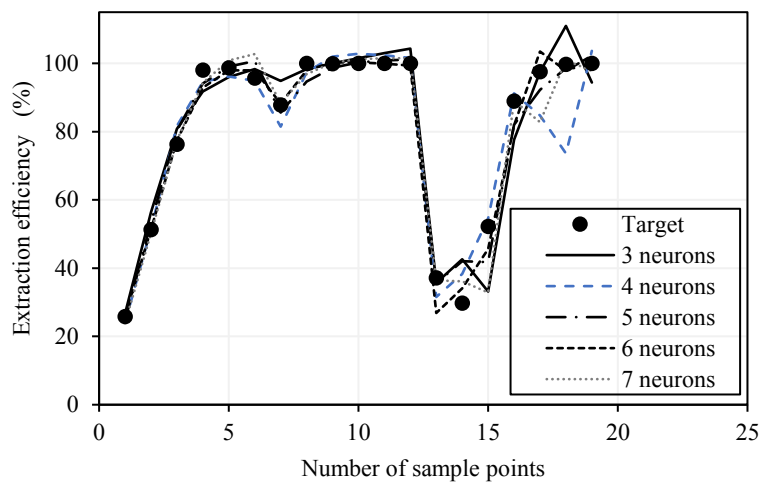


Figure 4.6. MISO topology prediction with the use of the BR algorithm

The BR algorithm again provided an excellent fit irrespective of the number of neurons used ($R^2 \geq 0.99$). According to Table 4.5 four hidden neurons gave the optimal fit (MAE = 1.22 and RMSE = 2.96), although the minimum point at sample point 14 was not captured properly. As a result, four hidden neurons were chosen as the optimal BR model.

Table 4.5. Validation of models and comparison of a range of hidden neuron results with the use of the BR algorithm

Hidden neurons	R ²	MAE	RMSE
3	0.99	2.59	3.81
4	0.99	1.22	2.96
5	0.99	2.32	3.22
6	0.99	2.55	3.72
7	0.99	2.25	2.96

4.3.2.4 Comparison and correlation of non-linear models

The best performance parameters of the three optimal ANN topologies (LM – with 3 hidden neurons, SCG – with 6 hidden neurons and BR – with 4 hidden neurons), using the MISO topology, are provided in Table 4.6. According to the performance parameters obtained ($R^2 = 0.99$, $RMSE \leq 4$ and $MAE \leq 3.5$), all three non-linear networks that had been optimised in terms of topology and number of hidden neurons, were essentially able to capture the relationships hidden in the data of the sample space. Although all three non-linear models proved to be suitable, when comparing the models, the BR topology was the most accurate with a low RMSE (3.0) and the lowest MAE (1.2) values, followed by the 2.7 (RMSE) and 2.0 (MAE) obtained when using the LM model.

Table 4.6. Overall comparison of ANN results when using the MISO topology with different algorithms

	LM	SCG	BR
R ²	0.99	0.99	0.99
RMSE	2.7	4.0	3.0
MAE	2.0	3.5	1.2

For the correlation study using the weights of the obtained optimal ANN in the Garson modified by Goh algorithm [1], the relative importance of the variables was assessed as presented in Figure 4.7. For this part of the study, the BR model was used. This was determined to ensure that the information obtained from the correlation coefficient is still valid when capturing hidden relationships in the data with the use of ANNs.

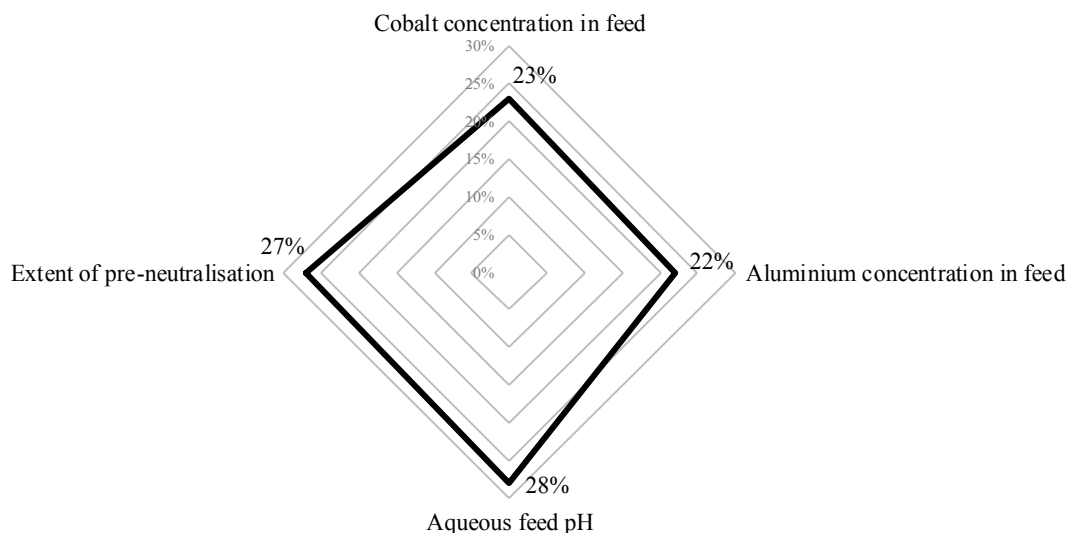


Figure 4.7. Illustration of the relative importance of variables to the extraction efficiency of aluminium

From this relative importance illustration, it can be deduced that (1) all four identified variables have a significant effect on the extraction efficiency of Al and (2) all four variables have a similar significance. According to the results obtained from the correlation and directionality study (Section 4.3.1) on the linear regression models, the pH had the most significant effect with the other three variables all similar.

However, although all variables had a similar influence when using the non-linear regression model (Figure 4.7), the influence of the pH on the extraction efficiency was again slightly larger (as indicated by the linear models), followed by the extent of pre-neutralisation and finally the Co and Al feed concentrations.

This implies that depending on the specific industrial application, the catalyst assay should be investigated to understand the metal competition and the amount of extracted metal which will then determine the required pH control. However, this can be seen as standard practice. It is however noteworthy that according to the analysis of the non-linear model, the initial feed metal concentration would be of similar significance than the pH and pre-neutralisation.

4.3.3 Linear and non-linear model comparison

In Figure 4.8, the best linear model (OLR) is compared with the best non-linear model, (BR algorithm) in terms of the target values, clearly showing the significantly closer fit obtained with the non-linear model.

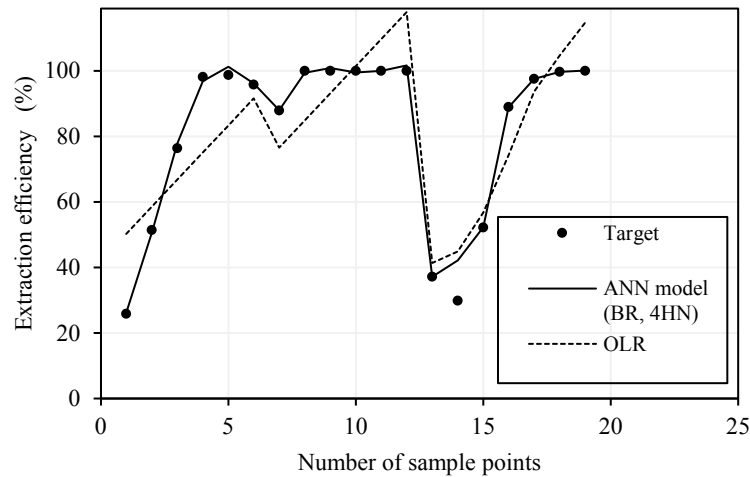


Figure 4.8. Comparison of the best performing linear regression model with the best non-linear regression model

This is confirmed when considering the calculated performance factors given in Table 4.7. The BR ANN ($R^2 = 0.99$, RMSE = 3.0 and MAE = 1.2) predicted significantly better than the OLR model. The BR model's RMSE is twenty-eight times smaller while the MAE is nine times smaller than that of the OLR model. As discussed previously, all three non-linear models outperformed the OLR, confirming the existence of non-linear relationships hidden in the data of the sample space. Although BR outperformed OLR, it is still important to acknowledge that with rudimentary equations, the ability to obtain directional results that are not prone to overfitting is a strength of the OLR technique.

Table 4.7. Overall comparison of linear and non-linear model performance

	Ordinary (Linear regression)	BR (Non-linear regression)
R^2	0.76	0.99
RMSE	84.2	3.0
MAE	10.9	1.2

4.4 Chapter conclusion

Using both linear and non-linear models, it was confirmed that the pH of an aqueous solution had the biggest impact on the extraction efficiency of Al from a Co-Al solution using SX followed by the effect of pre-neutralisation. It was however also confirmed that the concentration of both the aqueous feed metals (Al and Co) had a significant impact on the extraction efficiency. The ORL was found to be the best linear regression technique being able to capture 80% of the relationships in the data. However, the limitation of all the linear models was confirmed by the poor performance parameters (RMSE = 84.2% and MAE = 10.9%) obtained.

These performance results suggested the presence of non-linearity in the sample space. This was confirmed by the significant improvement in prediction capability when using ANNs. All three ANN, i.e. LM, SCG and BR, provided a significantly more accurate prediction than the ORL, with BR using the MISO topology and four hidden neurons providing the best fit of the ANNs by being able to capture all the relationships in the data with an $R^2 = 0.99$ and a high accuracy for both RMSE (3.0) and MAE (1.2). As a final thought, it is important to note that these models possess potential limitations, as extrapolation beyond the range of the input data carries an inherent risk of inaccuracy.

4.5 References

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5 Adapting the Sherwood number for mass transfer modelling in pertraction-based separation of cobalt and aluminium from spent catalyst leach solutions

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5.1 Introduction

While many literature articles found that the PX technology has multiple advantages over mixer-settlers (as highlighted in Section 2.7), no Co and Al separation commercial-scale facility is currently operational, nor is there any literature on separating these two metals with the PX technique. Consequently, this chapter has three objectives: (i) to confirm the suitability of PX technology for separating Co and Al, (ii) to develop an analytical model of the experimental setup (mainly focusing on the extraction phase) and (iii) to scale it up to an industrial-size facility, since the model will be used to size an industrial-scale PX facility (extraction phase) capable of delivering similar throughputs to the mixer-settler facility (sized in Chapter 3).

5.2 Method

This section contains a lot of mathematical equations and procedures. Therefore, a high-level procedure is provided in Section 5.2.5 to guide the reader on the flow of calculations provided in sections 5.2.1 and 5.2.2.

5.2.1 Experimental method

5.2.1.1 *Experimental setup*

The PX experiments conducted fulfilled mainly two purposes, (i) to test the technique's capability to separate Co and Al and (ii) to obtain overall equilibrium mass transfer coefficients that can act as validation for the analytical model as developed within this chapter. Similar to the SX experiments (see Section 3.2), cobalt(II)sulfate, aluminium sulfate and distilled water were used to prepare the aqueous phase solutions, while ShellSol2325, Cyanex272, tributyl phosphate and ammonium hydroxide (pre-conditioning) were used to prepare the organic phase solutions.

Additional details regarding the chemicals used for the synthetic aqueous and organic solutions can be obtained in Section 3.2.2 (Table 3.2). Aside from the membrane module, standard solvent extraction laboratory equipment was used to conduct the experiments, i.e. pH meter, scale, separation funnel and shaking incubator. To analyse the aqueous phase composition, ICP-OES was used. More detailed information regarding the equipment, manufacturers and the calibration thereof can be obtained in Section 3.2.

The PX experimental setup is provided in Figure 5.1 where a lab scale 1.4 m² 3M™ Liqui-Cel EXF-2.5x8 hydrophobic membrane module was used. Additional detail regarding the experimental module characteristics (as obtained from the manufacturer's datasheet [1]) is presented in Table 5.1. The circulating batch experiment was conducted at room temperature, using an O:A ratio of 1:1. Samples of

the extracted aqueous phase were taken at regular intervals over a period of two hours and analysed with ICP-OES (total volume of samples were negligible compared to the volume of the batch).

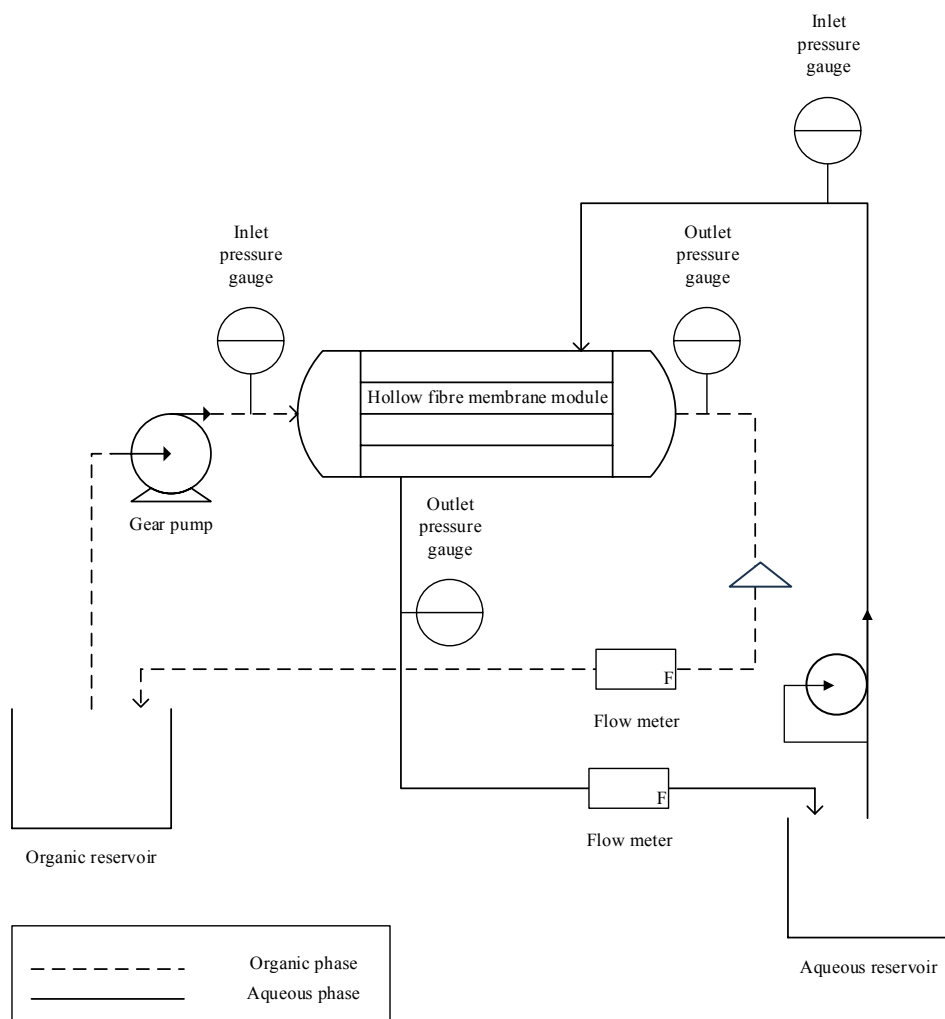


Figure 5.1. Benchtop pertraction experimental setup

Table 5.1. PX experimental bench-scale membrane module (1.4 m²) characteristics datasheet [1]

Parameter	Value	Unit
Membrane	3M™ Liqui-Cel EXF-2.5x8	-
Module diameter	6.7	cm
Membrane length	24.4	cm
Inner diameter of fibre	220	μm
Outside diameter of fibre	300	μm
Pore diameter	0.04	μm
Minimum flow rate	1000	ml/min
Tortuosity	2.5	-
Packing density	0.35	-
Porosity	0.4	-

5.2.1.2 Experimental conditions

The PX experimental conditions and synthetic solution composition are provided in Table 5.2. The optimal conditions were obtained using SX shake-out tests (Chapter 3) except for the contact temperature. An optimal temperature of 40°C was obtained in Chapter 3, whereas room temperature was chosen for the PX experiments due to the membrane heating complexity and to conduct the experimental runs at a constant temperature. Although the process fluid can be heated, the temperature within the membrane itself cannot be controlled and will decrease during operation.

Table 5.2. PX experimental conditions and synthetic solution composition

Parameter	Value	Unit
Temperature	25	°C
Aqueous flow rate	1000	mL/min
Organic flow rate	1000	mL/min
Aluminium feed concentration	0.9	g/L
Cobalt feed concentration	0.1	g/L
Aqueous feed pH	3.13	-
TBP	5	vol.%
Cyanex272	20	vol.%
Extent of pre-neutralisation (NH ₄ OH)	50	mol.%

5.2.1.3 Determination of experimental mass transfer coefficients ($k_{exp,ov}$)

Using the conditions and setup provided in Section 5.2.1.1 and 5.2.1.2, batch PX kinetics were measured to obtain an extraction efficiency of each metal as a function of time, which were used to determine the overall experimental mass transfer coefficient ($k_{exp,ov}$) of Co and Al. The combination of the mass balance and mass transfer equations (Equation (5-1) and (5-2) respectively) were used to obtain the overall experimental mass transfer coefficient ($k_{exp,ov}$) using Equation (5-3) [2].

$$V_{aq} \left(\frac{dx}{dt} \right) + V_{org} \left(\frac{dx}{dt} \right) = 0 \quad (5-1)$$

$$\frac{dx}{dt} = - \frac{k_{exp,ov} A}{V_{aq}} \left(x - \frac{y}{D} \right) \quad (5-2)$$

$$k_{exp,ov} = K = \frac{m Q_{org}}{A} \quad (5-3)$$

Where V refers to the volume (m³), x refers to the concentration (g/L), y the extraction efficiency (%), $k_{exp,ov}$ the overall mass transfer coefficient (m/s), D the distribution coefficient (-), m the slope [extraction efficiency (%)/time (s)], A the circular cross-sectional area of the shell, where $A = \frac{\pi d_{mod}^2}{4}$ (m²), d_{mod} the module diameter (m) and Q refers to the flow rate (m³/s).

5.2.2 Mathematical model development

5.2.2.1 Model philosophy

The mathematical model was developed to estimate the extraction efficiencies of Co and Al when using industry-scale membranes in series. It was based on results from benchtop experiments (Section 5.2.1). The model calculates the mass transfer coefficient using first principles, specifically the resistance-in-series approach, to determine the transferrate of each metal. The model setup consisted of two key steps: (i) validating the mathematically derived overall mass transfer coefficient (k_{var}) and (ii) applying the validated model to industry-scale membranes.

To determine k_{var} mathematically, an existing hollow-fibre membrane Sherwood model was adapted for PX applications. The model was first validated using a benchtop membrane by comparing the calculated overall mass transfer coefficient (k_{var}) with the experimentally determined coefficient ($k_{exp,ov}$).

Once the fit-for-purpose Sherwood equation and k_{var} (as a function of varying distribution coefficients) were established, the mathematical model was applied to industry-scale membrane modules. The relevant assumptions are detailed in Section 5.2.2.2.

5.2.2.2 Assumptions

The mathematical model relied on multiple inputs. The membrane characteristics were obtained from the manufacturer's datasheets, while key fluid characteristics were obtained from the fluid data sheets (as shown in Table 5.3). The plant online time was assumed to be 8000 h/a.

Table 5.3. Mathematical model assumptions

Assumption	Value/comment	Unit
Dynamic viscosity of Cyanex272	0.028	Pa·s
Dynamic viscosity of ShellSol2325	0.0016	Pa·s
Dynamic viscosity of TBP	0.002	Pa·s
Kinematic viscosity of organic fluid (20 vol.% Cyanex272)	7.45×10^{-6}	m ² /s
PX plant operating hours	8000	h/a

5.2.2.3 Determination of the overall mass transfer coefficient (k_{var})

5.2.2.3.1 Background and theory

For this section, it is important to revisit the working principle of the hollow fibre membrane since the design philosophy speaks directly to it. Computer Aided Design (CAD) drawings of the membrane module and the internals are provided in Figure 5.2 (i) providing a view of the fluid inlet and outlet

configuration for counter-current flow, whereas Figure 5.2 (ii) provides a cross-sectional view of the module, exposing the internals. The lumen side (also known as the tube/fibre side) is assumed to consist of laminar flow, which is confirmed during the model development by calculating the Reynolds number, whereas the baffle on the shell side will promote turbulent flow.

During the extraction step, the organic feed and the aqueous phase were circulated through the fibres and over the bank of fibres (shell side) respectively. The pores in the membrane then allow for contacting of the aqueous and the organic phase and hence the transfer of the desired metal.

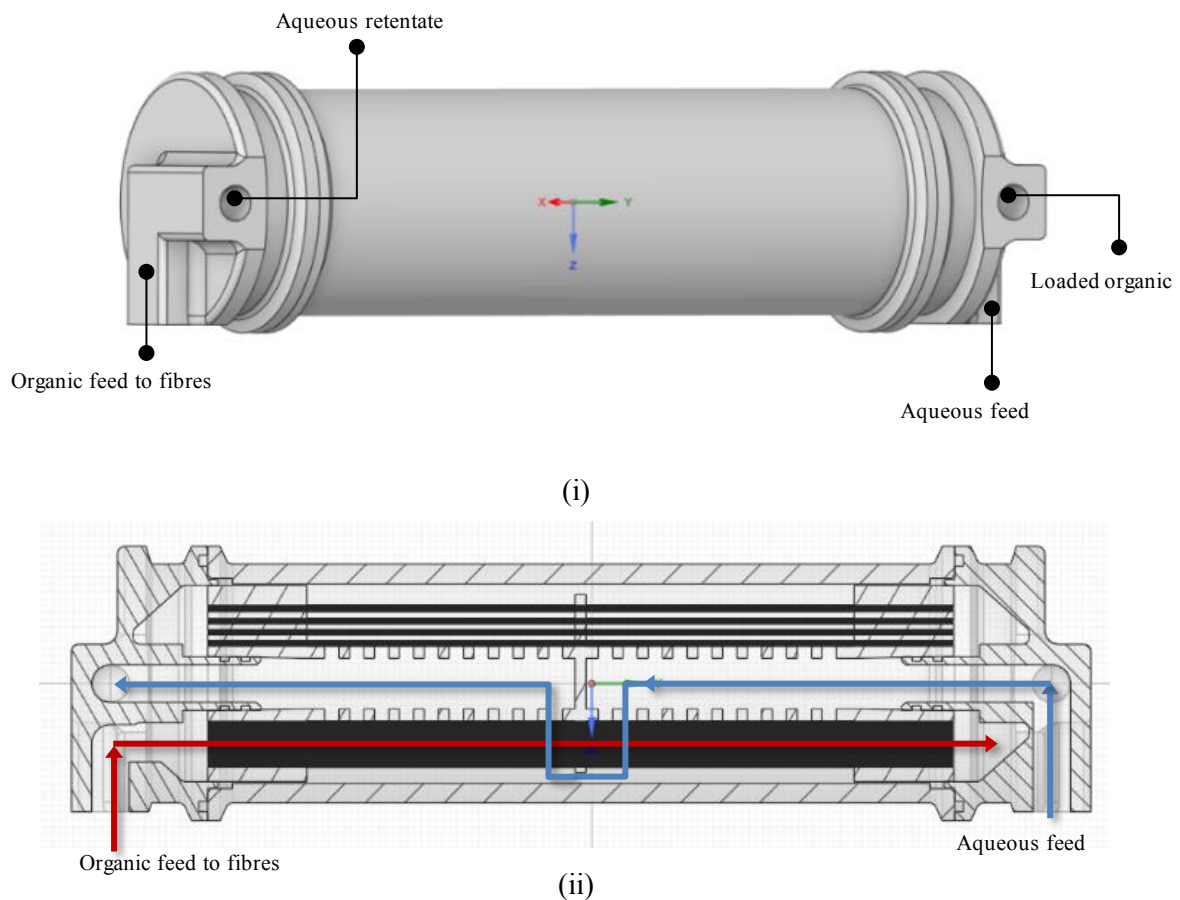


Figure 5.2. CAD drawings of the bench scale hollow fibre membrane with (i) representing the external view of the membrane and (ii) the internal cross-sectional view

While the membranes have numerous microscopic pores, it is assumed that the mass transfer concept remains the same across each. Hence, to simplify the working of the membrane, a single pore was used as a reference (Figure 5.3). The fixed and known number of pores per membrane allows for a constant and known contact area while keeping the phases separated from one another. To avoid phase entrainment, one side of the membrane was typically operated at a slightly higher pressure.

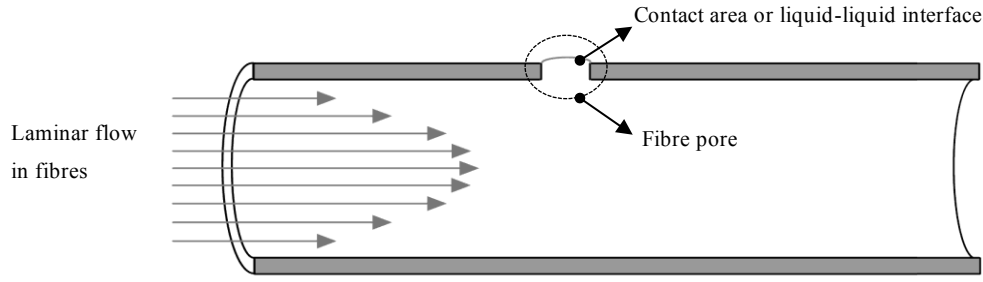


Figure 5.3. Illustration of a single fibre and a single pore

5.2.2.3.2 Mathematical philosophy to determine k_{var}

To describe the movement of a solute per unit area and unit time, a flux, (J) measured in ($\text{kg m}^{-2} \text{s}^{-1}$), was calculated. Considering mass transfer in a membrane, the flux can be calculated using Equation (5-4) [3]. Notice how the flux is only dependent on two factors, i.e. the mass transfer coefficient (K) and the driving force (F), one factor acting against and one acting for the movement.

$$J = K\Delta F \quad (5-4)$$

The mass transfer coefficient quantifies the resistance to flow due to friction against surfaces, other molecules, etc. With hollow fibre membranes, the solute needs to mainly overcome three steps (restrictions) in series (i) travel from the bulk of the feed to the fibre surface, (ii) travel across the boundary at the contact area, and lastly (iii) travel from the contact area into the bulk permeate. Based on the resistance-in-series model (depicted in Figure 5.4 and Equation (5-5)), the varying overall mass transfer coefficient can be expressed by Equation (5-6) [3].

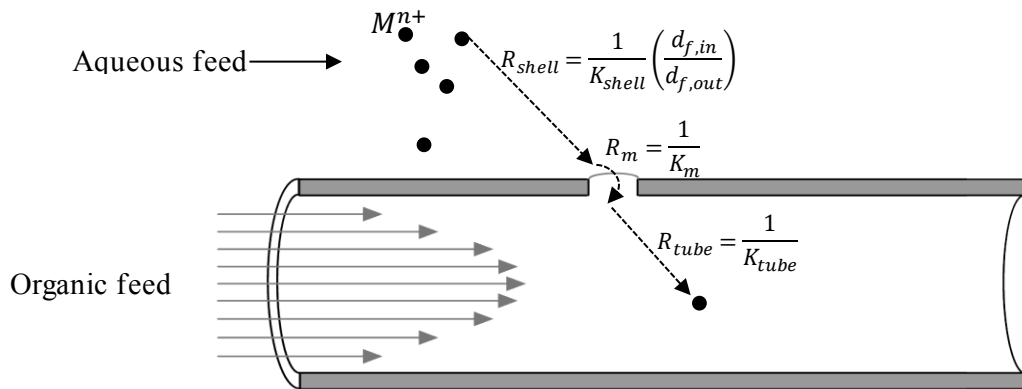


Figure 5.4. Illustration of the resistance steps relevant to the PX extraction step

$$R_{Total} = R_m + R_{tube} + R_{shell} \quad (5-5)$$

$$\frac{1}{K} = \frac{1}{K_m} + \frac{1}{K_{tube}} + \frac{1}{K_{shell}} \left(\frac{d_{f,in}}{d_{f,out}} \right) \quad (5-6)$$

Where K_m , K_{tube} and K_{shell} refers to the mass transfer coefficient of the membrane pore, tube side fluid (fibres) and shell side fluid respectively. Furthermore, $d_{f,in}$ and $d_{f,out}$ refers to the inner and outer diameter of the fibre (m). The individual factors forming the overall mass transfer coefficient K , as expressed in Equation (5-6), are illustrated below.

K_m is dependent on the distribution coefficient, D (-) as well as membrane characteristics including the membrane porosity, ϵ (-), the tortuosity, τ (-) and the membrane wall thickness, δ_m (m), which were obtained from the membrane manufacturer technical data sheets as presented in Table 5.5 [4], [5], [6], [7]. To calculate K_m , equations (5-7) to (5-9) can be used [3].

$$K_m = \frac{D\epsilon}{\tau\delta_m} \quad (5-7)$$

$$\epsilon = \frac{V_{pores}}{V_{tot}} \quad (5-8)$$

$$\delta_m = \frac{(d_{f,out} - d_{f,in})}{2} \quad (5-9)$$

Where D can be calculated with Equation (5-10), where c_{ext} and c_{raff} represents the concentration of species in the organic and aqueous phases respectively (kg/m^3).

$$D = \frac{c_{ext}}{c_{raff}} \quad (5-10)$$

K_{tube} is dependent on the fluid properties (i.e. density and viscosity), the distribution coefficient and other membrane properties (i.e. the inner diameter of the fibre and the length of the membrane) as shown in Equation (5-11) [3].

$$K_{tube} = 1.62 \left(\frac{D_t^2 \mu}{\rho L d_{f,in}} \right)^{0.33} \quad (5-11)$$

Where D_t refers to the distribution coefficient of the metals from the fibre side fluid perspective, μ refers to the dynamic viscosity of the mixture ($\text{Pa}\cdot\text{s}$) which can be calculated using Equation (5-12) and Equation (5-13) [8]. Furthermore ρ refers to the density of the mixture (kg/m^3) and L the length of the membrane module (m).

$$VBN_i = \ln \frac{(\mu_i)}{\ln(1000 \times \mu_i)} \quad (5-12)$$

$$VBN_{mix} = \sum_{i=0}^N v_i \times VBN_i \quad (5-13)$$

Where VBN_i indicates a viscosity blending number of component i in a mixture of N components, μ_i indicates the dynamic viscosity of the species i (Pa·s) and v_i indicates the percentage volume each component takes up in the mixture.

Finally, K_{shell} can be calculated using the Equation (5-14).

$$K_{shell} = Sh \times \frac{D}{L} \quad (5-14)$$

To determine K_{shell} , the relevant Sherwood (Sh) equation needs to be obtained. However, for hollow fibre membranes in the PX application, Sherwood approximations are scarce. In Table 5.4 Sherwood approximations for an applicable hollow fibre membrane were listed as a starting point. These approximations were varied within the model to find the Sherwood equation that most accurately captures the flow regime within the shell side of the membrane module. The optimal Sherwood equation was thereafter further adjusted to ensure its suitability for a liquid-liquid metal separation application.

The Sherwood number depends on the type of flow (flow regime), fluid velocity and type of packing of the membrane. The flow regime is characterised by the Reynolds number, as provided in Equation (5-15)³.

$$Re_{shell} = \frac{\rho \bar{u}_{max} d_{f,out}}{\mu} \quad (5-15)$$

$$\bar{u}_{max} = \frac{\sqrt{4b^2 + a} - 2}{a} \bar{u}_{mean} \quad (5-16)$$

Where $\bar{u}_{max}$ and $\bar{u}_{mean}$ indicate the average maximum and average mean velocities (m/s) of the fluid which is calculated with the use of $a = \frac{2b}{\sqrt{3}}$ and $a \times b = 1.563$ for compact packing.⁴

Regarding Table 5.4, ϕ represents packing density (generally within the range of 0.43% and 0.56% [9]), Re and Sc ($Sc = \frac{\nu}{D}$), indicate the Reynolds and Schmidt numbers respectively, where ν indicates the kinematic viscosity of the fluid (m²/s). For a comprehensive description of the symbols please see the List of symbols presented on pages xi-xii of this thesis.

³ The Reynolds number formula is applicable for external flow over a bank of tubes.

⁴ Solve for a and b simultaneously to use in Equation (5-16).

Table 5.4. Existing Sherwood approximations specifically relevant to hollow fibre membranes

Nr.	Sherwood approximation	Relevant when	Relevant case	Remarks	Ref
1	$Sh = \beta(1 - \phi)Re^{0.6}Sc^{0.33}\left(\frac{d_h}{L}\right)$	$Re > 500$	Shell-side axial flow	$\beta = 5.8$ for a hydrophobic membrane $\beta = 6.1$ for a hydrophilic membrane $\phi = 0.4\% - 40\%$	[10]
2	$Sh_r = \beta \left(\frac{1}{(0.86 - 0.3\phi_0)\phi_0} \right) \left(\frac{ReSc d_h}{L} \right)^{(0.3\phi_0 + 0.14)}$	$68 < Re < 1194$ $70 < Gz < 5039$	Including fibre and flow distribution randomness	β refers to a non-dimensional randomness factor $\phi = 20\% - 50\%$	[11]
3	$Sh = 0.09(1 - \phi)Re^{(0.8 - 0.16\phi)}Sc^{0.33}$	$Re_{16} < 10$	For regularly packed fibres	$\phi = 37\% - 97\%$	[3]
4	$Sh = (0.31\phi^2 - 0.34\phi + 0.10)Re^{0.9}Sc^{0.33}$	$32 < Re < 1287$	Flow maldistribution is considered	$\phi = 38\% - 70\%$	[12]

5.2.2.3.3 Approach to determine the distribution coefficient

Equations (5-7), (5-11) and (5-14) show the dependence of each step of the mass transfer resistance on the distribution coefficient. To ensure the correct approximation of the metal ion's distribution coefficient, three approaches were taken: (i) assume a static equilibrium distribution coefficient (as determined with SX shake-out tests), (ii) use isotherms (see Section 3.3.3.5) to obtain a varying distribution coefficient as a function of the metal concentration and (iii) calculate the distribution coefficients as obtained from the PX circulating batch experiment to also obtain a varying distribution coefficient as a function of metal concentration.

Since the distribution coefficient acts as a quantification of the metal ion's drive to transfer, the first approach should provide the model with a view of the extractant's selectivity. However, with a constant distribution coefficient, it is not expected that the mathematical model will be able to reach equilibrium. The second approach allows for a varying distribution coefficient as a function of metal concentration, which should scale the transfer rate accordingly. However, since the isotherm experiments were conducted separately with a single metal ion in solution, it is likely that the competition between metals is not captured, causing the model to predict higher transfer rates than what would have been obtained had metal mixtures been contacted to an extractant. This will however not affect the model development (refer to Section 5.3.2). Furthermore, the isotherm experiments at each concentration were conducted

before any extractant saturation occurred, which is also expected to lead to an overestimation of transfer rates.

Accordingly, the third approach aimed to capture metal competition and accurately quantify the distribution coefficients of metal ions in a mixture as a function of metal concentration while taking extractant saturation into account.

5.2.2.4 Prediction of extraction efficiencies as a function of time

In PX, the driving force, unlike reverse osmosis, is not a pressure difference but a concentration gradient forming across the contact area between the two fluids. This phenomenon is the foundation of many mathematical models developed and labelled as solution-diffusion models (commonly used to mathematically present liquid-liquid extraction in membranes as provided in Figure 5.5) [13], [14].

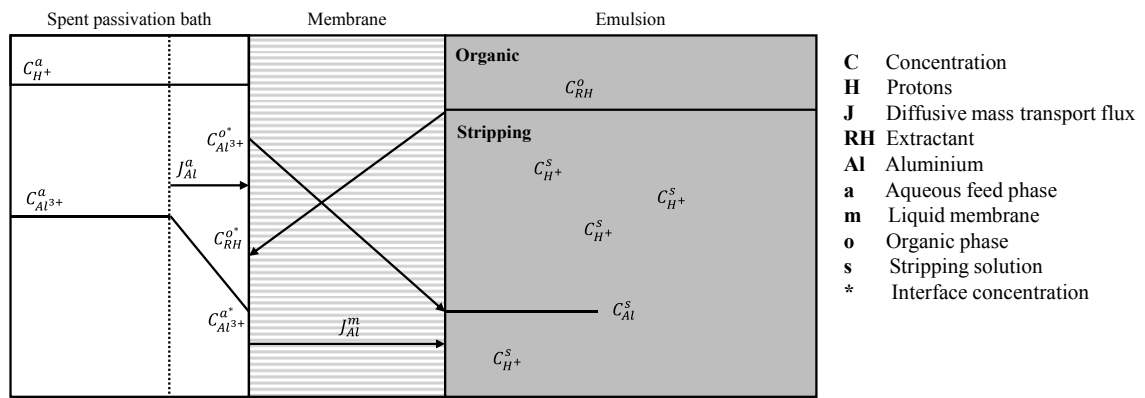


Figure 5.5. Enlarged view of a hollow fibre membrane (solution-diffusion model) as adapted from Bringas et al [14]

For hollow fibre membranes, a model provided in Equation (5-17) can be used to estimate the dependence of the solute concentration on the distance through the membrane [11].

$$C_s(z) = C_{s_i} \left(1 - \exp \left(- \frac{4Kz}{\bar{u}_{mean}d_{mod}} \right) \right) \quad (5-17)$$

Where C_s is the solute concentration (g/L) transferred to the permeate phase for the interval z , the distance travelled through the fibre (m), C_{s_i} the bulk concentration of the solute in the feed/retentate phase (g/L), $\bar{u}_{mean}$ the average mean velocity of the fluid on the shell side (m/s) and d_{mod} the diameter of the membrane (m).

The mass balance for a circulating batch system (as presented in Equation (5-18)) will then determine the C_{s_i} for the next interval. The concentration of the metal ion in the contacting fluid can be calculated with a standard mass balance, taking the O:A ratio into account and assuming no losses or bleed streams.

$$C_{s_{i+1}} = \frac{\left(C_s \times \left(\frac{z}{L_{mem}}\right) V_{mod}\right)}{V_{Batch}} + \frac{C_{s_i} \left(V_{Batch} - \left(\frac{z}{L_{mem}}\right) V_{mod}\right)}{V_{Batch}} \quad (5-18)$$

5.2.2.5 Pressure drop estimation

The pressure drop across the membrane is not only an operating expense for a PX facility but is also an important parameter to control to ensure breakthrough is avoided, which occurs if the pressure is less than the bubble point pressure. Since the flow behaviour in the fibres and the shell side of the module differ significantly, two different approaches were followed to determine the pressure drop through the fibres and the shell side.

The tube side of the membrane is filled with fibres, forming a porous structure. As fluid flows through the annular spaces between the fibres, it behaves like a fluid moving through a porous medium. The Ergun equation (Equation (5-19)) is well-suited for estimating the pressure drop (ΔP_{tube} in Pa/m) in such a system [15].

$$\Delta P_{tube} = \frac{150\mu(1-\epsilon)^2 \bar{u}_{mean}}{d_{f,in}^2 \epsilon^3} + \frac{1.75\rho(1-\epsilon) \bar{u}_{mean}^2}{d_{f,in} \epsilon^3} \quad (5-19)$$

On the shell side of a hollow fibre membrane, the flow is typically more complex because the fluid flows around the outside of the fibres, not through them. The shell side flow generally behaves differently than the flow through the porous media on the tube side, often resulting in less significant resistance compared to the tube side. The shell side typically involves more open flow paths with significantly less direct interaction with the membrane surface. In such cases, the pressure drop is often governed more by the flow distribution, bypass effects, and turbulent flow around the fibres, rather than the same kind of viscous and inertial effects seen inside the fibres.

Therefore, models like the Darcy-Weisbach equation (Equation (5-20)) or empirical correlations that account for flow patterns and shell-side geometry are often used instead of the Ergun equation [16].

$$\Delta P_{shell} = f \frac{L}{d_{f,out}} \left(\frac{\rho \bar{u}_{mean}^2}{2} \right) \quad (5-20)$$

Where f represent the Darcy-Weisbach friction factor (dimensionless) and is determined with Equation (5-21) for $Re < 2000$ or Equation (5-22) for $Re > 4000$.

$$f = \frac{64}{Re} \quad (5-21)$$

$$\frac{1}{\sqrt{f}} = -2 \log \left(\frac{\epsilon}{3.7 d_{f,out}} + \frac{2.51}{Re \sqrt{f}} \right) \quad (5-22)$$

5.2.3 Determination of an optimal industrial scale membrane

After the mathematical model has been validated with experimental results and its robustness confirmed, the model was applied to industrial-scale membranes. Four industry-scale membranes were identified (Table 5.5) for the evaluation. It is important to note that the X40 vs X50 membrane specifications are irrelevant to the liquid-liquid contacting principle as this is a method of distinguishment for gas-liquid contacting applications. The optimal membrane was determined and used to conduct the technology comparison study in Section 6.1.4. Note that the technical datasheets of the membranes are provided in Appendix C.

Table 5.5. Membrane specifications and relevant model inputs

Description	ϵ	Pore diameter (m) ⁶	τ	Inlet pipe diameter (m)	Q_{min} (m ³ /h)	L (m)	d_{mod} (m)	$d_{f,in}$ (m) ⁶	$d_{f,out}$ (m) ⁶
10x28 (X50)	0.4	0.04	2.5	0.248	10	1.186	0.28	300	220
8x80 (X40)	0.25	0.03	2.5	0.038	7	2.21	0.212	300	200
14x28 (X50)	0.4	0.04	2.5	0.104	16	1.156	0.356	300	220
14x40 (X40)	0.25	0.03	2.5	0.104	16	1.464	0.356	300	200

The membranes were evaluated based on four factors: (i) the maximum overall separation efficiency (as a function of extraction efficiency of Al and Co) along with (ii) the average overall mass transfer coefficient, (iii) the number of membranes required to achieve the optimal separation efficiency and (iv) the production rate of pure Al (<100 ppm Co).

5.2.4 Extraction phase PFD development

After the appropriate industry scale membrane has been obtained, high-level mass balances were conducted to determine the main equipment necessary to complete the desired separation. A high-level process flow diagram (PFD) was constructed to compare the Greenfields PX extraction step to conventional mixer-settler extraction. As mentioned in Chapter 3, only the extraction step for both mixer-settler and PX technologies was developed in further detail to obtain an estimated footprint of each facility while assuming that the findings for the extraction step will also apply for the scrubbing and stripping sections.

5.2.5 Summary procedure

Due to the mathematical nature of the previous sections in this chapter a summary of the procedure is provided below to (i) guide the reader and (ii) to ensure reproducibility.

Chapter 5 objective 1: Conduct PX benchtop experiments

Conditions	Use optimal conditions determined in Chapter 3 (also provided in Table 5.2).
Experimental setup	As provided in Figure 5.1.
<u>Return Objective 1</u>	Obtain PX benchtop extraction, scrubbing and stripping experimental results (<i>Objective 1 results</i>).

Chapter 5 objective 2: Calculated the overall experimental mass transfer coefficient ($k_{exp,ov}$) of Co and Al

Dataset	<i>Objective 1 results</i>
Data handling and preparation	Separate the data into two sections (i) the initial linear trend observed with the extraction efficiency results and (<i>Linear data set</i>) (ii) the point after equilibrium is being achieved.
Input data	Use the (<i>Linear data set</i>) as input into the mass transfer calculation
Calculate the overall experimental mass transfer coefficient	Calculate: (i) the slope of the <i>Linear data set</i> (ii) the radial cross-sectional area of the membrane module (iii) the flow rate Use (i) – (iii) as inputs into Equation (5-3)
<u>Return Objective 2</u>	Return $k_{exp,ov,Co}$ and $k_{exp,ov,Al}$

Chapter 5 objective 3: Develop a mathematical model that represents the results obtained from Objective 1 and Objective 2

Objective 3.1: Obtain a fit for purpose Sherwood approximation (repeat steps for Al and Co)

Input data	(i) Obtain fluid and membrane constant values in Table 5.3 and Table 5.5 Assume the distribution coefficient is constant as determined from Chapter 3
Calculate K_m	(i) Calculate the membrane mass transfer coefficient with Equation (5-7) while using Equation (5-8) and (5-9) to calculate ϵ and δ_m
Calculate K_{tube}	Calculate the fibre mass transfer coefficient with Equation (5-11) while using Equation (5-12) and (5-13) to obtain the mixture's viscosity
Calculate K_{shell}	(i) Calculate four different K_{shell} values by using Equation (5-14) and by varying the Sherwood approximations (as provided in Table 5.4). (ii) The Sherwood approximation is dependent on inputs such as the Reynolds and the maximum fluid velocity. Use Equation (5-15) and (5-16) to obtain these inputs
Calculate K_{var}	Calculate the varying overall mass transfer coefficient with Equation (5-6) Note, since four different Sherwood approximations were tested, four different K_{var} values will also be determined
Calculate the mass transfer as a function of distance travelled through the membrane	(i) Calculate the mass transfer of the metal as a function of the distance travelled through the membrane with Equation (5-17). (ii) Since the benchtop experiments were conducted as circulating batch, the concentration should be calculated along with Equation (5-18)
Compare to benchtop experiments	Plot the predicted mass transfer values as a function of distance through the membrane along with the experimental findings (<i>Objective 1 results</i>). Evaluate the accuracy with representative errors.
<u>Return Objective 3.1</u>	The Sherwood approximation that resulted in the highest prediction accuracy is chosen to continue further with the evaluation

Objective 3.2: Obtain a representative distribution coefficient equation (repeat steps for Al and Co)

Distribution coefficient	Using the most representative Sherwood <i>approximation</i> (Objective 3.1) vary the distribution coefficients using Equation (5-10): (i) Constant shake-out distribution coefficient (Chapter 3 – used in Objective 3.1) (ii) Isotherm distribution coefficient (Chapter 3) (iii) PX calculated distribution coefficients (Objective 1 results)
Calculate the mass transfer as a function of distance travelled through the membrane	Follow the steps from Objective 3.1 without varying the Sherwood approximation formula (keep constant as determined from Objective 3.1)
<u>Return Objective 3.2</u>	Obtain an optimal distribution coefficient equation as a function of metal concentration

Objective 3.3: Optimise the Sherwood approximation and finalise the model

Adapt Sherwood approximation	Optimise the Sherwood approximation by varying the β value to obtain the lowest error between the average predicted k_{var} and the determined $k_{exp,ov}$ (as obtained from Objective 2)
<u>Return Objective 3.3</u>	Obtain the ideal Sherwood approximation to use to predict mass transfer in industry scale membrane modules

5.3 Results

5.3.1 Circulating batch experimental results

The PX experiments were conducted according to the methodology explained in Section 5.2.1. Extraction (Section 5.3.1.1), scrubbing (Section 5.3.1.2) and stripping (Section 5.3.1.3) capabilities were experimentally evaluated to determine PX's capability to separate Co and Al. In Section 5.3.1.4, the determination of the mass transfer coefficient during extraction is presented.

5.3.1.1 Extraction

Figure 5.6 provides the extraction efficiency results of Co and Al when using a benchtop membrane and allowing the experiment to reach equilibrium. After a period of 150 min, 87% of the Al was extracted to the organic phase while 14% Co was co-extracted. The significant difference in extraction efficiencies of Co and Al provided in Figure 5.6 is proof that the PX technology is not only capable of separating the two metals but also delivers similar selectivity results at equilibrium as the mixer-settler separation mechanism. Hence, PX is just as capable as mixer-settlers to separate the two metal ions while not requiring mixing or downstream phase separation as would be required with mixer-settlers.

The Co and Al extraction efficiency results obtained from the PX experiments and the shake-out experiments were however expected to be similar since both experiments were conducted at similar conditions, with similar reagents and allowing ample time to reach equilibrium. Figure 5.6 therefore acts

as proof that the difference in the separation mechanism (phase mixture to create droplets with mixer-settlers vs. establishing contact across membrane pores with PX) that the PX technology offers, does not hinder the overall loading of the metal to the organic phase.

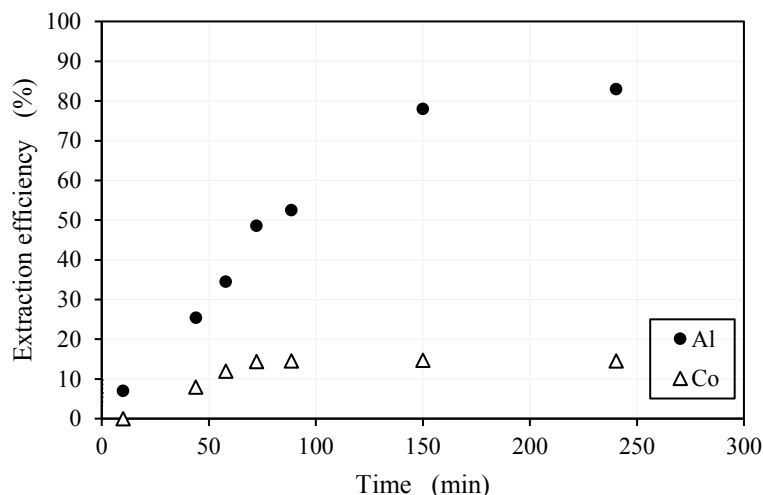


Figure 5.6. Experimental results of the PX extraction efficiency of cobalt and aluminium at 25°C, 1 atm, O:A ratio of 1:1 with 0.1 g/L of cobalt and 0.9 g/L of aluminium in the aqueous feed contacted to 20 vol.% Cyanex272, 5 vol.% TBP and the remainder ShellSol2325

Furthermore, due to the constant and known contact area that the PX technology offers, a more controlled environment is obtained in industry at any given time, allowing for precise optimisation at varying feed conditions. In contrast, the mixer-settler technology makes it difficult to determine the exact contact area during the mixing step, leading to uncertainty, reduced control, and ultimately a lower likelihood of achieving optimal separation efficiencies.

In conclusion, Figure 5.6 provided proof that the PX technology is just as capable of separating Co and Al from the sulphate solution while offering advantages like known contact area and therefore more precise control. However, resistance introduced by the separation does result in a significant time delay which should be compared to the residence time required by settler equipment on a mixer-settler facility. The difference in time can also be allocated to the small volumes used during the shake-out experimental runs compared to larger batch volumes used with PX.

5.3.1.2 Scrubbing

Figure 5.7 provides the scrubbing efficiency to remove Co from the loaded organic phase (obtained from the extraction step). The scrubbing kinetics indicated that equilibrium was reached (~2 min) whereby >96% of the Co was removed from the organic phase. This indicates that only one stage of scrubbing will be required. Note that negligible Al was removed during the scrubbing stage.

Membrane resistance appears to have a minimal impact on the scrubbing step compared to extraction, possibly due to the shorter diffusion path. Figure 5.8 (i) and (ii) illustrate the difference between hydrophobic and hydrophilic membranes. Since a hydrophobic membrane was used in these experiments, Figure 5.8 (i) is relevant. Therefore, when comparing the resistance between the scrubbing and extraction steps, observed differences may be attributed to variations in the metal ion's path to the interface and the difference in the pressure difference. To better understand the impact of membrane hydrophobicity, additional sensitivity analyses are recommended in future evaluations.

As more contact time is allowed a reduction in Co is also noted in Figure 5.7, which is likely due to the reloading of Co. Hence, one stage with short contact times 1-2 min is recommended to avoid reloading

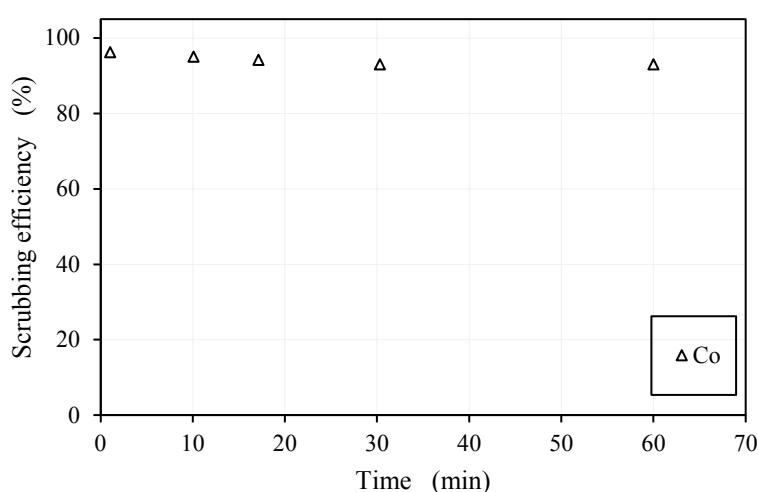


Figure 5.7. Experimental results of the PX scrubbing efficiency of cobalt and aluminium conducted at 25°C, 1 atm, O:A ratio of 1:1 contacted to a 50 g/L aluminium-rich solution

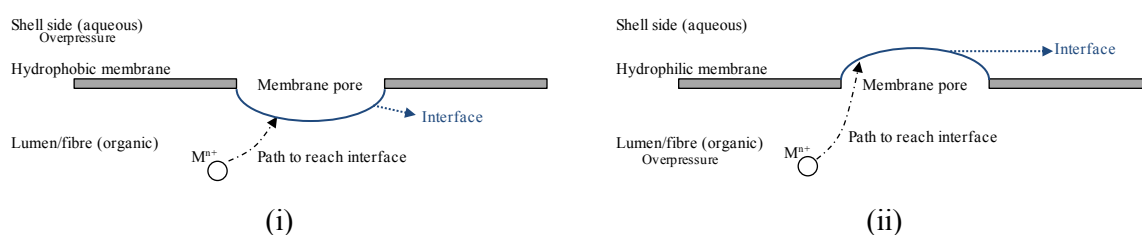


Figure 5.8. Depiction of interface location with respect to the membrane pore for (i) hydrophobic and (ii) hydrophilic membrane contactors

Scrubbing O:A ratios (conducted as a function of O:A flow rate) of 1:1 to 1:4 were also tested and found to produce similar results (seen in Figure 5.9). This can be expected due to the high scrubbing transfer rate (<2 min) that was observed in Figure 5.7.

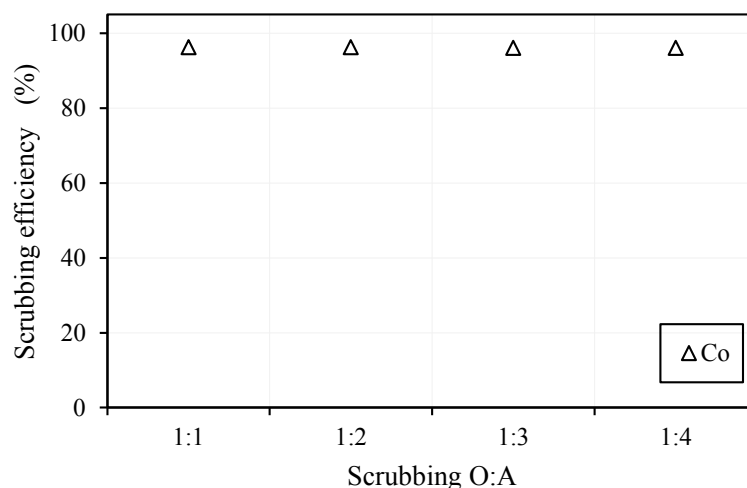


Figure 5.9. Experimental results of the PX scrubbing efficiencies at different O:A ratios (as a function of O:A flow rate) conducted at 25°C and 1 atm contacted with a 50 g/L aluminium-rich solution (samples taken after 5 min of contact)

5.3.1.3 Stripping

Stripping the scrubbed loaded organic using the PX technology was attained when stripping with 1 M H_2SO_4 as supported by Figure 5.10. Equilibrium is estimated to have been reached after ~150 min of contact time to establish a ~94% recovery of the Al from the scrubbed loaded organic phase at an O:A ratio of 1:4 (see Figure 5.11).

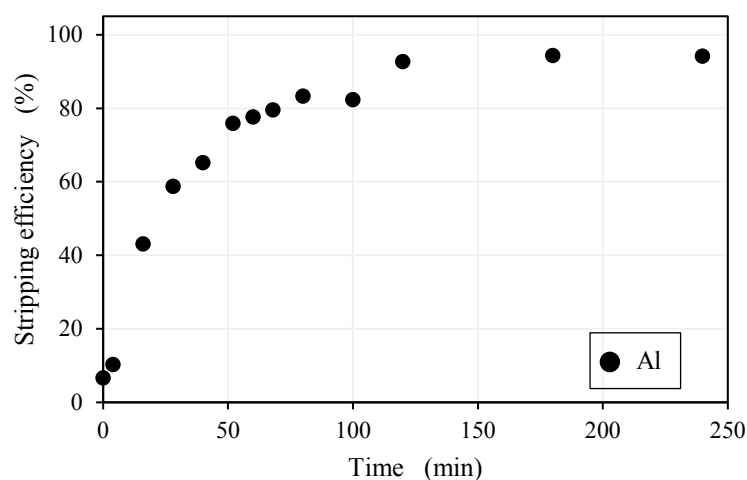


Figure 5.10. Experimental results of the PX stripping efficiency when contacting the loaded organic phase with 1 M H_2SO_4 at 25°C and 1 atm

O:A ratios of 1:1 to 1:4 were also tested and provided in Figure 5.11. An O:A ratio of 1:4 delivered the best stripping efficiency which can possibly be related to the highest concentration gradient at the contact interface.

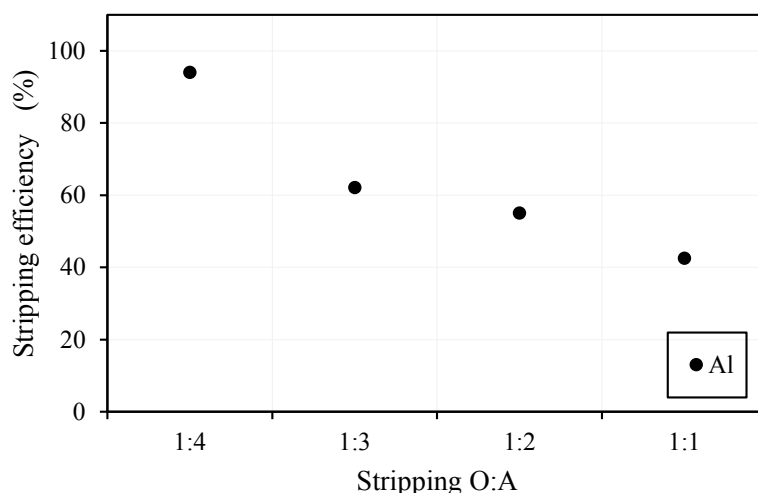


Figure 5.11. Experimental results of the PX stripping efficiencies at different O:A ratios when contacting the loaded organic phase with 1 M H₂SO₄ at 25°C and 1 atm

5.3.1.4 Determination of experimental mass transfer coefficients

In Section 5.3.1.1 to 5.3.1.3 it was shown that the PX technology is also capable of separating the two metals. Next, the overall experimental mass transfer coefficient ($k_{exp,ov}$) had to be determined to use as validation for the mathematic model (specifically focussing on the extraction step) that will be developed in the succeeding subsection.

The $k_{exp,ov}$ of Al and Co in the extraction step is shown in Figure 5.12 and Figure 5.13 respectively. The overall mass transfer coefficients for Al and Co using 20 vol.% Cyanex272 were calculated as 5.6×10^{-5} and 7.4×10^{-6} m/s respectively (with the use of equations (5-1) to (5-3)) comparing well with literature [2], [17]. These values were calculated by using the PX benchtop experimental results (determined in Section 5.3.1.1 to 5.3.1.3). Due to the selectivity of the extractant, from the experimental PX results, the mass transfer of Al was therefore estimated to be 8 times faster than that of Co, however, Co reaches equilibrium much quicker than Al indicating that the separation efficiency is likely both kinetically and thermodynamically driven. These results further agree well with the shake-out tests conducted in Section 3.3.3 whereby the difference in solubility of Al and Co led to the higher affinity of Al to the organic phase, driving the chemical separation of the ions across the phases.

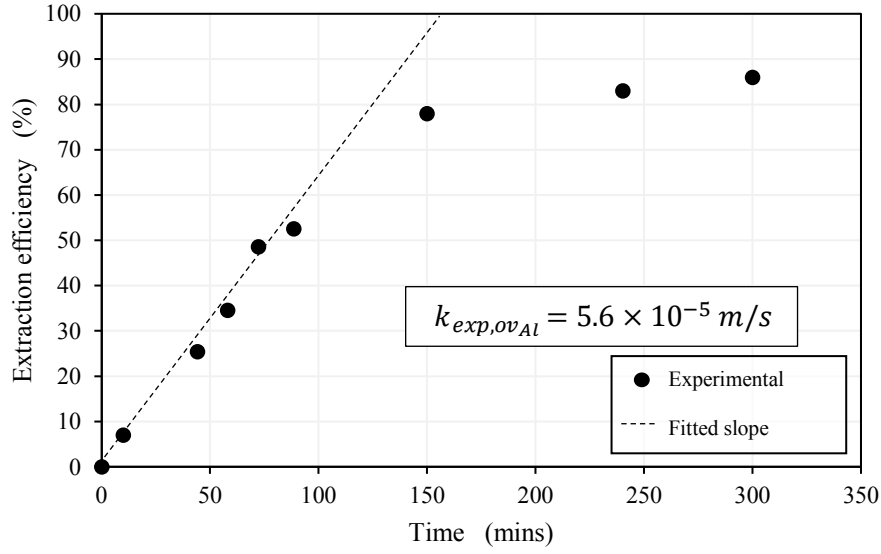


Figure 5.12. Determination of the overall experimental transfer coefficient of aluminium in the extraction phase

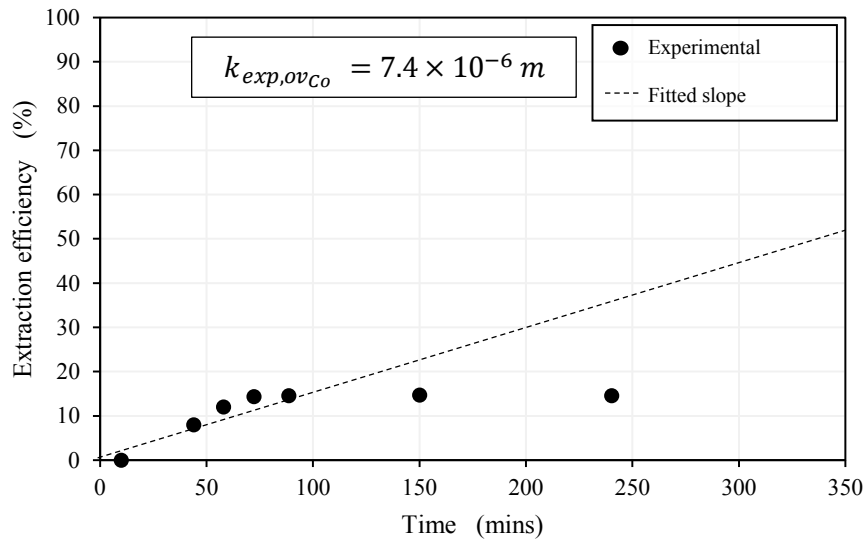


Figure 5.13. Determination of the overall experimental transfer coefficient of cobalt in the extraction phase

5.3.2 Mathematical modelling results

In the previous section (Section 5.3.1) the PX benchtop experimental results were provided along with the experimentally determined overall mass transfer coefficient. In this section, the overall varying mass transfer coefficient is determined from a mathematical perspective where the resistance in series model is used to estimate the resistance to mass transfer. The modelling of these resistance steps sets the foundation to the mass transfer rate. The mathematically determined varying mass transfer coefficient

is thereafter compared with the experimentally determined overall mass transfer coefficient to validate the model.

5.3.2.1 Obtaining fit for purpose Sherwood approximation

The overall mass transfer coefficient according to Equation (5-6), is not only a function of the fibre's inner and outer diameter but also a function of (i) the membrane pore mass transfer coefficient (K_m), (ii) the fibre fluid flow mass transfer coefficient (K_{tube}) and (iii) the shell side fluid mass transfer coefficient (K_{shell}). K_m and K_{tube} are mainly driven by the metal's affinity to remain in its current fluid or to move over to the contacting fluid (as quantified by the distribution coefficient). Furthermore, fibre and fluid characteristics including the porosity, tortuosity, fluid viscosity, density and fibre wall thickness (fluid properties are provided in Table 5.3 and membrane properties are provided in Table 5.5) also influence the mass transfer coefficient.

Unlike K_m and K_{tube} , K_{shell} is also influenced by the flow regime as quantified by the Sherwood number, which is a function of the Reynolds number. Due to the complexity of the specific flow regime, considering that thousands of thin fibres are spread across the shell side of the module, four different hollow fibre Sherwood approximations (as provided in Table 5.4) were used to approximate the extraction efficiencies. On a first pass, the distribution coefficients were assumed to be constant and equal to the equilibrium coefficients determined in Chapter 3 ($D_{Al, equilibrium} = 4.8$ and $D_{Co, equilibrium} = 0.15$).

While the first Sherwood approximation (Sherwood 1 – in Table 5.4) is a standard equation used in hydrophobic/hydrophilic membranes with highly turbulent applications ($Re > 500$), Sherwood 2 accounts for fibre and flow distribution randomness while applying to a wide range of Reynolds ($68 < Re < 1194$). Sherwood 2 also allows for a Beta (β) value that captures the extent of deviation from a uniformly packed module. Sherwood 3 focussed on regularly packed fibres and assumed laminar flow in the shell side ($Re < 10$), whereas Sherwood 4 accounts for maldistribution and turbulent flow.

The model predictions based on each Sherwood are presented in Figure 5.14 (conducted at constant equilibrium distribution coefficients – obtained in Section 3.3.3). Most of the models underpredict the resistance for mass transfer which can be attributed to a difference in applications (specifically due to the difference in viscous fluids being used in the hollow fibre membranes). With PX, the viscous fluid adds a significant amount of resistance, rendering Sherwood approximations 1, 3 and 4 not fit for purpose for this application.

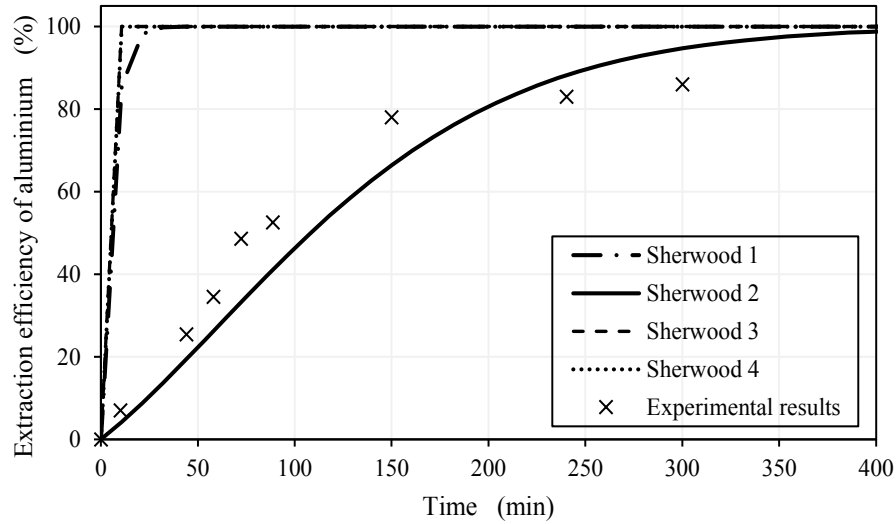


Figure 5.14. Approximation of aluminium extraction efficiency as a function of time based on constant equilibrium distribution coefficients and varying Sherwood approximations for shell side mass transfer coefficients

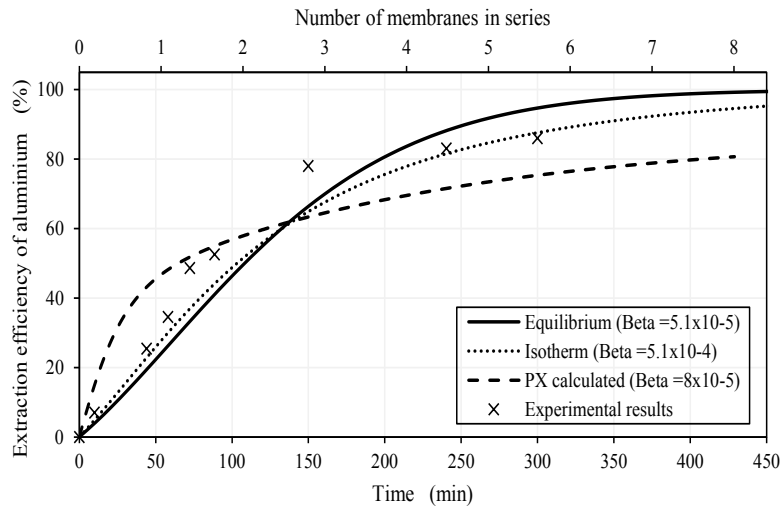
Since Sherwood 2 allows for a dimensionless factor which can also act as a scaling for the Sherwood itself, it was the best predictive model in this case. However, the Sherwood still needs to be optimised to ensure the model truly captures the driving force behind the mass transfer.

5.3.2.2 Optimising Sherwood approximation and mass transfer coefficient by varying distribution coefficient relationship

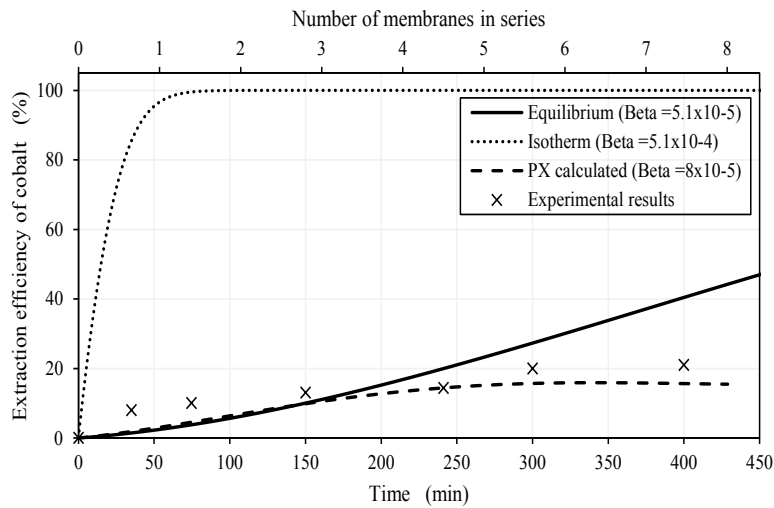
The distribution coefficient plays a key role in computing the mass transfer coefficient as it quantifies the metal ion's affinity to remain in its current phase or to move over to the contacted phase. As discussed in Section 5.2.2.3.3, three different distribution coefficient approaches were taken, i.e. (i) use static equilibrium distribution coefficient from SX shake-out tests ("Equilibrium"), (ii) use isotherms (see Section 3.3.3.5) providing a varying distribution coefficient as a function of the metal concentration ("Isotherm") and (iii) calculate the distribution coefficients as obtained from the PX circulating batch experiments ("PX calculated"). The results of these three predicted extraction efficiencies as well as the experimental data for the extraction of Al and Co are shown in Figure 5.15 (i) and (ii) respectively.

The equilibrium distribution coefficient (solid line) initially predicts the drive in mass transfer well, however since the equilibrium distribution coefficient is a constant value, the model will consist of a constant drive to transfer the metal ion (irrespective of the metal concentration). This results in a constant k_{var} throughout the membrane, which is not representative of the experimental findings. It can therefore be seen in Figure 5.15, that the equilibrium distribution coefficient (solid line) of both Al and Co overshoots the point of equilibrium and will continue to transfer until all the metal is removed. The

model however still predicts an exponential extraction efficiency and not linear, which is due to the nature of the mass transfer equation (Equation (5-17) and (5-18)) as a function of a constant k_{var} .



(i)



(ii)

Figure 5.15. Prediction of extraction efficiency of (i) aluminium and (ii) cobalt using three different distribution coefficient approaches

To capture the change in the metal ion's distribution coefficient, shake-out isotherms (Figure 5.15 - dotted lines) were used. According to the results, this approach ensured a slight improvement of the predictability for Al extraction, however, it overestimates extraction of Co significantly. This can be attributed to the way the shake-out tests were conducted, where only a single metal in solution was contacted with the extractant, leading to the lack of capturing metal ion competition. Furthermore, the

shake-out tests were also conducted at the optimal separation pH for the individual metals, which was not the case here, which would explain the significant overestimation of the Co extraction efficiency.

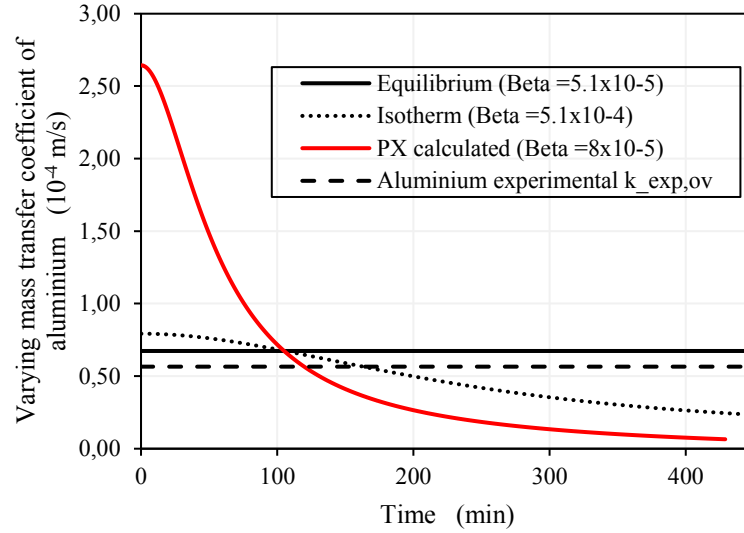
To capture the metal ion competition, the PX extraction results were used to obtain another set of distribution coefficients (Figure 5.15 - dashed lines). These distribution coefficients should capture existing metal competition as a mixture of metals in solution were used during the PX experiments. It is hence understandable that the PX distribution coefficient provided the highest predictability.

The PX distribution coefficient as a function of remaining aqueous metal concentration was furthermore able to capture the change from kinetically to thermodynamically driven mass transfer while taking metal competition into account. This results in a more robust model that can quantify the drive behind the mass transfer properly.

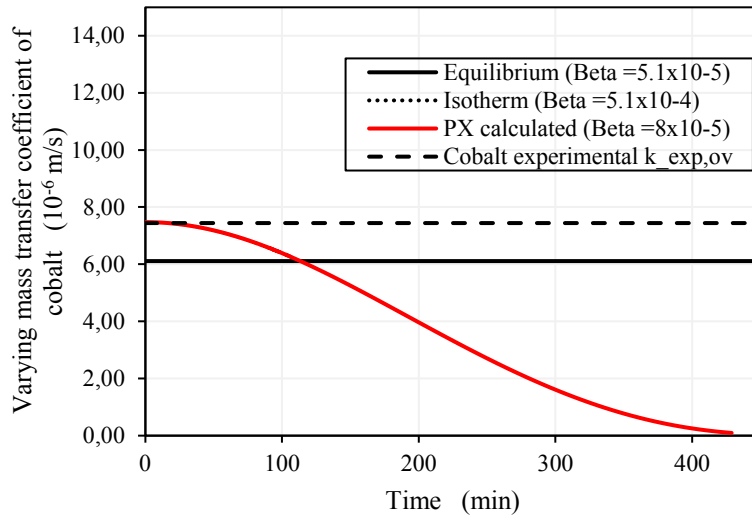
The calculated k_{var} for each approach (“Equilibrium” – solid black line, “Isotherm” – dashed line and “PX calculated” – solid red line) are provided in Figure 5.16. The overall mass transfer coefficient ($k_{exp,ov}$) of Al and Co (as determined in Section 5.3.2.1) are also added to Figure 5.16 (dashed line) to act as reference. The k_{var} of Al was thereafter calculated, by obtaining the average from the “PX calculated” data, as 5.4×10^{-5} m/s (equivalent to a 4% error with the experimentally determined $k_{exp,ov}$).

The mass transfer coefficient results (presented in Figure 5.16 (i) and (ii)) aim to show the reader what the k_{var} results were as calculated with the resistance of series model (Equation (5-6)). It furthermore aims to act as support to the results provided in Figure 5.15 since these results were fed into the solution-diffusion model (Equation (5-17)) to obtain the results shown in Figure 5.15.

Figure 5.16 demonstrates that the “Equilibrium” line resulted in a constant k_{var} when introducing a constant distribution coefficient into the resistance in series model, while varying distribution coefficients, obtained from either “Isotherm” or “PX experimental” data, result in a varying k_{var} . A constant k_{var} implies that the rate of mass transfer is identical at each point in the membrane module, regardless of flow regime or metal concentration, which is not true. A varying mass transfer coefficient represents varying flow regimes and the drive to transfer (because of varying metal concentration) more elegantly.



(i)



(ii)

Figure 5.16. Mass transfer coefficient of (i) aluminium and (ii) cobalt using different distribution coefficient approaches

The “PX calculated” k_{var} for both Al and Co (Figure 5.16) furthermore portrays an initially high mass transfer rate which decreases as the distance through the membranes increases. This is due to the co-current membrane configuration in the model since the concentration of the metal ions decrease as the membrane length increase, resulting in a reduction of the concentration gradient. With counter current configurations (not in the scope of this study) the data provided in Figure 5.16 is expected to be different.

These findings (Figure 5.15 and Figure 5.16) also resonate in the parity plots as shown in Figure 5.17. Although the PX distribution coefficient obtained the lowest coefficient of determination (Figure 5.17 (i) (3)), it is more robust and representative of reality as explained earlier. The model resulted in a RMSE

= 3.5% compared to the experimental data. The risk of using the isotherm distribution coefficient approach lies in overestimating the extraction efficiency of Al as it will approach complete metal extraction and therefore not capture the equilibrium of the system.

Although the calculated PX model underperformed slightly when predicting the Co extraction (Figure 5.17 (ii)), yielding an R^2 of 0.66, a low RMSE of 1.4% was obtained rendering the model adequate to deliver representative results for the remainder of this chapter. The R^2 values of Figure 5.17 (ii) can be misleading, as a reminder, R^2 measures only the strength of a linear relationship but does not necessarily indicate a good model fit [18]. The results should be interpreted along with the RMSE measurement.

Figure 5.15, Figure 5.16 and Figure 5.17 not only justifies using the metal ion's distribution coefficient as a function of metal concentration obtained from PX experiments, but it also reveals how sensitive the model is to the distribution coefficient. It is therefore recommended that in future studies, a higher frequency of sampling intervals is used to capture each step of the extraction.

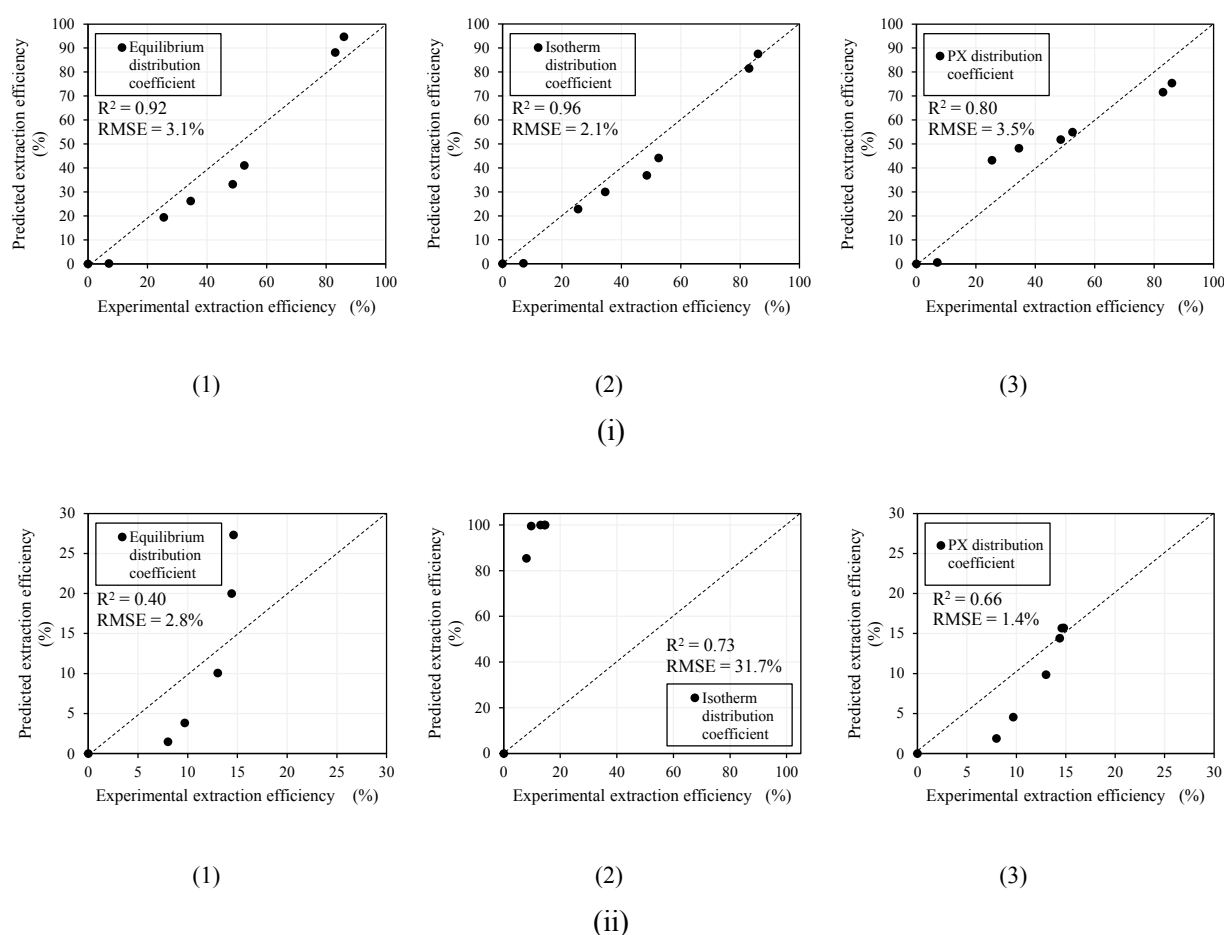


Figure 5.17. Parity plots of predicting extraction efficiency of (i) aluminium and (ii) cobalt when using three different distribution coefficient approaches

The optimal β value was determined to be 8×10^{-5} (to obtain an optimal fit while using PX experimental distribution coefficients) and the resulting mass transfer coefficient together with the Sherwood approximation that represents Co and Al separation in a hollow fibre membrane with 20 vol.% Cyanex272 as developed within this chapter are provided in Equation (5-23) and Equation (5-24).

$$\frac{1}{K} = \frac{\tau t_{fibre}}{D\epsilon} + \left(\frac{L}{D Sh} \right) \left(\frac{d_{in}}{d_{out}} \right) + \frac{1}{1.62} \left(\frac{D^{-2}v}{L d_{in}} \right)^{-0.33} \quad (5-23)$$

$$Sh = \left(8 \times 10^{-5} ((0.86 - 0.3\phi)\phi)^{-1} \right) \left(\frac{Re Sc d_h}{L} \right)^{0.3\phi+0.14} \quad (5-24)$$

5.3.3 Optimal industrial scale membrane

According to Section 5.2.3, the membranes were compared based on four factors, i.e. (i) the maximum overall separation efficiency, (ii) the average overall mass transfer coefficient, (iii) the number of membranes required for optimal separation efficiency and (iv) the production rate of pure Al (<100 ppm Co), to obtain a view of what an industrial PX extraction stage footprint will entail. The results from this section will be used to conduct a high-level comparative study with the mixer-settler technology (Section 6.1.4).

The resulting k_{var} of Al and Co for the four industry-scale membranes tested (characteristics and model inputs given in Table 5.5) are given in Figure 5.18, while the average k_{var} of each is provided in Table 5.6. The resulting k_{var} of Al and Co was obtained by calculating the mean of the data presented in Figure 5.18.

Table 5.6. Average overall mass transfer coefficients of aluminium and cobalt in different industry scale membrane modules

Industrial membrane	$\bar{k}_{var,Al}$ (m/s)	$\bar{k}_{var,Co}$ (m/s)
<i>Experimental (2.5x8)</i>	<i>5.7E-05</i>	<i>7.4E-06</i>
10x28 (X50)	1.30E-05	9.09E-07
8x80 (X40)	5.20E-06	1.23E-07
14x28 (X50)	1.33E-05	3.89E-07
14x40 (X40)	1.06E-05	2.75E-07

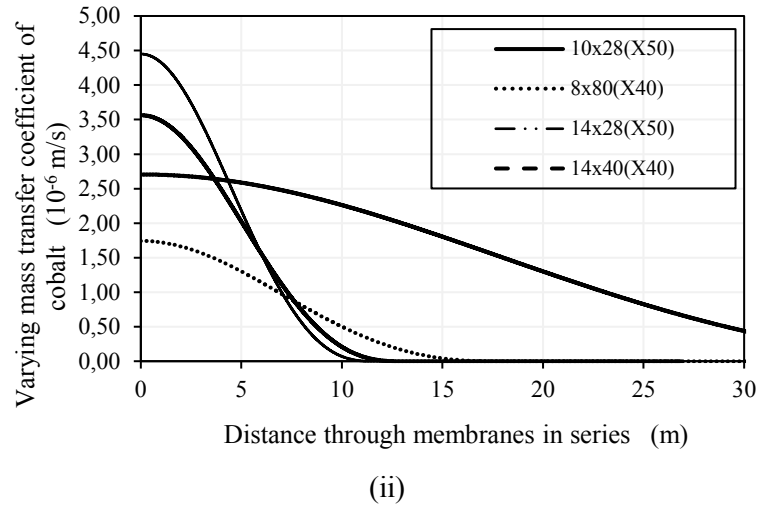
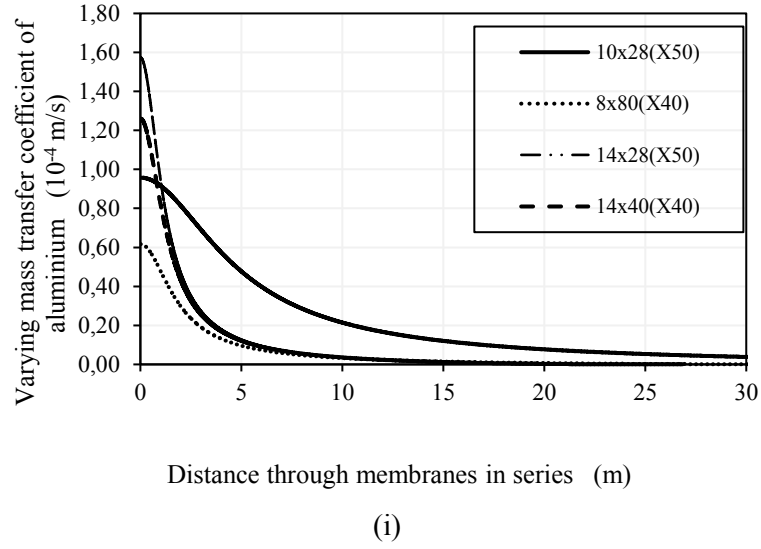
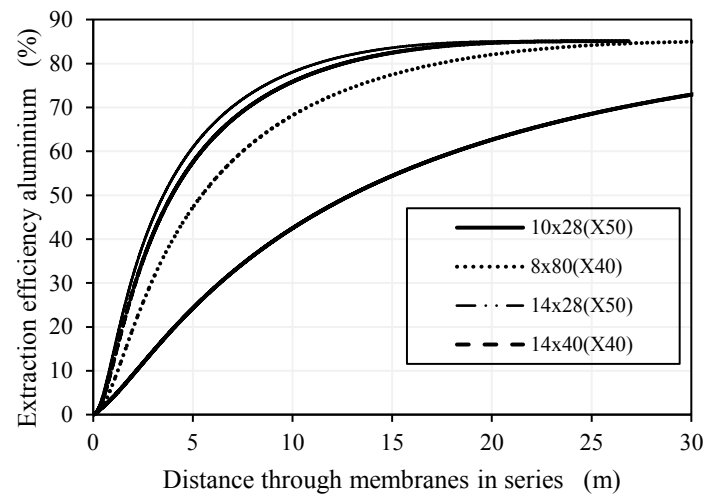


Figure 5.18. Predicted mass transfer coefficients in different industrial scale hollow fibre membranes of (i) aluminium and (ii) cobalt

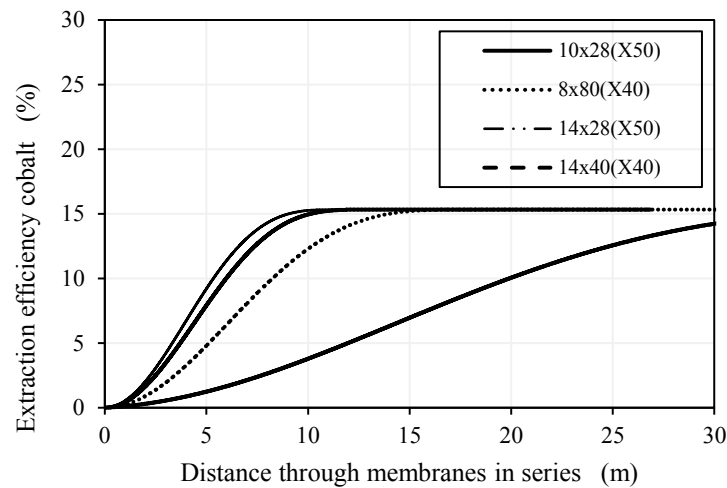
The membranes delivered different k_{var} results, which is likely due to varying contact areas per meter of membrane length, along with other factors like porosity. From Table 5.6, the industrial scale membranes 14x28, 10x28 resulted in the quickest mass transfer rates for aluminium with the 14x40 presenting similar rates. However, the benchtop experimental membrane (2.5x8 – denoted as “Experimental”) presented the best mass transfer rates. In a future study, it is recommended to take the lucrative qualities from the benchtop experimental module (i.e. length to width ratio) and apply it to the industrial membrane module decision making framework.

The extraction efficiency of Co and Al for each membrane are provided in Figure 5.19. Both figures provide a clearer view of membrane capability as a function of the distance through the membrane. The 10x28 membrane module clearly performed the worst amongst the four membrane modules whereby the main difference was noticed in the inlet pipe diameter size which likely resulted in low entrance velocities of the fluids. The 10x28 module also had a low minimum recommended flow rate compared

to the 14x28 and 14x40 modules. Furthermore, the 10x28 membrane module required significantly more membrane length than the other modules.



(i)



(ii)

Figure 5.19. Calculated extraction efficiencies of (i) aluminium and (ii) cobalt with the use of different industrial scale hollow fibre membranes

However, all four membrane modules proved to be capable and comparable. A more conclusive way of comparing the modules will be based on capital efficiency which is a function of the number of membranes required and the production rate of pure aluminium (as provided in Table 5.7).

Table 5.7. Comparison of industry scale membranes on factors that will influence the economic viability of the facility

Industrial membrane	Number of membranes in series required to reach optimal separation efficiency	Total pressure drop (bar)	Al recovery (%)	Co recovery (%)	Pure Al production rate (t/a)
10x28(X50)	25	10	73%	86%	52
8x80(X40)	14	60	85%	85%	43
14x28(X50)	17	10	85%	85%	98
14x40(X40)	13	8	85%	85%	98

Since the 14x40 membrane module requires the least number of membranes in series while delivering high recovery and production rates with an estimated low total pressure drop, this module was chosen as the optimal industry scale membrane among the four modules evaluated. The consequent estimated footprint of the extraction phase of the PX technology is $\sim 0.6 \text{ m}^3$, which is required for 13 membrane modules and will replace a mixer and a settler of $\sim 16.7 \text{ m}^3$ (as determined in Section 3.3.6).

5.3.4 Extraction phase PFD

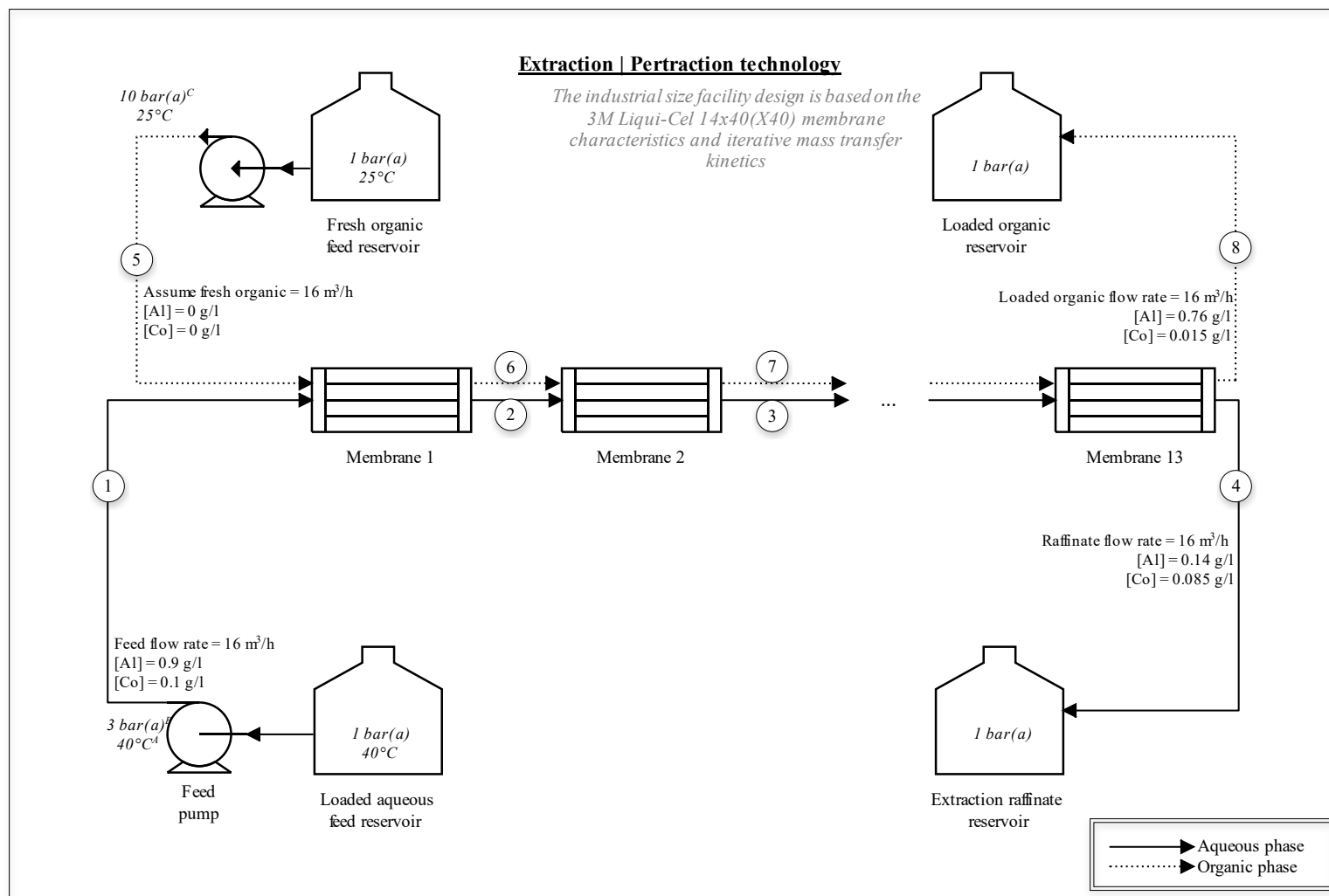
The process flow diagram of the extraction phase is provided in Figure 5.20 while the mass balance is provided in Table 5.8. A co-current membrane configuration is provided in Figure 5.20 to provide a conservative estimate. After extraction only, the desired Al product specifications are not met making the scrubbing step (at optimal conditions determined in Chapter 3) a requirement to reach the purity specification.

Two feed tanks are required, one for the aqueous feed solution and one for the fresh or regenerated organic feed. This process assumes fresh organic feed will be required, but more detailed work can be conducted to weigh up additional capital on equipment vs. operating expense savings. Two intermediate tanks are also required, one for the raffinate and another for the loaded organic.

For future studies, the raffinate can be connected to a separate train to recover the Co as well as improve the viability of the plant. The loaded organic reservoir will act as feed to the stripping section that will transfer the Al to an aqueous medium. At an aqueous and organic flow rate of $16 \text{ m}^3/\text{h}$ each (minimum recommended flow rate) the estimated pure Al production rate will be 12 kg/h or 98 t/a when the plant online time is 8000 h/a .

Table 5.8. Extraction phase of a pertraction facility stream composition

Stream	Units	1	2	3	4	5	6	7	8
Flow rate	m ³ /h	16	16	16	16	16	16	16	16
Composition									
Cyanex272	vol. %	-	-	-	-	20	20	20	20
ShellSol2325	vol. %	-	-	-	-	85	85	85	85
Tributyl phosphate	vol. %	-	-	-	-	5	5	5	5
Aluminium	g/L	0.90	0.72	0.54	0.14	-	0.18	0.36	0.76
Cobalt	g/L	0.10	0.099	0.097	0.085	-	0.001	0.003	0.015
Flow rate	kg/h	15892	15889	15886	15879	14720	14723	14726	14732
Component flow rate									
Cyanex272	kg/h	-	-	-	-	2944	2944	2944	2944
ShellSol2325	kg/h	-	-	-	-	12512	12512	12512	12512
Tributyl phosphate	kg/h	-	-	-	-	736	736	736	736
Aluminium	kg/h	14.40	11.55	8.60	2.22	-	2.85	5.80	12.18
Cobalt	kg/h	1.60	1.59	1.55	1.35	-	0.01	0.05	0.25
Water	kg/h	15876	15876	15876	15876	-	-	-	-



^A Ignoring temperature addition due to pump energy loss

^B Friction losses in pipes are ignored. Membrane modules assumed to be the predominant cause of pressure drop

^C Breakthrough pressure only expected to occur at pressure difference $> 16.5 \text{ bar}$ according to manufacturer data sheet, therefore one feed pump should suffice without causing breakthrough in the first membrane in series

Figure 5.20. Conceptual process flow diagram of an extraction step in a PX facility

5.4 Chapter conclusion

The PX technology was proven to be just as capable of separating the Co and Al as the mixer-settler technology. Furthermore, the experimental $k_{exp,ov}$ for Al and Co was determined as 5.7×10^{-5} and 7.4×10^{-6} m/s respectively which was then used to validate the approach for the mathematical model.

The “PX calculated” distribution coefficient approach resulted in the most accurate, representative and robust mass transfer coefficient of both metal ions. This approach inherently captured the metal competition that exists if metals in a mixture are exposed to an extractant. This phenomenon was also noted in Chapter 3 when conducting pH dependence tests. After the development of an adapted Sherwood approximation the developed model resulted in an overall extraction efficiency prediction accuracy of 4% on Al and 1.4% on Co (RMSE).

Furthermore, the 3M Liqui-Cel 14x40(X40) membrane was the optimal industry scale membrane of choice amongst those evaluated due to its ability to deliver high production rates at a low overall pressure drop (~8 bar), high recovery (85%) and the least number of membranes required in series (13). The total volume/footprint required for the extraction phase of the PX technology was ~0.6 m³

5.5 References

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6 Evaluation, conclusion and recommendations

This chapter is divided into an in-depth evaluation of the results (Chapter 6.1), followed by a thesis conclusion (Chapter 6.2) and finally the general recommendations (Chapter 6.3).

6.1 Evaluation

During this study, Al was recovered to the specified purity (containing <100 ppm Co), where both investigated technologies (mixer-settlers in Chapter 3 and PX in Chapter 5) were demonstrated to effectively separate Co and Al. Furthermore, the experiments conducted on both technologies allowed for the successful sizing of the mixer-settler and pertraction extraction stages, where the mixer-settler sizing was conducted with well-established and known guidelines (Chapter 3) [1]. While the conceptual design of hollow-fibre membranes in liquid-liquid extraction application was more complex due to the novelty of the application to which this technology is applied. A more applicable Sherwood model was successfully adapted, leading to accurate (4% RMSE) model predictability and robustness.

In this section (Sections 6.1.1 – 6.1.3), the three experimental chapters are evaluated, which leads to a comparison of an industry scale mixer-settler and PX plant (Section 6.1.4).

6.1.1 Liquid-liquid solvent extraction (Chapter 3)

Chapter 3 entailed (i) experimental planning, (ii) determination of optimal separation conditions with shake-out tests and (iii) sizing of an industrial scale mixer-settler and attempted to address objective 1 as set out in Section 1.3. Section 6.1.1.1 – 6.1.1.4 elaborates on how each of these objectives was met.

6.1.1.1 *Metal speciation*

The use of OLI's database provided valuable insights into metal speciation under varying conditions, which, in conjunction with the literature, informed the experimental planning. Pourbaix diagrams for Al and Co indicated that the desired species (Al^{3+} and Co^{2+}) are expected to coexist at pH values ranging from 0 to 3.4, potentially leading to competition for binding to the extractant. Furthermore, neither Al nor Co species were present under basic pH conditions ($\text{pH} > 7.8$), where precipitation was anticipated. The data confirmed that experiments should be conducted within the low pH range to ensure the presence of the desired metal species while avoiding precipitation losses. It is also crucial to avoid using single metals in solution when conducting experiments, as this may not accurately reflect the dynamics of the Co-Al separation system, particularly if metal competition is involved. To further enhance the understanding of metal speciation, it is recommended to confirm which desired Al and Co species exists in the presence of sulfates.

6.1.1.2 Extraction stage

The extraction kinetics revealed that the batch volumes used required approximately 15 min to reach equilibrium. Consequently, the contact time for all subsequent experiments was set to a minimum of 1 h to ensure that equilibrium was achieved. Pre-neutralisation of the extractant phase with NH_4OH significantly improved the extraction efficiency of Al, increasing it from 26% to 87% at 50 mol.% addition of NH_4OH relative to Cyanex272 volume.

This 50 mol.% addition confirmed the manufacturer's datasheet, which also recommended this level to prevent potential issues with viscosity and selectivity loss. However, experimental results showed that selectivity remained intact up to a 60 mol.% addition of NH_4OH (resulting in 98% extraction of Al), indicating that higher concentrations did not significantly affect selectivity until exceeding 60 mol.%. It is therefore recommended to conduct additional experiments to evaluate the effect of operating with more than 50 mol.% of NH_4OH .

The pH dependence studies were consistent with the metal speciation results, showing a distinct variation in pH dependence when single metals were in solution compared to the metal mixture. Metal competition was observed and an optimal pH of 3.13 was identified for a solution containing a mixture of metals. These findings highlight the critical importance of experimental planning, as the dynamics of metal competition would not have been evident had the pH dependence been investigated using single metals in solution.

No significant improvement in extraction efficiency was observed at temperatures above 40°C, making 40°C the optimal temperature for extraction. Isotherm data for Al and Co showed that a 20 vol.% concentration of Cyanex272 did not reach saturation and provided the best extraction efficiencies.

6.1.1.3 Scrubbing and stripping stages

The loaded organic phase from the extraction stage was subjected to two scrubbing methods. Scrubbing with H_2SO_4 , as recommended by the literature [2], proved unsuccessful, as no selectivity was achieved, leading to the stripping of both metals. In contrast, scrubbing with a solution containing 50 g/L Al at a pH of 2.8 resulted in 99.7% removal of Co 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. Using the Al loaded scrubbing liquor, a Co concentration of 54 ppm (with respect to Al concentration) was attained, meeting the <100 ppm of Co target set. Optimal stripping of Al was achieved using a 1 M H_2SO_4 solution, which resulted in approximately 80% recovery of Al.

6.1.1.4 Mixer-settler sizing

The McCabe-Thiele method indicated that two mixer stages would be required to achieve 87% extraction efficiency of Al (sized only for Al recovery). According to the design, the mixer effluent would be directed to a settler, which was sized at 1.5 m x 1.5 m x 6 m to facilitate effective phase separation, which was found to be equivalent to $\sim 16.7 \text{ m}^3$.

6.1.2 Linear and non-linear modelling of variables affecting the extraction efficiency of liquid-liquid extraction (Chapter 4)

Chapter 4 employed (i) linear regression and (ii) non-linear regression techniques by utilising the results obtained from the shake-out tests performed in Chapter 3, which created the database for this section. This was done to address objective 2 as set out in Section 1.3. Section 6.1.2.1 and 6.1.2.2 elaborate on how this objective was met. The purpose of the modelling was to evaluate the effect of the operating variables on the extraction efficiency.

6.1.2.1 Linear modelling performance

The Ordinary Linear Regression (OLR), Ridge Regression (RR) and Lasso Regression (LR), all performed poorly in terms of the R^2 , RMSE, and MAE, achieving a correlation of 0.8 or lower, with an $\text{RMSE} > 84\%$ and an $\text{MAE} > 10\%$. The linear regression models were inadequate due to the nature of the data, which inherently exhibited non-linearity, that cannot be captured by simple linear regression techniques. As a result, non-linear modelling techniques were also employed.

6.1.2.2 Non-linear modelling performance

The Levenberg-Marquardt, Scaled Conjugate Gradient, and Bayesian Regularisation algorithms significantly outperformed the linear models, achieving optimal results with six or fewer hidden neurons (one hidden layer). All three algorithms achieved a coefficient of determination of ~ 1 , with an $\text{MAE} < 3.5\%$. Among these, the Bayesian Regularisation algorithm was the best performer, yielding the lowest errors ($\text{RMSE} = 3\%$, $\text{MAE} = 1.2\%$) and requiring the fewest neurons (4).

Using the weights from the optimal Bayesian Regularisation neural network, the relative importance of variables in determining Al and Co extraction efficiency was quantified (with the use of Equation (2-17)). The significance of aqueous feed pH, a well-known factor, was once again confirmed, as it produced the highest relative importance. Nearly as important, was the extent of pre-neutralisation, which plays a crucial role in stabilising the contact pH during extraction. Finally, the metal composition in the feed, although still significant, had the least importance. All the factors confirmed that variations in the feed metal composition in industrial processes would influence extraction efficiencies. Since the shake-out

tests were conducted using a synthetic solution free of impurities, it is recommended that a catalyst assay be performed to capture the effects of metal impurities.

6.1.3 Liquid-liquid extraction with pertraction technology (Chapter 5)

Chapter 5 entailed (i) benchtop PX experiments, (ii) determination of the experimental mass transfer coefficient and (iii) developing a fit for purpose, robust model to predict the extraction efficiency of Co and Al in spent FTS leach solutions with industrial scale membranes. This chapter therefore attempted to address objective 3 as set out in Section 1.3. Section 6.1.3.1 – 6.1.3.3 elaborate on how this objective was met.

The optimal conditions for separation as determined in Chapter 3 were used as the conditions of separation within this chapter. A comparison between the experimental results obtained in Chapter 3 and Chapter 5 will be provided in Section 6.1.3.4 while the technology comparison based on the sizing of each facility were conducted in Section 6.1.4.

6.1.3.1 Experimentally determined overall mass transfer coefficient

Pertraction experiments yielded an overall experimental mass transfer coefficient of 5.6×10^{-5} m/s for Al and 7.4×10^{-6} m/s for Co during the extraction stage. As a result, the extraction of Al is expected to initially be eight times faster than that of Co. However, Co reached equilibrium quicker than Al (>50 min vs >150 min respectively), suggesting that the separation process is influenced by both kinetic and thermodynamic factors. The successful difference in extraction efficiencies of Co and Al also formed proof of the pertraction technology's capability to separate the two metals.

6.1.3.2 Mathematically determined overall mass transfer coefficient and adapted Sherwood approximation

The overall mass transfer coefficient is influenced by both the metal distribution coefficient and the Sherwood number (inputs into the solution-diffusion model provided in Equation (5-17)). Three approaches were followed to quantify the distribution coefficient (i) equilibrium distribution coefficients obtained from the shake-out tests conducted in Chapter 3, (ii) varying distribution coefficients obtained for the single metal isotherms conducted in Chapter 3 and (iii) varying distribution coefficients as obtained from the benchtop experiments in Chapter 5.

Using the equilibrium distribution coefficients obtained from the shake-out tests, conducted in Chapter 3, ($D_{Al} = 4.8$ and $D_{Co} = 0.15$) partially provided accurate predictions (MAE = 7%) of extraction and separation efficiencies. However, a constant distribution coefficient implies a constant driving force for the metal transfer to the contacting phase, limiting the model's ability to predict equilibrium accurately.

Incorporating shake-out isotherm distribution coefficients (Chapter 3), which account for variations in the distribution coefficient as a function of metal concentration, allow for a dynamic mass transfer coefficient. This modification might have enabled the model to predict equilibrium more accurately, but the isotherms were conducted with single metals in solution, which does not account for the additional restriction posed by metal competition. As a result, the model overestimated the extraction efficiency of Co, leading to poor separation between the metals, which did not align with the experimental results.

To better capture the interactions between metal ions, distribution coefficients were recalculated using the pertraction experiments conducted with metal mixtures. This adjustment introduced greater robustness and improved the model's predictability. The model was able to achieve an average overall mass transfer coefficient for Al of 5.4×10^{-5} m/s (with a 4% error), while also demonstrating a strong correlation with the experimental data. This model was considered representative of the experimental results and was used to predict the industrial scale pertraction for Co-Al separation. The correct distribution coefficient function was critical for ensuring the model's accuracy and robustness. It is recommended to conduct pertraction kinetic experiments with higher granularity for Co and Al to further refine the model fit.

The Sherwood approximation was further adapted using pertraction-based distribution coefficients. Since large-scale liquid-liquid extraction with hollow-fibre membranes is largely unexplored, obtaining relevant Sherwood approximations for such applications remains challenging. Three of the four existing hollow-fibre membrane Sherwood models underestimated flow resistance, as demonstrated in Chapter 5.

The Sherwood approximation developed in Chapter 5 provided mass transfer coefficients tailored for hollow-fibre membranes operating with highly viscous flow, liquid-liquid contact, and metal separation. It was considered fit for purpose due to its high predictive accuracy, with an RMSE of 4% for Al and 1.4% for Co. To further refine mass transfer predictions and optimise membrane length for future applications, it is recommended to test this new Sherwood approximation in additional scenarios, such as Co-Ni separation or alternative membrane modules.

6.1.3.3 Conceptual design of an industry scale pertraction plant

The optimised and validated model was used to evaluate four industry-scale membranes. The Liqui-Cel 14x40(X40) membrane was found to be superior, based on its low overall pressure drop (~8 bar), the fewest number of membranes required in series (13 modules), high Al recovery (85%) and high production rate at the minimum recommended flow rate of 16 m³/h. Consequently, the resulting industrial-scale facility would require 13 Liqui-Cel 14x40(X40) membranes in series to produce 98 t/a of Al.

6.1.3.4 Comparison of shake-out experimental results (Chapter 3) and PX benchtop experimental results (Chapter 5)

A synthetic spent catalyst leach solution containing a 0.9 g/L Al and 0.1 g/L Co underwent extraction, scrubbing and stripping with typical SX shake-out tests (Chapter 3) and PX benchtop experiments with a Liqui-Cel 2.5x8 module (Chapter 5). At equilibrium both techniques obtained similar extraction efficiencies for Al (87 wt.%) and Co (shake-out: 17 wt.% and PX: 14 wt.%), however, the two techniques differed in terms of time required to reach equilibrium. The shake-out experiments reached equilibrium in >15 min while the PX experiments reached equilibrium for Co >50 min and Al >150 min.

The extended time to reach equilibrium with PX can be attributed to the additional resistance induced by the membrane component or it can be due to the small volume (50 ml per phase) that were used to conduct the shake-out experiments. It is recommended to evaluate how the shake-out kinetics change as more volume is required to contact.

6.1.4 Comparison of industry scale mixer-settlers and pertraction facilities as new Greenfields investment options

Since both technologies have proven their capability to separate Co and Al and each technology has been sized on a high level, a qualitative pre-feasibility study (PFS) can be conducted to compare the technologies. To recall what was mentioned in Section 2.8, factors that need to be quantified or addressed in the PFS include the eight listed below. This comparison addressed the final objective (objective 4) of the study as outlined in Section 1.3.

1. Scope of the project
2. Marketing concept
3. Raw materials and supply
4. Location, site and environment
5. Engineering and technology
6. Organisation and overhead cost
7. Human resources (labour cost)
8. Project implementation

6.1.4.1 Qualitative pre-feasibility study and initial technology selection

A qualitative PFS was conducted to compare the two competing technologies on a high level and to identify important areas that will require more detailed analysis in future studies. The comparison based on the eight factors is presented in Table 6.1.

Table 6.1. Preliminary qualitative feasibility study comparing a mixer-settler facility with a PX facility

	Description	Mixer-settler	Pertraction	Justification
1	Scope of the project			
	Size of process equipment	-	✓	According to the completed sizing of the technologies, the mixer-settler plant is estimated to be ~ 30 times larger than the PX plant. This is critical when limited space is available on a brownfields plant. The footprint also plays a role in overheads construction costs like pipeline, cabling, ground preparation, etc.
	Number of process equipment components	-	✓	Both will require extraction, scrubbing and stripping stages. For the mixer-settler, an impeller is necessary whereas the PX plant does not require this additional component. It can be assumed that the same number of auxiliary equipment will be required.
	Installation complexity of the process equipment	-	✓	Conventional mixer-settler installation contains more internal components that need to be assembled whereas PX membranes are purchased as a module. The mixer-settlers also have larger structures that will need to be installed with the proper foundation and groundwork. This extensive groundwork will not be necessary for PX installation. To overcome the extensive groundwork, newer designs allow the use of carbon steel structures eliminating the extensive foundation works.
	Conclusion	Since the mixer-settler plant is larger in size and contains more complex equipment to install, it can be concluded that it will be the more labour-intensive option to construct.		
2	Raw materials and supply			
	Amount of raw material necessary	-	-	If it is assumed that the position of equilibrium during separation is similar for mixer-settlers and PX, the losses each plant will produce during normal, steady operation should be similar if no evaporation or entrainment occurs in mixer-settler facilities. However, open to atmosphere settlers will experience evaporation of their extractant (rates will differ based on application, use of extractants and atmospheric conditions) which will result in a top-up requirement. To initially start up the mixer-settler plant, ‘metal lock-up’ will be a significant expense, especially for the PGM industry. However, PX plants have been proven to decrease the metal lock-up. Lastly, a significant running cost for PX will be the membrane replacement. Due to the acidic nature of the system, the polypropylene fibres deteriorate over time.
	Conclusion	Additional work will be required to compare the metal lock-up and top-up cost, with the membrane replacement cost to derive a clear conclusion.		

	Description	Mixer-settler	Pertraction	Justification
3	Location, site and environment			
	The size of the area that the plant will utilise	-	✓	As mentioned, the mixer-settler plant should utilise a significantly larger area to complete the task at hand.
	Emissions	-	✓	Due to the open nature of the settlers used at the SX plant, volatile organic carbons (VOCs) will evaporate into the atmosphere and cause organic emissions. With increasing stringent environmental rules and carbon tax increases, the existing metal industry might come under increased pressure to close the settlers and avoid VOC emissions. Furthermore, more customers are requesting manufacturers to disclose their product carbon footprint, which will be negatively influenced by the VOC emissions. For metal industries exporting their products to countries like Europe, cross border taxes based on the product carbon footprint will also directly affect the cost competitiveness of the manufacturer.
	Product nature	-	✓	Both plants should have products of a similar nature, but the product carbon footprint is expected to be higher for mixer-settler facilities than PX facilities due to the increased VOC emissions.
	Conclusion	Due to the larger size and higher emissions expected from the mixer-settler plants, the PX facility will be the more sustainable solution.		
4	Engineering and technology			
	Sustainability of the technology	-	✓	Due to the environmental factors mentioned (reduced emissions), PX is a more sustainable choice of technology.
	Complexity of technology	✓	-	Both mixer-settlers and PX plants are considered easy operation plants, however, the PX plants are relatively new where the lack of experience can cause additional challenges.
	Stability of operation	-	✓	Due to uncontrollable factors like contact area during agitation, improper fluid distribution, etc., the mixer-settlers probably cause more unstable operation.
	Proven technology	✓	-	Mixer-settlers have been in operation for decades, and with time comes experience and trust.
	Reliability of equipment	✓	-	Due to the lack of historical data to prove the reliability of process equipment, it needs to be assumed that the PX equipment is less reliable.
	Conclusion	Due to the proven technology, accompanied by decades of use, the mixer-settler plant has the upper hand for this section.		

	Description	Mixer-settler	Pertraction	Justification
5	Organisation, overhead and labour cost			
	Electricity	✓	-	The additional rotary equipment necessary to agitate the two phases at the mixer-settler plant will need to be evaluated against potential additional pumping capacity required to overcome the resistances introduced by the membranes. It is estimated that more pressure drop will be present in a PX facility, potentially requiring more pumping capacity and consequently more electricity. This should be confirmed in a future study.
	Labour cost	-	✓	On most accounts, during normal operation, labour costs should be similar since the process equipment to control is similar. During maintenance and cleaning plant shutdowns, the mixer-settler plant will however be more labour-intensive due to the larger footprint.
	Conclusion	The labour costs should potentially be less for the PX plant. However, electricity costs are expected to be higher for PX facilities due to the additional resistance. Depending on the location, the difference in labour vs electricity cost will need to be evaluated.		

A summary of the evaluation conducted in Table 6.1 is provided in Table 6.2.

Table 6.2. Summary of the findings from the qualitative comparison between mixer-settlers and pertraction

Factor	Superior technology	Comment
Scope of the project	Pertraction	Due to smaller volume and less complex installation
Raw materials and supply (running cost)	-	Additional work will be required to compare the metal lock-up and top-up cost, with the membrane replacement cost to obtain a clear economic conclusion
Location, site and environment	Pertraction	PX facilities is expected to operate with a lower environmental footprint (due to the low size requirement and enclosed nature). This factor can partially be addressed in mixer-settlers where mitigation elements like floating roofs can be employed, which will however come at additional capital.
Engineering and technology	Mixer-settlers	Due to the proven technology and the robustness that comes with decades of operation that benefitted from operation learnings
Organisational, overheads and labour costs (Location dependent) In the case of high cost of energy In the case of high cost of labour	Mixer-settlers Pertraction	Due to the additional resistance that membranes induce, pertraction is expected to be more energy intensive. However, the facility is smaller and more simplistic which should result in less labour required

These results indicate that both pertraction and mixer-settlers contain advantages and disadvantages. The information available in literature on PX is simply not granular enough to conduct a representative economic evaluation. More detailed studies must be conducted to quantify the running cost of a PX facility, specifically the rate and cost of membrane replacement and consequent plant downtime. This should be compared to the extraction top-up and metal lock-up required for mixer-settlers to provide a view on which technology will be the cost leader.

However, considering the volatile space of environmental legislation, alternative factors should also be considered such as carbon taxes, product carbon footprints etc.

Decades ago, when existing mixer-settler facilities were designed, the emissions did not bear the same level of importance in the design stage. Today, emissions are not only a waste stream, but it is also a strict specification that you need to adhere to under the minimum emission standard (of which the allowable limit is continually decreasing) to ensure that your licence to operate remains valid [3]. It is furthermore an input into each facility's product carbon footprint which is not only becoming the norm to disclose to the market but is also a customer requirement. Furthermore, with increasing country-specific carbon taxes as well as the carbon border adjustment mechanisms that are being introduced for exported products, emissions also directly reduce your margin per ton of product. This, in short means that high emissions can lead to high carbon tax penalties (which is only expected to increase into the future) and a reduction of customers willing to buy the product. Based on the qualitative assessment for a Greenfields project, both technologies have merit. Table 6.3 provided a superior choice of technology based on specific drivers behind an investment decision.

Table 6.3. Superior technology based on specific drivers behind the investment decision

Investment decision main driver	Technology choice
Plant footprint is size constrained	Pertraction
Customer specific need to purchase low carbon products	Pertraction
Modular and flexible location of the technology required i.e. to run campaign mode or move during its lifetime	Pertraction
High granularity in control required during separation	Pertraction
Higher selectivity needed to improve product purity	Pertraction
Lower solvent inventory and losses required	Pertraction
Continuous operation with minimal phase disengagement concerns	Pertraction
Reduction of hazardous solvent exposure and emissions	Pertraction
Low technology risk (i.e. commercial packages available - proven and well-understood technology required)	Mixer-settlers
Solvents with high viscosities	Mixer-settlers
Ease of troubleshooting and process visibility	Mixer-settlers
High mechanical reliability with minimal fouling risk	Mixer-settlers
Lower sensitivity to feed variability	Mixer-settlers
Easier retrofitting into existing solvent extraction circuits	Mixer-settlers
Handling of large flow rates with minimal complexity	Mixer-settlers
Easier maintenance and lower technical expertise required	Mixer-settlers

The choice between pertraction (PX) and mixer-settlers depends on process needs and constraints. Pertraction is preferred when space is limited, solvent losses must be minimised (due to cost or availability), high selectivity is required, or modularity and sustainability are priorities. It is ideal for processes requiring lower environmental impact, improved process control, and reduced solvent exposure.

Mixer-settlers, on the other hand, are better for large-scale operations and handling of systems with high viscosities. They offer proven reliability, easier troubleshooting, and are more suitable for high-throughput processes where footprint and solvent inventory are less of a concern.

6.2 Conclusion

Section 1.3 outlines the overall aim and objectives of this thesis. The aim was to establish the capability of both technologies and to compare solvent extraction and pertraction technologies for conducting similar separations, while evaluating their respective advantages and shortcomings. Chapters 3-5 are evidence that the thesis successfully met its aim. Chapter 3 determined the optimal conditions of separation that were used in Chapter 5 to set up the pertraction experiments. It also provided the necessary data to size the extraction phase of the mixer-settler and to be able to apply linear and non-linear regression techniques in Chapter 4. The results of Chapter 4 were used to improve the understanding of variable dependency on separation efficiency in liquid-liquid extraction processes. Chapter 5 results were used together with Chapter 3 to compare the two technologies (Section 6.1.4).

6.3 Recommendation

This study suggests several key areas for future research to further optimise and refine the liquid-liquid solvent extraction and pertraction processes for Al-Co separation.

Mixer-settlers/shake-out experiments

- Additional isotherm experiments should be conducted to obtain a more detailed view of the isotherms, ensuring the optimal extractant concentration is selected.
- Investigations into metal speciation are also recommended to confirm which Al and Co species in sulfate-rich environments are present.
- Since the shake-out tests were conducted using synthetic solutions free of impurities, catalyst assays should be performed to assess the impact of metal impurities on extraction efficiencies. This will provide a more realistic understanding of system performance under industrial conditions.
- Furthermore, additional shake-out tests should be conducted to determine the necessity and optimal requirement of TBP in the extraction process.

- It is also recommended to evaluate how the shake-out kinetics change as more volume is required to contact.
- It is recommended that experiments are conducted at smaller intervals and to repeat the runs to ensure statistical confidence is obtained when applying linear and non-linear modelling to the results.

Pertraction

- Experiments should be performed to evaluate the effects of operating with NH_4OH concentrations above 50 mol.% on extraction efficiency and selectivity.
- Pertraction kinetic experiments with higher granularity for both Co and Al are recommended to refine the model fit and improve prediction accuracy.
- Additionally, computational fluid dynamics (CFD) modelling should be conducted to evaluate the flow regime within the membrane module, providing a deeper understanding of mass transfer limitations.
- Further applications should also be tested against the new Sherwood approximation to enhance mass transfer predictions and optimise membrane length for large-scale implementation.
- A crucial area for future evaluation is the economic comparison between PX and mixer-settler technologies. This should include an assessment of membrane lifetime under various operating conditions, particularly as a function of strip liquor pH. A proper economic evaluation should compare PX membrane replacement costs to mixer-settler extractant top-up costs, electricity usage and additional carbon tax penalties associated with mixer-settler operations.
- Additionally, an overall residence time comparison between PX and mixer-settler facilities should be conducted to understand process efficiencies better.
- A key upcoming research objective will be to model the mass transfer coefficient and the resulting extraction efficiency, with the aim of supporting process scale-up.
- Furthermore, while this study considered a co-current membrane configuration, a counter-current system is expected to be more effective in practice. A comparative study of co-current vs. counter-current configurations is therefore recommended to optimise the design for industrial applications.

By addressing these recommendations, future research can enhance the efficiency, scalability, and economic viability of Al-Co separation through mixer-settler and pertraction technologies.

6.4 References

- [1] P. J. Rydberg, M. Cox, C. Musikas, and G. R. Choppin, *Principles and Practices of Solvent Extraction*, 2nd ed., revised and expanded. New York, NY, USA: Marcel Dekker, 2004, p. 760. ISBN: 0-8247-5053-2.
- [2] P. E. Tsakiridis and S. Agatzini-Leonardou, “Solvent extraction of aluminium in the presence of cobalt, nickel and magnesium from sulphate solutions by Cyanex 272,” *Hydrometallurgy*, vol. 80, no. 1–2, pp. 90–97, 2005. doi: 10.1016/j.hydromet.2005.07.002.
- [3] B. E. E. Molewa, “Listed Activities and Associated Minimum Emission Standards Identified in Terms of Section 21 of the National Environmental Management: Air Quality Act, 2004 (Act 39 of 2004),” *Government Gazette*, no. 37054, Nov. 22, 2013. [Online]. Available: [http://jutastat.juta.co.za/nxt/gateway.dll/strg/sargstat/full_notice/3956_full_notice?f=templates\\$fn=default.htm](http://jutastat.juta.co.za/nxt/gateway.dll/strg/sargstat/full_notice/3956_full_notice?f=templates$fn=default.htm).

APPENDIX A

This Appendix provides the MSDSs of the chemicals used within this study.

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

Version 6.6

Revision Date 02.06.2023

Print Date 21.03.2025

GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SECTION 1: Identification of the substance/mixture and of the company/undertaking**1.1 Product identifiers**

Product name : Aluminum sulfate

Product Number : 202614

Brand : Aldrich

REACH No. : 01-2119531538-36-XXXX

CAS-No. : 10043-01-3

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Merck Life Science (Pty) Ltd.
1 Friesland Drive
Longmeadow Business Estate
MODDERFONTEIN
1609
SOUTH AFRICA

Telephone : +27 +27 (0) 8600 63725

Fax : +27 +27 (0) 860 522 329

E-mail address : Melissa.byrne@merckgroup.com

1.4 Emergency telephone

Emergency Phone # : 0-800-983-611

SECTION 2: Hazards identification**2.1 Classification of the substance or mixture****Classification according to Regulation (EC) No 1272/2008**

Corrosive to Metals (Category 1), H290

Serious eye damage (Category 1), H318

For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2 Label elements**Labelling according Regulation (EC) No 1272/2008**

Pictogram



Signal Word

Danger

Hazard statement(s)

H290

May be corrosive to metals.

H318

Causes serious eye damage.

Precautionary statement(s)

P234

Keep only in original packaging.

P280

Wear eye protection/ face protection.

P305 + P351 + P338

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

P390

Absorb spillage to prevent material damage.

Supplemental Hazard Statements

none

Reduced Labeling (<= 125 ml)

Pictogram



Signal Word

Danger

Hazard statement(s)

H318

Causes serious eye damage.

Precautionary statement(s)

P280

Wear eye protection/ face protection.

P305 + P351 + P338

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard Statements

none

2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

SECTION 3: Composition/information on ingredients

3.1 Substances

Formula : $\text{Al}_2\text{O}_3 \cdot \text{S}_3$
Molecular weight : 342,15 g/mol
CAS-No. : 10043-01-3
EC-No. : 233-135-0

Component	Classification	Concentration
aluminium sulfate		
CAS-No.	10043-01-3	Met. Corr. 1; Eye Dam. 1; <= 100 %



EC-No.	233-135-0	H290, H318	
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For the full text of the H-Statements mentioned in this Section, see Section 16.

SECTION 4: First aid measures

4.1 Description of first-aid measures

General advice

Show this material safety data sheet to the doctor in attendance.

If inhaled

After inhalation: fresh air.

In case of skin contact

In case of skin contact: Take off immediately all contaminated clothing. Rinse skin with water/ shower.

In case of eye contact

After eye contact: rinse out with plenty of water. Immediately call in ophthalmologist. Remove contact lenses.

If swallowed

After swallowing: immediately make victim drink water (two glasses at most). Consult a physician.

4.2 Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed

No data available

SECTION 5: Firefighting measures

5.1 Extinguishing media

Suitable extinguishing media

Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.

Unsuitable extinguishing media

For this substance/mixture no limitations of extinguishing agents are given.

5.2 Special hazards arising from the substance or mixture

Sulfur oxides

Aluminum oxide

Not combustible.

Ambient fire may liberate hazardous vapours.

5.3 Advice for firefighters

In the event of fire, wear self-contained breathing apparatus.



5.4 Further information

Suppress (knock down) gases/vapors/mists with a water spray jet. Prevent fire extinguishing water from contaminating surface water or the ground water system.

SECTION 6: Accidental release measures

6.1 Personal precautions, protective equipment and emergency procedures

Advice for non-emergency personnel: Avoid inhalation of dusts. Avoid substance contact. Ensure adequate ventilation. Evacuate the danger area, observe emergency procedures, consult an expert.

For personal protection see section 8.

6.2 Environmental precautions

Do not let product enter drains.

6.3 Methods and materials for containment and cleaning up

Cover drains. Collect, bind, and pump off spills. Observe possible material restrictions (see sections 7 and 10). Take up dry. Dispose of properly. Clean up affected area. Avoid generation of dusts.

6.4 Reference to other sections

For disposal see section 13.

SECTION 7: Handling and storage

7.1 Precautions for safe handling

For precautions see section 2.2.

7.2 Conditions for safe storage, including any incompatibilities

Storage conditions

No metal containers.

Tightly closed. Dry.

hygroscopic Store under inert gas.

Storage class

Storage class (TRGS 510): 8B: Non-combustible, corrosive hazardous materials

7.3 Specific end use(s)

Apart from the uses mentioned in section 1.2 no other specific uses are stipulated



SECTION 8: Exposure controls/personal protection

8.1 Control parameters

Ingredients with workplace control parameters

8.2 Exposure controls

Personal protective equipment

Eye/face protection

Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU). Tightly fitting safety goggles

Body Protection

protective clothing

Respiratory protection

required when dusts are generated.

Our recommendations on filtering respiratory protection are based on the following standards: DIN EN 143, DIN 14387 and other accompanying standards relating to the used respiratory protection system.

Recommended Filter type: Filter type P2

The entrepreneur has to ensure that maintenance, cleaning and testing of respiratory protective devices are carried out according to the instructions of the producer. These measures have to be properly documented.

Control of environmental exposure

Do not let product enter drains.

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

- | | |
|---|---|
| a) Physical state | powder |
| b) Color | white |
| c) Odor | odorless |
| d) Melting point/freezing point | Melting point/range: 770 °C - dec. |
| e) Initial boiling point and boiling range | 112 - 116 °C |
| f) Flammability (solid, gas) | The product is not flammable. - Flammability (solids) |
| g) Upper/lower flammability or explosive limits | No data available |
| h) Flash point | No data available |
| i) Autoignition | No data available |



	temperature	
j)	Decomposition temperature	No data available
k)	pH	No data available
l)	Viscosity	Viscosity, kinematic: No data available Viscosity, dynamic: No data available
m)	Water solubility	ca.0,00001 g/l at 21,5 °C - insoluble
n)	Partition coefficient: n-octanol/water	Not applicable for inorganic substances
o)	Vapor pressure	No data available
p)	Density	2,71 g/mL at 25 °C - lit.
	Relative density	No data available
q)	Relative vapor density	No data available
r)	Particle characteristics	No data available
s)	Explosive properties	No data available
t)	Oxidizing properties	none

9.2 Other safety information

No data available

SECTION 10: Stability and reactivity

10.1 Reactivity

No data available

10.2 Chemical stability

The product is chemically stable under standard ambient conditions (room temperature) .

10.3 Possibility of hazardous reactions

No data available

10.4 Conditions to avoid

Air Exposure to moisture.
no information available

10.5 Incompatible materials

No data available

10.6 Hazardous decomposition products

In the event of fire: see section 5



SECTION 11: Toxicological information

11.1 Information on toxicological effects

Acute toxicity

LD50 Oral - Rat - male and female - > 2.000 mg/kg

(OECD Test Guideline 401)

Inhalation: No data available

LD50 Dermal - Rabbit - male and female - > 5.000 mg/kg

(OECD Test Guideline 402)

Skin corrosion/irritation

Skin - Rabbit

Result: No skin irritation - 4 h

(OECD Test Guideline 404)

Serious eye damage/eye irritation

Eyes - Rabbit

Result: Irreversible effects on the eye

(OECD Test Guideline 405)

Respiratory or skin sensitization

Local lymph node assay (LLNA) - Mouse

Result: negative

(OECD Test Guideline 429)

Germ cell mutagenicity

Test Type: Ames test

Test system: Escherichia coli/Salmonella typhimurium

Metabolic activation: with and without metabolic activation

Method: OECD Test Guideline 471

Result: negative

Test Type: In vitro mammalian cell gene mutation test

Test system: mouse lymphoma cells

Metabolic activation: with and without metabolic activation

Method: OECD Test Guideline 476

Result: negative

Test Type: Micronucleus test

Test system: Human lymphocytes

Metabolic activation: with and without metabolic activation

Method: OECD Test Guideline 487

Result: negative

Test Type: Micronucleus test

Species: Rat

Application Route: Oral

Method: OECD Test Guideline 474

Result: negative

Remarks: (in analogy to similar products)

The value is given in analogy to the following substances: aluminium hydroxide

Species: Rat



Application Route: Oral

Remarks: Cytogenetic analysis

Carcinogenicity

No data available

Reproductive toxicity

No data available

Specific target organ toxicity - single exposure

No data available

Specific target organ toxicity - repeated exposure

No data available

Aspiration hazard

No data available

11.2 Additional Information

Endocrine disrupting properties

Product:

Assessment

The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

Repeated dose toxicity - Rat - male - Oral - NOAEL (No observed adverse effect level) - 18 mg/kg - LOAEL (Lowest observed adverse effect level) - 90 mg/kg

Remarks: (in analogy to similar products)

The value is given in analogy to the following substances: aluminium(III) chloride, anhydrous

RTECS: BD1700000

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

SECTION 12: Ecological information

12.1 Toxicity

Toxicity to fish	semi-static test LC50 - Danio rerio (zebra fish) - > 87,5 mg/l - 96 h (OECD Test Guideline 203)
Toxicity to daphnia and other aquatic invertebrates	static test EC50 - Daphnia magna (Water flea) - > 200 mg/l - 48 h (OECD Test Guideline 202)
Toxicity to algae	static test ErC50 - Pseudokirchneriella subcapitata (microalgae) -



	0,24 mg/l - 72 h (OECD Test Guideline 201)
Toxicity to bacteria	static test EC50 - activated sludge - > 200 mg/l - 3 h (OECD Test Guideline 209)
Toxicity to fish(Chronic toxicity)	semi-static test NOEC - <i>Salvelinus fontinalis</i> (Brook trout) - 0,024 mg/l - 60 d Remarks: (ECHA)
	semi-static test NOEC - <i>Salvelinus fontinalis</i> (Brook trout) - 0,024 mg/l - 60 d Remarks: (ECHA)
	semi-static test NOEC - <i>Salvelinus fontinalis</i> (Brook trout) - 0,024 mg/l - 60 d Remarks: (ECHA)
Toxicity to daphnia and other aquatic invertebrates(Chronic toxicity)	semi-static test NOEC - <i>Ceriodaphnia dubia</i> (water flea) - 3,8 mg/l - 8 d (US-EPA)

12.2 Persistence and degradability

The methods for determining biodegradability are not applicable to inorganic substances.

12.3 Bioaccumulative potential

No data available

12.4 Mobility in soil

No data available

12.5 Results of PBT and vPvB assessment

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

12.6 Endocrine disrupting properties

Product:

Assessment

: The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

12.7 Other adverse effects

No data available



SECTION 13: Disposal considerations

13.1 Waste treatment methods

No data available

SECTION 14: Transport information

14.1 UN number

ADR/RID: 3260

IMDG: 3260

IATA: 3260

14.2 UN proper shipping name

ADR/RID: CORROSIVE SOLID, ACIDIC, INORGANIC, N.O.S. (aluminium sulfate)

IMDG: CORROSIVE SOLID, ACIDIC, INORGANIC, N.O.S. (aluminium sulfate)

IATA: Corrosive solid, acidic, inorganic, n.o.s. (aluminium sulfate)

14.3 Transport hazard class(es)

ADR/RID: 8

IMDG: 8

IATA: 8

14.4 Packaging group

ADR/RID: III

IMDG: III

IATA: III

14.5 Environmental hazards

ADR/RID: no

IMDG Marine pollutant: no

IATA: no

14.6 Special precautions for user

Tunnel restriction code : (E)

Further information : No data available

SECTION 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

This material safety data sheet complies with the requirements of Regulation (EC) No. 1907/2006.

Other regulations

Take note of Dir 94/33/EC on the protection of young people at work.

15.2 Chemical Safety Assessment

For this product a chemical safety assessment was not carried out

SECTION 16: Other information

Full text of H-Statements referred to under sections 2 and 3.

H290

May be corrosive to metals.

H318

Causes serious eye damage.



Full text of other abbreviations

ADN - European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways; ADR - Agreement concerning the International Carriage of Dangerous Goods by Road; AIIC - Australian Inventory of Industrial Chemicals; ASTM - American Society for the Testing of Materials; bw - Body weight; CMR - Carcinogen, Mutagen or Reproductive Toxicant; DIN - Standard of the German Institute for Standardisation; DSL - Domestic Substances List (Canada); ECx - Concentration associated with x% response; ELx - Loading rate associated with x% response; EmS - Emergency Schedule; ENCS - Existing and New Chemical Substances (Japan); ErCx - Concentration associated with x% growth rate response; GHS - Globally Harmonized System; GLP - Good Laboratory Practice; IARC - International Agency for Research on Cancer; IATA - International Air Transport Association; IBC - International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk; IC50 - Half maximal inhibitory concentration; ICAO - International Civil Aviation Organization; IECSC - Inventory of Existing Chemical Substances in China; IMDG - International Maritime Dangerous Goods; IMO - International Maritime Organization; ISHL - Industrial Safety and Health Law (Japan); ISO - International Organisation for Standardization; KECI - Korea Existing Chemicals Inventory; LC50 - Lethal Concentration to 50 % of a test population; LD50 - Lethal Dose to 50% of a test population (Median Lethal Dose); MARPOL - International Convention for the Prevention of Pollution from Ships; n.o.s. - Not Otherwise Specified; NO(A)EC - No Observed (Adverse) Effect Concentration; NO(A)EL - No Observed (Adverse) Effect Level; NOELR - No Observable Effect Loading Rate; NZIoC - New Zealand Inventory of Chemicals; OECD - Organization for Economic Co-operation and Development; OPPTS - Office of Chemical Safety and Pollution Prevention; PBT - Persistent, Bioaccumulative and Toxic substance; PICCS - Philippines Inventory of Chemicals and Chemical Substances; (Q)SAR - (Quantitative) Structure Activity Relationship; REACH - Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals; RID - Regulations concerning the International Carriage of Dangerous Goods by Rail; SADT - Self-Accelerating Decomposition Temperature; SDS - Safety Data Sheet; TCSI - Taiwan Chemical Substance Inventory; TECI - Thailand Existing Chemicals Inventory; TSCA - Toxic Substances Control Act (United States); UN - United Nations; UNRTDG - United Nations Recommendations on the Transport of Dangerous Goods; vPvB - Very Persistent and Very Bioaccumulative

Further information

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.

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SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

Version 7.8

Revision Date 17.03.2025

Print Date 21.03.2025

GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SECTION 1: Identification of the substance/mixture and of the company/undertaking**1.1 Product identifiers**

Product name : Ammonium hydroxide solution

Product Number : 221228

Brand : Sigma-Aldrich

UFI : 4HVY-A508-P991-RPHH

REACH No. :

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

Uses advised against : This product is not intended for consumer use.

1.3 Details of the supplier of the safety data sheet

Company : Merck Life Science (Pty) Ltd.
1 Friesland Drive
Longmeadow Business Estate
MODDERFONTEIN
1609
SOUTH AFRICA

Telephone : +27 +27 (0) 8600 63725

Fax : +27 +27 (0) 860 522 329

E-mail address : Melissa.byrne@merckgroup.com

1.4 Emergency telephone

Emergency Phone # : 0-800-983-611

SECTION 2: Hazards identification**2.1 Classification of the substance or mixture**

Skin corrosion, (Category 1) H314: Causes severe skin burns and eye damage.

Serious eye damage, (Category 1) H318: Causes serious eye damage.

Specific target organ toxicity - single exposure, (Category 3), Respiratory system H335: May cause respiratory irritation.



Short-term (acute) aquatic hazard, (Category 1)

H400: Very toxic to aquatic life.

Long-term (chronic) aquatic hazard, (Category 1)

H410: Very toxic to aquatic life with long lasting effects.

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008

Pictogram



Signal Word

Danger

Hazard Statements

H314

Causes severe skin burns and eye damage.

H335

May cause respiratory irritation.

H410

Very toxic to aquatic life with long lasting effects.

Precautionary Statements

P261

Avoid breathing mist or vapors.

P271

Use only outdoors or in a well-ventilated area.

P273

Avoid release to the environment.

P280

Wear protective gloves/ protective clothing/ eye protection/ face protection.

P303 + P361 + P353

IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.

P305 + P351 + P338

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard Statements

none

Reduced Labeling (<= 125 ml)

Pictogram



Signal Word

Danger

Hazard Statements

H314

Causes severe skin burns and eye damage.

Precautionary Statements

P280

Wear protective gloves/ protective clothing/ eye protection/ face protection.

P303 + P361 + P353

IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.

P305 + P351 + P338

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard Statements

none



2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

Ecological information:

The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

Toxicological information:

The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.
Lachrymator.

SECTION 3: Composition/information on ingredients

3.2 Mixtures

Formula : H_5NO
Molecular weight : 35,05 g/mol

Component		Classification	Concentration
ammonia solution			
CAS-No.	1336-21-6	Acute Tox. 4; Skin Corr. 1B; Eye Dam. 1; STOT SE 3; Aquatic Acute 1; Aquatic Chronic 1; H332, H314, H318, H335, H400, H410 Concentration limits: >= 5 %: STOT SE 3, H335; M-Factor - Aquatic Acute: 10 M-Factor - Aquatic Chronic: 1	>= 30 - < 50 %
EC-No.	215-647-6		
Index-No.	007-001-01-2		
Registration number	01-2119488876-14-XXXX		

For the full text of the H-Statements mentioned in this Section, see Section 16.

SECTION 4: First aid measures

4.1 Description of first-aid measures

General advice

First aiders need to protect themselves. Show this material safety data sheet to the doctor in attendance.

If inhaled

After inhalation: fresh air. Call in physician.

In case of skin contact

In case of skin contact: Take off immediately all contaminated clothing. Rinse skin with water/ shower. Call a physician immediately.



In case of eye contact

After eye contact: rinse out with plenty of water. Immediately call in ophthalmologist.
Remove contact lenses.

If swallowed

After swallowing: make victim drink water (two glasses at most), avoid vomiting (risk of perforation). Call a physician immediately. Do not attempt to neutralise.

4.2 Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed

No data available

SECTION 5: Firefighting measures**5.1 Extinguishing media****Suitable extinguishing media**

Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.

Unsuitable extinguishing media

For this substance/mixture no limitations of extinguishing agents are given.

5.2 Special hazards arising from the substance or mixture

Nitrogen oxides (NO_x)

Not combustible.

Ambient fire may liberate hazardous vapours.

5.3 Advice for firefighters

Stay in danger area only with self-contained breathing apparatus. Prevent skin contact by keeping a safe distance or by wearing suitable protective clothing.

5.4 Further information

Suppress (knock down) gases/vapors/mists with a water spray jet. Prevent fire extinguishing water from contaminating surface water or the ground water system.

SECTION 6: Accidental release measures**6.1 Personal precautions, protective equipment and emergency procedures**

Advice for non-emergency personnel: Do not breathe vapors, aerosols. Avoid substance contact. Ensure adequate ventilation. Evacuate the danger area, observe emergency procedures, consult an expert.

For personal protection see section 8.

6.2 Environmental precautions

Do not let product enter drains.

6.3 Methods and materials for containment and cleaning up

Cover drains. Collect, bind, and pump off spills. Observe possible material restrictions (see sections 7 and 10). Take up with liquid-absorbent and neutralising material (e.g. Chemizorb® OH⁻, Merck Art. No. 101596). Dispose of properly. Clean up affected area.

6.4 Reference to other sections

For disposal see section 13.



SECTION 7: Handling and storage

7.1 Precautions for safe handling

Advice on safe handling

Avoid contact with skin and eyes. Always open containers slowly to allow any excess pressure to vent.

Hygiene measures

Immediately change contaminated clothing. Apply preventive skin protection. Wash hands and face after working with substance.

For precautions see section 2.2.

7.2 Conditions for safe storage, including any incompatibilities

Storage conditions

Tightly closed.

Storage stability

Recommended storage temperature

2 - 8 °C

May develop pressure. Refrigerate before opening. Handle and open container with care.

Storage class

Storage class (TRGS 510): 8B: Non-combustible, corrosive hazardous materials

7.3 Specific end use(s)

Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

SECTION 8: Exposure controls/personal protection

8.1 Control parameters

Ingredients with workplace control parameters

8.2 Exposure controls

Personal protective equipment

Eye/face protection

Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU). Tightly fitting safety goggles

Skin protection

Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

The selected protective gloves have to satisfy the specifications of Regulation (EU) 2016/425 and the standard EN 374 derived from it.

Full contact

Material: butyl-rubber

Minimum layer thickness: 0,3 mm

Break through time: 480 min

Material tested: Butoject® (KCL 897 / Aldrich Z677647, Size M)

Splash contact

Material: Nitrile rubber



Minimum layer thickness: 0,11 mm

Break through time: 240 min

Material tested: Dermatril® (KCL 740 / Aldrich Z677272, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 87300, e-mail sales@kcl.de, test method: EN374

If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the EC approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.

Body Protection

protective clothing

Respiratory protection

required when vapours/aerosols are generated.

Our recommendations on filtering respiratory protection are based on the following standards: DIN EN 143, DIN 14387 and other accompanying standards relating to the used respiratory protection system.

Recommended Filter type: Filter type ABEK

The entrepreneur has to ensure that maintenance, cleaning and testing of respiratory protective devices are carried out according to the instructions of the producer. These measures have to be properly documented.

Control of environmental exposure

Do not let product enter drains.

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

- | | |
|---|--|
| a) Physical state | liquid |
| b) Color | colorless |
| c) Odor | No data available |
| d) Melting point/freezing point | -60 °C |
| e) Initial boiling point and boiling range | 38 - 100 °C at 1.013 hPa |
| f) Flammability (solid, gas) | No data available |
| g) Upper/lower flammability or explosive limits | Upper explosion limit: 27 %(V)
Lower explosion limit: 16 %(V) |
| h) Flash point | Not applicable |
| i) Autoignition temperature | Not applicable |
| j) Decomposition temperature | No data available |
| k) pH | 11,7 at 20 °C |



- | | |
|--|--|
| l) Viscosity | Viscosity, kinematic: No data available
Viscosity, dynamic: No data available |
| m) Water solubility | at 20 °C soluble |
| n) Partition coefficient:
n-octanol/water | No data available |
| o) Vapor pressure | 153 hPa at 20 °C |
| p) Density | 0,9 g/cm ³ at 25 °C - lit. |
| Relative density | No data available |
| q) Relative vapor
density | No data available |
| r) Particle
characteristics | No data available |
| | |
| s) Explosive properties | Not classified as explosive. |
| t) Oxidizing properties | none |

9.2 Other safety information

Relative vapor density 1,21 - (Air = 1.0)

SECTION 10: Stability and reactivity

10.1 Reactivity

No data available

10.2 Chemical stability

The product is chemically stable under standard ambient conditions (room temperature) .

10.3 Possibility of hazardous reactions

Violent reactions possible with:
The generally known reaction partners of water.

10.4 Conditions to avoid

no information available

10.5 Incompatible materials

Copper, Iron, Zinc

10.6 Hazardous decomposition products

In the event of fire: see section 5

SECTION 11: Toxicological information

11.1 Information on toxicological effects

Mixture

Acute toxicity

Oral: No data available



Inhalation: No data available

Acute toxicity estimate Inhalation - 4 h - > 5 mg/l - dust/mist(Calculation method)

Symptoms: mucosal irritations, Cough, Shortness of breath, Possible damages:, damage of respiratory tract

Dermal: No data available

Skin corrosion/irritation

No data available

Serious eye damage/eye irritation

Remarks: Mixture causes serious eye damage.

Risk of blindness!

Respiratory or skin sensitization

No data available

Germ cell mutagenicity

No data available

Carcinogenicity

No data available

Reproductive toxicity

No data available

Specific target organ toxicity - single exposure

Mixture may cause respiratory irritation.

Specific target organ toxicity - repeated exposure

No data available

Aspiration hazard

No data available

11.2 Additional Information

Endocrine disrupting properties

Product:

Assessment

The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Other dangerous properties can not be excluded.

Handle in accordance with good industrial hygiene and safety practice.

Components

ammonia solution

Acute toxicity

Oral: No data available

LC50 Inhalation - Rat - male - 4 h - 4,9 mg/l - dust/mist

Remarks: (ECHA)



Acute toxicity estimate Inhalation - 4,9 mg/l - dust/mist
(ATE value derived from LD50/LC50 value)

Dermal: No data available

Skin corrosion/irritation

Remarks: Causes skin burns.

Classified according to Regulation (EU) 1272/2008, Annex VI (Table 3.1/3.2)

Serious eye damage/eye irritation

No data available

Respiratory or skin sensitization

No data available

Germ cell mutagenicity

No data available

Carcinogenicity

No data available

Reproductive toxicity

No data available

Specific target organ toxicity - single exposure

May cause respiratory irritation.

Specific target organ toxicity - repeated exposure

No data available

Aspiration hazard

No data available

SECTION 12: Ecological information

12.1 Toxicity

Mixture

No data available

12.2 Persistence and degradability

No data available

12.3 Bioaccumulative potential

No data available

12.4 Mobility in soil

No data available

12.5 Results of PBT and vPvB assessment

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

12.6 Endocrine disrupting properties

Product:

Assessment

: The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.



12.7 Other adverse effects

No data available

Components

ammonia solution

Toxicity to fish

flow-through test LC50 - Pimephales promelas (fathead minnow) - 0,068 mg/l - 96 h

Remarks: (ECHA)

The value is given in analogy to the following substances:
ammonium sulphate

Toxicity to daphnia
and other aquatic
invertebrates

static test LC50 - Daphnia magna (Water flea) - 101 mg/l - 48 h

Remarks: (ECHA)

anhydrous

Toxicity to
fish(Chronic toxicity)

flow-through test NOEC - Ictalurus punctatus - 0,048 mg/l - 31 d

(OECD Test Guideline 215)

Remarks: anhydrous

Toxicity to daphnia
and other aquatic
invertebrates(Chronic
toxicity)

flow-through test LC50 - Daphnia magna (Water flea) - 4,07 mg/l - 96 h

(US-EPA)

Remarks: The value is given in analogy to the following substances:

The value is given in analogy to the following substances:
ammonium chloride

flow-through test NOEC - Daphnia magna (Water flea) - 0,79 mg/l - 96 h

(US-EPA)

Remarks: The value is given in analogy to the following substances:

The value is given in analogy to the following substances:
ammonium chloride

SECTION 13: Disposal considerations

13.1 Waste treatment methods

No data available



SECTION 14: Transport information

14.1 UN number

ADR/RID: 2672

IMDG: 2672

IATA: 2672

14.2 UN proper shipping name

ADR/RID: AMMONIA SOLUTION

IMDG: AMMONIA SOLUTION

IATA: Ammonia solution

14.3 Transport hazard class(es)

ADR/RID: 8

IMDG: 8

IATA: 8

14.4 Packaging group

ADR/RID: III

IMDG: III

IATA: III

14.5 Environmental hazards

ADR/RID: yes

IMDG Marine pollutant: yes

IATA: no

14.6 Special precautions for user

Tunnel restriction code : (E)

Further information : No data available

14.7 Maritime transport in bulk according to IMO instruments

Not applicable for product as supplied.

SECTION 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

This material safety data sheet complies with the requirements of Regulation (EC) No. 1907/2006.

Authorisations and/or restrictions on use

National legislation

Seveso III: Directive 2012/18/EU of the European Parliament and of the Council on the control of major-accident hazards involving dangerous substances.

E1

ENVIRONMENTAL HAZARDS

E1

ENVIRONMENTAL HAZARDS

Other regulations

Take note of Dir 94/33/EC on the protection of young people at work.

15.2 Chemical Safety Assessment

For this product a chemical safety assessment was not carried out

SECTION 16: Other information

Full text of H-Statements

H314 Causes severe skin burns and eye damage.

H318 Causes serious eye damage.

H332 Harmful if inhaled.

H335 May cause respiratory irritation.



H400	Very toxic to aquatic life.
H410	Very toxic to aquatic life with long lasting effects.

Full text of other abbreviations

ADN - European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways; ADR - Agreement concerning the International Carriage of Dangerous Goods by Road; AIIC - Australian Inventory of Industrial Chemicals; ASTM - American Society for the Testing of Materials; bw - Body weight; CMR - Carcinogen, Mutagen or Reproductive Toxicant; DIN - Standard of the German Institute for Standardisation; DSL - Domestic Substances List (Canada); ECx - Concentration associated with x% response; ELx - Loading rate associated with x% response; EmS - Emergency Schedule; ENCS - Existing and New Chemical Substances (Japan); ErCx - Concentration associated with x% growth rate response; GHS - Globally Harmonized System; GLP - Good Laboratory Practice; IARC - International Agency for Research on Cancer; IATA - International Air Transport Association; IBC - International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk; IC50 - Half maximal inhibitory concentration; ICAO - International Civil Aviation Organization; IECSC - Inventory of Existing Chemical Substances in China; IMDG - International Maritime Dangerous Goods; IMO - International Maritime Organization; ISHL - Industrial Safety and Health Law (Japan); ISO - International Organisation for Standardization; KECI - Korea Existing Chemicals Inventory; LC50 - Lethal Concentration to 50 % of a test population; LD50 - Lethal Dose to 50% of a test population (Median Lethal Dose); MARPOL - International Convention for the Prevention of Pollution from Ships; n.o.s. - Not Otherwise Specified; NO(A)EC - No Observed (Adverse) Effect Concentration; NO(A)EL - No Observed (Adverse) Effect Level; NOELR - No Observable Effect Loading Rate; NZIoC - New Zealand Inventory of Chemicals; OECD - Organization for Economic Co-operation and Development; OPPTS - Office of Chemical Safety and Pollution Prevention; PBT - Persistent, Bioaccumulative and Toxic substance; PICCS - Philippines Inventory of Chemicals and Chemical Substances; (Q)SAR - (Quantitative) Structure Activity Relationship; REACH - Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals; RID - Regulations concerning the International Carriage of Dangerous Goods by Rail; SADT - Self-Accelerating Decomposition Temperature; SDS - Safety Data Sheet; TCSI - Taiwan Chemical Substance Inventory; TECI - Thailand Existing Chemicals Inventory; TSCA - Toxic Substances Control Act (United States); UN - United Nations; UNRTDG - United Nations Recommendations on the Transport of Dangerous Goods; vPvB - Very Persistent and Very Bioaccumulative

Classification of the mixture

Skin Corr.1	H314
Eye Dam.1	H318
STOT SE3	H335
Aquatic Acute1	H400
Aquatic Chronic1	H410

Classification procedure:

Based on product data or assessment
Based on product data or assessment
Calculation method
Calculation method
Calculation method

Further information

The information is believed to be correct but is not exhaustive and will be used solely as a guideline, which is based on current knowledge of the chemical substance or mixture and is applicable to appropriate safety precautions for the product. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact



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SAFETY DATA SHEET

COBALT SULPHATE



The safety data sheet is in accordance with Commission Regulation (EU) 2015/830 of 28 May 2015 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

SECTION 1: Identification of the substance / mixture and of the company / undertaking

Date issued 14.06.2017

1.1. Product identifier

Product name	COBALT SULPHATE
REACH Reg. No.	01-2119517426-41-0003
CAS no.	10026-24-1
EC no.	233-334-2
Extended SDS with ES incorporated	Yes

1.2. Relevant identified uses of the substance or mixture and uses advised against

Use of the substance/preparation	• Use of cobalt sulfate in the production of cobalt carbonate • surface treatment processes (intermediate use) • inorganic pigments & frits, glass and ceramic ware (intermediate use) • dyes for the textile, leather, wood and/or paper industry (intermediate use) • industrial use of cobalt sulfate in the manufacture of chemicals and in other wet-chemical processes as intermediate • fertilizers and/or feed grade materials • catalyst in synthesis processes • fermentation processes and/or biogas production • Formulation and industrial use of as water treatment chemical, oxygen scavenger, corrosion inhibitor • Manufacture and industrial use of batteries using cobalt sulfate (intermediate use) • Professional use of fertilizers containing cobalt sulfate
Uses advised against	None.

1.3. Details of the supplier of the safety data sheet

Manufacturer

Company name	Norilsk Nickel Harjavalta Oy
Postal address	Teollisuuskatu 1
Postcode	29200
City	Harjavalta
Country	Finland
Tel	+358 2 537 11
E-mail	product.safety@nornickel.fi
Enterprise no.	F115917284

1.4. Emergency telephone number

Emergency telephone

Description: 3E EH&S Mission Control Center: +44 20 35147487 / Access Code: 334656

SECTION 2: Hazards identification

2.1. Classification of substance or mixture

Classification according to
Regulation (EC) No 1272/2008
[CLP / GHS]

Acute tox. 4; H302,H302

Eye Irrit. 2; H319,H319

Resp. Sens. 1A; H334,H334

Skin Sens. 1; H317,H317

Repr. 1B; H360F,H360F

Muta. 2; H341,H341

Carc. 1B; H350i,H350i

Aquatic Acute 1; H400,H400

Aquatic Chronic 1; H410,H410

2.2. Label elements

Hazard Pictograms (CLP)



Signal word

Danger

Hazard statements

H302 Harmful if swallowed.
H319 Causes serious eye irritation.
H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H317 May cause an allergic skin reaction.
H360F May damage fertility.
H341 Suspected of causing genetic defects
H350i May cause cancer by inhalation.
H400 Very toxic to aquatic life.
H410 Very toxic to aquatic life with long lasting effects.
H410 Very toxic to aquatic life with long lasting effects.

Precautionary statements

P202 Do not handle until all safety precautions have been read and understood.
P261 Avoid breathing dust / fume / gas / mist / vapours / spray.
P270 Do not eat, drink or smoke when using this product.
P280 Wear protective gloves / protective clothing / eye protection / face protection.
P309+P311 IF exposed or if you feel unwell: Call a POISON CENTER or doctor / physician.
P273 Avoid release to the environment.

2.3. Other hazards

PBT / vPvB

The PBT and vPvB criteria of Annex XIII to the regulation does not apply to inorganic substances.

SECTION 3: Composition/information on ingredients

3.1. Substances

Substance	Identification	Classification	Contents
Cobalt sulphate heptahydrate	CAS no.: 10026-24-1 EC no.: 233-334-2 REACH Reg. No.: 01-2119517426-41-0003	Carc. 1B; H350i Muta. 2; H341 Repr. 1B; H360F Acute tox. 4; H302 Resp. Sens. 1; H334 Skin Sens. 1; H317 Eye Irrit. 2; H319 Aquatic Acute 1; H400; M-factor 10 Aquatic Chronic 1; H410; M-factor 10	> 99,9 %
Substance comments	CoSO ₄ · 7H ₂ O		

SECTION 4: First aid measures

4.1. Description of first aid measures

Inhalation	Remove affected person from the immediate area. Ensure supply of fresh air. If breathing is irregular or stopped, administer artificial respiration. Consult a physician.
Skin contact	Wash off with soap and plenty of water. Remove soiled or soaked clothing immediately. Wash contaminated clothing before re-use.
Eye contact	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. If easy to do, remove contact lens, if worn. If eye irritation persists, consult a specialist.
Ingestion	Rinse mouth. Consult a physician.

4.2. Most important symptoms and effects, both acute and delayed

General symptoms and effects	If inhaled : Cough ; Shortness of breath If swallowed : Vomiting ; Abdominal pain Eyes / Skin : Redness If symptoms persist, call a physician. Treat symptomatically.
------------------------------	--

4.3. Indication of any immediate medical attention and special treatment needed

Medical treatment	None.
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SECTION 5: Firefighting measures

5.1. Extinguishing media

Suitable extinguishing media	The product itself does not burn. Powder. Carbon dioxide (CO ₂). Water spray.
Improper extinguishing media	None.

5.2. Special hazards arising from the substance or mixture

Fire and explosion hazards	In case of fire, toxic gases may be formed. Sulphurous gases (SO _x). Cobalt oxides
----------------------------	--

5.3. Advice for firefighters

Personal protective equipment	Use personal protective equipment as required.
Other Information	Collect contaminated fire extinguishing water separately. Do not discharge into the drains/surface waters/groundwater.

SECTION 6: Accidental release measures

6.1. Personal precautions, protective equipment and emergency procedures

General measures	Avoid contact with skin, eyes and clothing. Ensure adequate ventilation. Avoid dust formation. Avoid breathing dust.
------------------	---

6.2. Environmental precautions

Environmental precautionary measures	Do not allow to enter drains, sewers or watercourses.
--------------------------------------	---

6.3. Methods and material for containment and cleaning up

Other information	Send in suitable containers for recovery or disposal.
-------------------	---

6.4. Reference to other sections

Other instructions	See also section 7, 8,13
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SECTION 7: Handling and storage

7.1. Precautions for safe handling

Handling	Take note of Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work. Avoid inhalation of dust and contact with skin and eyes. Use mechanical ventilation in case of handling which causes formation of dust. Avoid spread of dust.
----------	---

Protective Safety Measures

Advice on general occupational hygiene	Private clothes and working clothes should be kept separately.
--	--

7.2. Conditions for safe storage, including any incompatibilities

Storage	Store in tightly closed original container in a dry, cool and well-ventilated place.
Conditions to avoid	Keep away from Strong oxidizing agents.

7.3. Specific end use(s)

Specific use(s)	Industrial use ; professional use
-----------------	-----------------------------------

SECTION 8: Exposure controls/personal protection

8.1. Control parameters

Substance	Identification	Value	TWA Year
Cobalt and its inorganic compounds*		TWA (8h): 0,02 mg/m ³ Exposure Limit Letter Letter description: Co Source: HTP Finland	TWA Year: 2012

DNEL / PNEC

Substance	Cobalt sulphate heptahydrate
DNEL	Group: Consumer Route of exposure: Long-term inhalation (local) Value: 16.6 µg/m ³ Group: Professional Route of exposure: Long-term inhalation (local)

PNEC	Value: 105,2 µg/m ³
	Value: 25 µg/kg bw/day
	Comment : long-term oral (local)
	Route of exposure: Saltwater
	Value: 2,36 µg Co/L
	Route of exposure: Freshwater
	Value: 0.51 µg/L
	Route of exposure: Freshwater sediments
	Value: 9,5 mg Co/kg dw
	Route of exposure: Saltwater sediments
	Value: 9,5 mg Co/kg dw
	Comment : PNEC Soil = 7.9 mg/kg dw
	Water treatment plant micro organisms = 0.373 µg Co/l

8.2. Exposure controls

Precautionary measures to prevent exposure

Product-related measures to prevent exposure	Avoid contact with skin and eyes. Do not breathe dust.
--	--

Eye / face protection

Suitable Eye Protection	Wear tight-fitting goggles or face shield.
-------------------------	--

Hand protection

Suitable gloves type	Wear protective gloves. Avoid prolonged skin contact.
Suitable materials	Butyl rubber. Polyvinyl chloride (PVC).

Skin protection

Suitable protective clothing	Wear appropriate clothing to prevent reasonably probable skin contact. Wear special protective clothing.
------------------------------	--

Respiratory protection

Recommended type of equipment	Use respiratory equipment with particle filter, type P3.
-------------------------------	--

Hygiene / environmental

Specific hygiene measures	Wash contaminated clothing before reuse. Personal protection must be kept separate from other clothes. When using do not eat, drink or smoke.
---------------------------	---

Appropriate environmental exposure control

Environmental exposure controls	The employer shall fulfill requirements of IPPC Directive.
---------------------------------	--

SECTION 9: Physical and chemical properties

9.1. Information on basic physical and chemical properties

Physical state	Crystals or crystalline.
----------------	--------------------------

Colour	Red.
Odour	Odourless.
Odour limit	Comments: Not relevant.
pH	Status: In delivery state Comments: 5.11 (100 g/l)
Melting point / melting range	Comments: 96.8°C CoSO ₄ · 7H ₂ O
Boiling point / boiling range	Comments: Not relevant.
Flash point	Comments: Not relevant.
Evaporation rate	Comments: Not relevant.
Flammability (solid, gas)	does not ignite
Vapour pressure	Comments: No data available.
Vapour density	Comments: No data available.
Density	Value: 1.948 g/cm ³ Comments: (CoSO ₄ · 7H ₂ O)
Solubility	Medium: Water Value: 376,7 g/l Temperature: 20 °C
Partition coefficient: n-octanol/water	Comments: Not applicable.
Spontaneous combustability	Comments: Not applicable.
Decomposition temperature	Comments: No data available.
Viscosity	Comments: Not applicable. Solid
Explosive properties	Not explosive
Oxidising properties	no oxidizing

9.2. Other information

SECTION 10: Stability and reactivity

10.1. Reactivity

Reactivity	No specific reactivity hazards associated with this product.
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10.2. Chemical stability

Stability	Stable under recommended storage conditions.
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10.3. Possibility of hazardous reactions

Possibility of hazardous reactions	No dangerous reaction known under conditions of normal use.
------------------------------------	---

10.4. Conditions to avoid

Conditions to avoid	Heat.
---------------------	-------

10.5. Incompatible materials

Materials to avoid	Strong oxidizing agents
--------------------	-------------------------

10.6. Hazardous decomposition products

Hazardous decomposition products Sulphurous gases (SO_x). Cobalt oxides

Other information

SECTION 11: Toxicological information

11.1. Information on toxicological effects

Other information regarding health hazards

Assessment of acute toxicity classification	LD50/oral/rat = 768 mg/kg
Assessment of skin corrosion / irritation, classification	Not classified as Corrosive. Causes serious eye irritation.
Sensitisation	May cause allergy or asthma symptoms or breathing difficulties if inhaled. May cause an allergic skin reaction.
Mutagenicity	Suspected of causing genetic defects.
Carcinogenicity	May cause cancer by inhalation. Animal experiments showed a statistically significant number of tumours. Concentration 0,3 mg/m ³
Reproductive toxicity	May damage fertility
Assessment of specific target organ toxicity RE, classification	No data available.
Aspiration hazard, comments	Not relevant.

SECTION 12: Ecological information

12.1. Toxicity

Ecotoxicity	LC50/96t/mutu (Fathead minnows) = 3.61 mg/L (CoSO ₄) LC50/96h/Salmo gairdneri: 1.5 mg/l (CoCl ₂) NOEC: 351.4 mg/L (Fresh water , fish)(Chemical Safety Report) NOEC: 31802 mg/L (Sea water , fish) (Chemical Safety Report) EC/LC50: 0.61 mg/L (Fresh water , Invertebrates.) (Chemical Safety Report) EC/LC50: 2.23 mg/L(Sea water , Invertebrates.) (Chemical Safety Report)
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12.2. Persistence and degradability

Persistence and degradability	No data available.
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12.3. Bioaccumulative potential

Bioaccumulative potential	Cobalt water plants BCF: > 100 – 5000 Invertebrates. , Water BCF < 300 fish Fresh water BCF/BAF : <10 fish Sea water BCF/BAF : <10
---------------------------	--

12.4. Mobility in soil

Mobility	No data available.
----------	--------------------

12.5. Results of PBT and vPvB assessment

PBT assessment results	The PBT and vPvB criteria of Annex XIII to the regulation does not apply to inorganic substances.
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12.6. Other adverse effects

Other adverse effects / Remarks	no data available
------------------------------------	-------------------

SECTION 13: Disposal considerations

13.1. Waste treatment methods

Specify the appropriate methods of disposal	Contaminated packaging should be emptied as far as possible. Packaging that cannot be cleaned should be disposed as special waste in compliance with local and national regulations.
Other Information	Contact manufacturer. Dispose of as special waste in compliance with local and national regulations.

SECTION 14: Transport information

14.1. UN number

Comments	UN3077
----------	--------

14.2. UN proper shipping name

Comments	ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S. (Cobalt sulphate)
----------	--

14.3. Transport hazard class(es)

Class Code IMDG	9
-----------------	---

14.4. Packing group

Comments	III
----------	-----

14.5. Environmental hazards

Comments	Environmentally hazardous substance – marine pollutant
----------	--

14.6. Special precautions for user

Special safety precautions for user	None. Tunnel restriction code (-)
--	-----------------------------------

14.7. Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code

Transport In Bulk Value (Yes/No)	No
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SECTION 15: Regulatory information

15.1. Safety, health and environmental regulations/legislation specific for the substance or mixture

Legislation and regulations	Candidate list : Cobalt sulphate EC no 233-334-2 http://echa.europa.eu/web/guest/candidate-list-table
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15.2. Chemical safety assessment

Chemical safety assessment performed	Yes
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SECTION 16: Other information

List of relevant H-phrases (Section 2 and 3).	H302 Harmful if swallowed. H317 May cause an allergic skin reaction. H319 Causes serious eye irritation. H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled. H341 Suspected of causing genetic defects H350i May cause cancer by inhalation. H360F May damage fertility. H400 Very toxic to aquatic life. H410 Very toxic to aquatic life with long lasting effects.
Classification according to Regulation (EC) No 1272/2008 [CLP / GHS]	Acute tox. 4; H302,H302 Eye Irrit. 2; H319,H319 Resp. Sens. 1A; H334,H334 Skin Sens. 1; H317,H317 Repr. 1B; H360F,H360F Muta. 2; H341,H341 Carc. 1B; H350i,H350i Aquatic Acute 1; H400,H400 Aquatic Chronic 1; H410,H410
Additional information	Disclaimer The information in this document is believed to be correct as of the date issued. However, no warranty of merchantability, fitness for any particular purpose, or any other warranty is expressed or is to be implied regarding the accuracy or completeness of this information, the results to be obtained from the use of this information or the product, the safety of this product, or the hazards related to its use. This information and product are furnished on the condition that the person receiving them shall make his own determination as to the suitability of the product for his particular purpose and on the condition that he assume the risk of his use thereof.
Key literature references and sources for data	Chemical Safety Report
Exposure scenario	 ES_0_COBALT SULPHATE [FI-FIN].pdf

File No: NA291

Date: 5 March 1996

**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION
AND ASSESSMENT SCHEME**

FULL PUBLIC REPORT

Bis (2,4,4-trimethylpentyl) phosphinic acid

This Assessment has been compiled in accordance with the provisions of *the Industrial Chemicals (Notification and Assessment) Act 1989*, and Regulations. This legislation is an Act of the Commonwealth of Australia. The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) is administered by Worksafe Australia which also conducts the occupational health & safety assessment. The assessment of environmental hazard is conducted by the Department of the Environment, Sport, and Territories and the assessment of public health is conducted by the Department of Human Services and Health.

For the purposes of subsection 78(1) of the Act, copies of this full public report may be inspected by the public at the Library, Worksafe Australia, 92-94 Parramatta Road, Camperdown NSW 2050, between the hours of 10.00 a.m. and 12.00 noon and 2.00 p.m. and 4.00 p.m. each week day except on public holidays.

For Enquiries please contact the Administration Coordinator at:

Street Address: 92 Parramatta Rd Camperdown, NSW 2050, AUSTRALIA

Postal Address: GPO Box 58, Sydney 2001, AUSTRALIA

Telephone: (61) (02) 565-9466 **FAX (61) (02) 565-9465**

Director
Chemicals Notification and Assessment

FULL PUBLIC REPORT**Bis (2,4,4-trimethylpentyl) phosphinic acid****1. APPLICANT**

Cytec Australia Limited of Suite 1, 1st Floor, 7-11 Railway St, Baulkham Hills, NSW 2153 has submitted a standard notification statement in support of their application for an assessment certificate for Bis (2,4,4-trimethylpentyl) phosphinic acid.

2. IDENTITY OF THE CHEMICAL

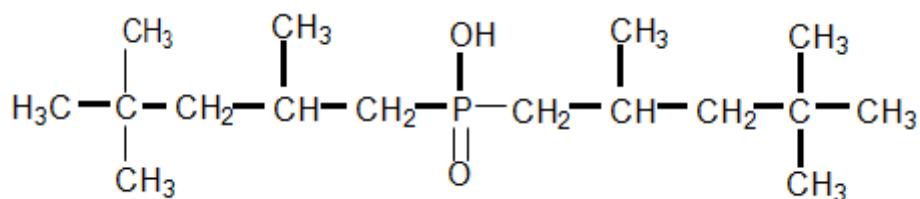
Chemical name: Bis (2,4,4-trimethylpentyl) phosphinic acid

Chemical Abstracts Service (CAS) Registry No.: 83411-71-6

Other names: None known

Trade name: Cyanex 272 Extractant

Molecular formula: $C_{16}H_{35}PO_2$



Structural formula:

Molecular weight: 290

Method of detection and determination: The chemical can be detected by infrared spectroscopy, titration and gas chromatography. Methodology was provided for the latter two.

Spectral data: An infrared spectrum was provided for the chemical with peaks at 1670, 2300 and 2650 cm^{-1} (characteristic for phosphinic acids).

3. PHYSICAL AND CHEMICAL PROPERTIES

Appearance at 20⁰C and 101.3 kPa:	Colourless to light amber liquid
Boiling Point:	>300 °C (at 760 mm Hg)
Specific Gravity:	0.92 at 24 °C
Vapour Pressure:	Not determined but expected to be very low due to the high boiling point
Water Solubility:	16 mg/L at pH 2.6; 38 mg/L at pH 3.7; with increasing pH, solubility is expected to increase
Partition Co-efficient (n-octanol/water) log P_{ow}:	K _{ow} >450; log P _{ow} >2.7 (determined by shake-flask method)
Hydrolysis as a function of pH:	See Comments Below
Adsorption/Desorption:	Not determined. The applicant states that due to extensive recycling, releases to the environment are likely to be insignificant
Dissociation Constant pKa:	4 x 10 ⁻⁶ (at 25 °C; solvent 75% isopropanol:water by volume)
Flash Point:	108 °C
Flammability Limits:	Non-flammable
Autoignition Temperature:	Non-flammable
Explosive Properties:	Stable
Reactivity/Stability:	Not reactive

Comments on Physico-Chemical Properties

The technical bulletin on Cyanex 272 Extractant presented by the notifier indicates that the notified chemical is stable at pH 5 and 50 °C for four weeks. Under environmental conditions hydrolysis of Cyanex 272 Extractant is not expected.

Adsorption/desorption was not determined but the notified substance may be expected to moderately attach to the organic fraction in soil due to the moderate octanol/water coefficient. Cyanex 272 Extractant is also likely to attach to soil cations, reducing its mobility in soil (based on technical bulletin provided by the notifier).

4. PURITY OF THE CHEMICAL

Degree of purity: 85-87%

Toxic or hazardous impurity/impurities: None known

Non-hazardous impurity/impurities (> 1% by weight):

Chemical name:	Tris (2,4,4-trimethylpentyl) phosphine oxide
Weight percentage:	10-12%

Additives/Adjuvants: None known

5. INDUSTRIAL USE

The notified chemical will be used in the mineral processing industry where it will be used as an extractant in mining operations. A 10% solution with an organic liquid detergent will be used to separate zinc and iron from cobalt solutions.

The chemical has been confirmed for use at one site Australia in the purification of cobalt from iron and zinc. Potentially it could be used at approximately 5 other sites for the separating/purification of a number of base metals.

The notified chemical will be imported in 200 L tight-head high density polyethylene drums at a rate of > 1 tonne per annum.

6. OCCUPATIONAL EXPOSURE

It will be imported to Australia in 200 L tight head density polyethylene drums in containers and transported to Cytec Australia's warehouse in Sydney. At the warehouse the containers will be unpacked and the drums either stored or transported

to the industrial customers. Ten to 20 workers (including waterside workers, drivers and warehouse workers) will be involved in transport and handling of the material from the wharf to the warehouse and another 10 to 15 (warehouse workers and drivers) from the warehouse to industry. As no repacking or reformulation will be carried out by these workers, exposure to the chemical will result only in the event of accidental spillages.

At the customer sites process operators (numbers not specified) will attach and disconnect automatic dosing systems into the imported drums (approximately 10 times per year). Exposure during these operations will be of very short duration and should not result in any significant exposure.

The automatic dosing systems will deliver the chemical directly into enclosed extraction systems. The extractant will then be recycled via an enclosed stripping system. As both these processes are completely enclosed and automated, no worker exposure is anticipated. Workers will however be required to sample the liquor in the extraction systems into bottles via sample valves (approximately 6 times a week; 1 minute per sampling). These workers will be required to wear eye protection, gloves, safety boots, overalls and a canister face mask (if necessary).

7. PUBLIC EXPOSURE

No public exposure to the notified chemical is expected during its distribution.

The solvent extraction process is stated to be highly automated and will be conducted in enclosed systems, and therefore no public exposure to the notified chemical is expected to occur. Minimal waste is anticipated during the extraction process as a 'solvent recycle system' will be employed which is known to reduce Cyanex 272 Extractant in waste streams to <1 mg/L. Any waste will be treated at the effluent treatment plant, and the resultant solid waste, containing the notified chemical, will be disposed in accordance with relevant local, state and federal government requirements. Industrial use and disposal of the notified chemical are not expected to result in any significant public exposure.

8. ENVIRONMENTAL EXPOSURE

The process at the customer site involves extraction of the iron and zinc impurities from the raw aqueous cobalt solution using the notified chemical and organic solvents. The organic solvent and Cyanex 272 Extractant from the extraction section are sent to the stripping section, where the iron, zinc and other impurities are removed from the solvent/Cyanex 272 Extractant, before the organic phase is returned for reuse. The aqueous streams from the extractor and the stripping section are passed through two further separators to recover the maximum amount of solvent and Cyanex 272 Extractant, which are reused. The other potential users are expected to use similar methodology and technology in their operations. (The other potential users are currently in either the design or construction phase of their processing facilities.)

Release

Release to the environment during the transport and storage of the product would be confined to breakages caused by transport accidents. Release from the imported containers is expected to be rare. Dispensing is to be done in closed systems which are largely automated, therefore minimising possible spills. Any spills that do occur during transport or formulation are to be treated according to instructions in the Material Safety Data Sheet (MSDS). Spills are to be adsorbed using sand or earth and transferred to drums. Disposal of spilt material is to be in accordance with federal, state and local regulations.

As a result of the high cost of the notified chemical, releases to the environment are expected to be kept to a minimal. Almost all of the Cyanex 272 Extractant used is recycled within the plant with the solvent. The notifier estimates that approximately 10% of the initial charge will be required as a top-up per annum.

Releases from the customer site are expected to be minimal. As a result of the low pH used in the extractor (approximately pH 3), the concentration of Cyanex 272 Extractant in the aqueous extract is expected to be <2 ppm (technical bulletin on Cyanex 272 Extractant presented by the notifier). The aqueous solution from the separator, containing the cobalt, is further treated to remove the cobalt. It is unclear what happens to the waste from the cobalt recovery plant but it is expected to eventually end up in the tailings dam, from which the effluent liquid is returned to the processing plant. The other aqueous stream from the stripping area (where the iron/zinc is stripped from the organic extract) is stated by the applicant to contain <1 ppm of Cyanex 272 Extractant and is returned to the main nickel processing plant.

The waste iron and zinc solids from the stripping plant are disposed of as solid waste in accordance with relevant local, state and federal government requirements. It is anticipated that most of this solid waste will be sent to the tailings dam or landfilled in a pit. The amounts of Cyanex 272 Extractant in this solid waste is unknown.

Fate

The fate of most of the notified chemical is disposed in the tailings dam, where it will be adsorbed to particles in the tailings. The applicant states that the effluent from the tailings dam is returned to the processing plant for reuse. Some of the notified chemical will be disposed of with the iron-zinc solid waste.

There is no information on the degradation of the notified chemical. However, the notifier has presented the results (no report) of a similar chemical, Cyanex 301, in the OECD Closed Bottle Test as 13% BOD in 28 days. (Cyanex 301 is the dithio analogue of Cyanex 272.) Phosphate esters are known to oxidise from the thio form to the oxo and a similar reaction could occur for dithiophosphinic acids, which could be attributed to the percentage degradation noted.

The moderate solubility and log P_{ow} together with the molecular weight indicate that bioaccumulation is possible. However, bioaccumulation is not expected due to the

limited environmental exposure anticipated.

9. EVALUATION OF TOXICOLOGICAL DATA

9.1 Acute Toxicity

Table 1 Summary of the acute toxicity of Cyanex 272 Extractant

Test	Species	Outcome	Reference
Acute oral toxicity	Rat	LD ₅₀ > 3500 mg/kg	(1)
Acute dermal toxicity	Rat	LD ₅₀ > 2000 mg/kg	(1)
Skin Irritation	Rabbit	severe irritant	(2)
Eye irritation	Rabbit	severe irritant	(1)
Skin sensitisation	Guinea-pig		(3)

9.1.1 Oral Toxicity (1)

LD₅₀: > 3500 mg/kg

Result. low oral toxicity

Species/strain. Rat, Sprague-Dawley

Number/sex of animals: SM, SF

Observation period: 14 days

Method of administration (vehicle): gavage

Mortality: 2F (day 1), 1M (day 2)

Test Method. based on OECD Guidelines for Testing Chemicals (4).

9.1.2 Dermal Toxicity (1)

LD₅₀: > 2000 mg/kg

Result: severe irritant

Species/strain: Albino rabbits

Number/sex of animals: 10 males

Observation period. 14 days

Method of administration (vehicle): By occluded patch to abraded skin; 24 hour exposure.

Modality: no deaths

Clinical signs: this was a combined dermal toxicity/irritation study see below for irritant effects.

Draize Scores' (5):

Time after treatment (days)	Animal #									
	1	2	3	4	5	6	7	8	9	10
ERYTHEMA										
1	2	2	4	4	4	3	4	4	3	3
2	2	4	4	4	4	2	4	4	2	3
3	2	4	4	4	4	2	4	4	2	3
OEDEMA										
1	4	3	4	4	4	4	4	4	4	4
2	3	3	3	3	3	4	4	3	3	3
3	3	3	3	3	2	4	4	3	3	3

¹ See Attachment 1 for Draize Scales.

Test Method: based on OECD Guidelines for Testing Chemicals

9.1.4 Skin Irritation (2)

Result: slight irritant

Species/strain. ' Albino rabbit

Number/sex of animals: 6 males

Method of administration: a neat sample of the notified chemical was applied under occluded dressing for 24 hours.

Draize Scoresⁱ (5):

Time after treatment (days)	Animal #					
	1	2	3	4	5	6
ERYTHEMA						
1	1	1	1	1	1	1
3	0	0	0	0	0	1
OEDEMA						
1	2	1	2	1	2	2
3	1	1	0	1	1	1

ⁱSee Attachment 1 for Draize Scales

Test Method. based on OECD Guidelines for Testing Chemicals (4).

9.1.5 Eye Irritation (1)

Result: Severe irritant

Species/strain. ' Albino rabbits

Number of animals: 9 males

Method of administration: 0.1 mL into conjunctival sac of one eye. For 6 animals the treated eyes were not irrigated; for 3 animals the treated eyes were irrigated for 1 minute, 20-30 seconds after instillation.

Test Method. ' based on OECD Guidelines for Testing Chemicals (4).

Draize Scores' (5):

Unirrigated Eyes

Animal	Time after instillation											
	1 day		2 days		3 days		4 days		7 days			
CORNEA	opacity		opacity		opacity		opacity		opacity			
	area		area		area		area		area			
1	0		1	4	1	4	0		0			
2	0		1	2	1	3	1	3	0			
3	0		1	4	1	4	2	4	3	4		
4	0		1	3	1	4	2	4	1	3		
5	1	4	2	4	2	2	1	2	0			
6	2	4	2	4	2	4	1	4	0			
IRIS												
1	0		0		0		0		0			
2	0		0		0		0		0			
3	0		0		0		0		0			
4	0		0		0		0		0			
5	0		0		0		0		0			
6	0		0		0		0		0			
CONJUNCTIVA	r ^a	c ^b	d ^c	r ^a	c ^b	d ^c	r ^a	c ^b	d ^c	r ^a	c ^b	d ^c
1	2	3		1	1	2	1	1	1	0	1	1
2	2	3	3	2	2	2	2	2	2	1	2	2
3	1	2	2	1	1	1	3	2	1	3	2	2
4	2	2	2	1	2	2	2	2	1	2	2	1
5	1	2	2	1	2	1	1	2	1	0	1	0
6	2	4	3	2	3	2	2	3	2	2	2	1

^aredness chemosis ^cdischarge

'See Attachment 1 for Draize Scales

Irrigated Eyes: No corneal or iridal effects; 2 animals exhibited no conjunctival redness, 1

animal slight redness on days 1 and 2; 2 animals exhibited slight chemosis on day 1, 1 animal moderate chemosis on day 1 and mild chemosis on days 2 and 3; 2 animals exhibited slight discharge on day 1, 1 animal mild discharge on day 1 and slight discharge on days 2 and 3.

9.1.6 Skin Sensitisation (3)

Result: non-sensitiser

Species/strain. Guinea pig/ Dunkin/Hartley *Number of animals:* 20 test, 10 control

Induction. Three pairs of injections of 0.1 mL: FCA in water (1:1); 0.25% notified chemical in Alembicol D with and without FCA (1:1). Topical induction: at day 6, 0.2 mL 10% sodium lauryl sulphate in petrolatum followed 1 day later by 0.4 mL neat notified chemical for 48 hours.

Results. use of 50% and 100% v/v notified chemical produced reactions in the controls which, while not suggestive of sensitisation, made scoring imprecise. Therefore a second challenge was conducted one week later as follows:

Challenge Concentration	24 hrs		48 hrs	
	test	control	test	control
25%	0/20	0/10	0/20	0/10
50%	0/20	0/10	0/20	0/10

Test Method. based on OECD Guidelines for Testing Chemicals (4).

9.2 Repeated Dose Toxicity

Not supplied. This was acceptable as there will be minimal potential for repeated occupation exposure under normal use situations.

9.3 Genotoxicity

9.3.1 Salmonella typhimurium Reverse Mutation Assay (6)

Result: non-mutagenic

Strains. *Salmonella typhimurium* TA 98, TA 100, TA 1S3S, TA 1S37, TA 1S38 and *Escherichia coli* WP2uvrA

Concentration range. 33 - 10000 ~ig/ plate with and without rat liver S9

Test Method. based on OECD Guidelines for Testing Chemicals (4).

9.3.2 Micronucleus Assay in the Bone Marrow Cells of the Mouse (7)

Result. ' negative (sampling times 24, 48 and 72 hours post-dosing). A borderline result at the 48 hour time point was confirmed as negative in a second study.

Species/strain. ' mouse/ Swiss SPF CD-i

Number and sex: SM, SF

Doses. ' 900 mg/kg

Method of administration (vehicle). ' gavage (1 % methylcellulose)

Test Method. ' based on OECD Guidelines for Testing Chemicals (4).

9.4

Overall Assessment of Toxicological Data

Cyanex 272 Extractant showed low oral toxicity ($LD_{50} > 3500$ mg/kg) and dermal toxicity ($LD_{50} > 2000$ mg/kg) in rats. When tested in rabbits it was a severe skin irritant, a severe eye irritant to non-irrigated eyes and a moderate eye irritant following irrigation. The chemical was not a skin sensitiser in guinea pigs. In the presence and absence of metabolic activation, the chemical was not mutagenic in bacteria and did not produce chromosome aberrations in a mouse micronucleus study. No repeat dose toxicity study was provided.

On the basis of submitted data, the notified chemical would not be classified as hazardous in accordance with Worksafe Australia's *Approved Criteria for Classifying Hazardous Substances* (8) in relation to Acute lethal effects (oral, dermal); Sensitising effects (skin) or Mutagenic effects. However based on the chemosis scores presented in the submitted eye irritancy test, as well as the skin irritancy reported in the submitted acute dermal toxicity study, the chemical would be classified as hazardous.

10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

The following ecotoxicity studies have been provided by the notifier. The fish studies are old studies (December 1981) and were conducted according to US EPA "Methods for acute toxicity test with fish, 197S". Small globules of the test material were noted on the surface in the fish studies. The results are also based on the nominal concentrations for these studies.

The *daphnia* studies were performed to modern standards (OECD and US EPA requirements). The *daphnia* results are actual concentrations in solution as measured.

Test	Species	Results
Acute toxicity	Rainbow trout	96h LC_{50} 22 mg.L ⁻¹ NOEC = 7.7 mg.L ⁻¹
Acute toxicity	Bluegill	96h LC_{50} 46 mg. L ⁻¹ NOEC = 22 mg. L ⁻¹
Acute toxicity	<i>Daphnia magna</i>	48h EC_{50} > 9.9 mg. L ⁻¹ NOEC = 2.9 mg. L ⁻¹

The ecotoxicity studies show that the notified chemical's toxicity to fish was higher than the solubility in the test media and the results could reflect the physical effect of the oily globules on the fish's gills. The results show that Cyanex 272 Extractant is slightly toxic to aquatic organisms. Effects on aquatic organisms are possible when the chemical is released to waterways.

There was no information on algae toxicity.

11. ASSESSMENT OF ENVIRONMENTAL HAZARD

With the continuous reuse of Cyanex 272 Extractant, releases of chemical from the plants where it is to be used is expected to be minimal. At the proposed customer, the two aqueous solutions (one from the extractor and the other from stripping the organic/Cyanex 272 Extractant phase) will be treated before being reused within the facility. The Cyanex 272 Extractant in these aqueous streams is expected to be diluted in the facility before being sent to the tailings area, where the water will be returned to the processing facility. Some of the chemical is expected to be adsorbed to the solids in the tailings dam. The solids waste from the stripping plant is also expected to contain some Cyanex 272 Extractant. These solids are expected to be sent to the tailings dam or buried in a pit. The concentration of Cyanex 272 Extractant in the tailings dam is unknown but there is expected to be between 200-500 kg per annum of chemical added each year as a top-up. This amount includes some losses due to degradation in use and that disposed of via the tailings dam.

In normal operations there should not be any releases from the tailing dam to the environment on an ongoing basis. Release could occur during heavy rain due to flooding of the tailings dam. In this case there would be large dilution of the overflow from the tailings dam in the flooded streams, which would reduce the hazard to low levels and reduce the risk to negligible.

At the end of the mine's life, the processing plant will be decommissioned. The solvent used containing the notified chemical is expected to be disposed of according to the relevant federal, state and local government regulations. Currently disposal would be by incineration or sent to a solvent recycler for reuse.

Similarly the tailings dam will be decommissioned according to relevant federal, state and local government requirements. It is expected this will involve stabilising the dam and site rehabilitation. Leaching of the notified chemical is possible; however as other phosphoric acid compounds, eg glyphosate (9) are known to bind strongly to soil cations to form adsorbent-cation-complex, a similar process is expected for the notified chemical due to the strong affinity to iron and aluminium, major soil cations (technical bulletin on Cyanex 272 Extractant presented by the notifier). Leaching of the notified chemical from the tailings dam is not expected.

Degradation of the notified chemical within the tailings dam is not known but it is unlikely due to the low biological activity within the tailings dam.

The environmental exposure is expected to be limited and therefore the hazard is negligible.

The only other sources of environmental contamination during normal usage is from accidental spills etc. The MSDS is adequate to limit the environmental exposure from spills etc and together with the expected strong binding to soil and moderate Kow the environmental effects from possible accidentals should be negligible.

The overall environmental hazard can be rated as negligible.

12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS

Cyanex 272 Extractant is stable, non-flammable and is expected to exhibit low volatility. Based on the submitted data, the major toxicological concerns associated with Cyanex 272 Extractant will be severe skin and eye irritation.

During the use of the chemical, occupational exposure will be limited to workers involved with the extraction process. This process will be conducted in an enclosed mineral extraction system in which the extractant is recycled. Workers may be potentially exposed via dermal or eye exposure while fitting dosing system connections to the imported drums. They may also be exposed via these routes during liquor sampling. Inhalational exposure is unlikely as the chemical is a nonvolatile liquid and is unlikely to form aerosols or mists during normal use.

The personal protective equipment stipulated in the MSDS (impervious gloves and chemical splash goggles or full face shield) should be adequate to minimise exposure during the extraction process. Therefore, under normal use conditions, the notified chemical is not expected to present any significant health or safety risk to workers.

Given the industrial use pattern of Cyanex 272 Extractant, no significant public exposure is expected to occur.

13. RECOMMENDATIONS

To minimise occupational exposure to Cyanex 272 Extractant the following guidelines and precautions should be observed:

if engineering controls and work practices are insufficient to reduce exposure to Cyanex 272 Extractant to a safe level, then the following personal protective equipment which conforms to Australian Standard (AS) or Australian/New Zealand Standard (AS/NZS) should be worn:

safety goggles should be selected and fitted in accordance to AS 1336 (10) to comply with AS/NZS 1337 (11).

industrial clothing must conform to the specifications detailed in AS 2919 (12) and AS 376S.1 (13).

impermeable gloves or mittens conforming to AS 2161 (14) and AS 376S.1 (13).

all occupational footwear should conform to AS/NZS 2210 (15).

spillage of the notified chemical should be avoided.

good personal hygiene should be practised to minimise the potential for ingestion.

a copy of the Material Safety Data Sheet should be easily accessible to employees.

14. MATERIAL SAFETY DATA SHEET

The MSDS for Cyanex 272 Extractant was provided in Worksafe Australia format (16).

This MSDS was provided by Cytec Australia Limited as part of their notification statement. The accuracy of this information remains the responsibility of Cytec Australia Limited.

15. REQUIREMENTS FOR SECONDARY NOTIFICATION

Under the *Industrial Chemicals (Notification and Assessment) Act 1989*, secondary notification of Cyanex 272 Extractant shall be required if any of the circumstances stipulated under subsection 64(2) of the Act arise. No other specific conditions are prescribed.

16. REFERENCES

1. Bioassay Systems Corp. Project Number 11273, August 1982, *Single dose oral toxicity, primary eye irritation and combined dermal toxicity and irritation tests performed on [Cyanex 272 Extractant]*..
2. Bioassay Systems Corp. Project Number 11452, December 1982, *Primary dermal irritation test performed on Cyanex 272, Sample No. N-805-1-P*.
3. Huntington Research Centre, CTI 4/950098/SS,1995, *Cyanex 272 Extractant Skin sensitisation in the guinea pig*.
4. Organisation for Economic Co-operation and Development, *OECD Guidelines for Testing of Chemicals*, OECD, Paris, France.
5. Draize JH, 1959, 'Appraisal of the Safety of Chemicals in Foods, Drugs and Cosmetics', *Association of Food and Drug Officials of the US*, 49.
6. Huntington Research Centre, CTI-567-94, 1995, *Salmonella/Escherichia coli plate incorporation mutagenicity assay*.

7. Huntington Research Centre, CTI 3/9S0462, 1995, *Cyanex 272 Extractant Mouse micronucleus test*.
8. National Occupational Health and Safety Commission, 1994, *Approved Criteria for Classifying Hazardous Substances*. Australian Government Publishing Service, Canberra.
9. 5. M. Carlisle and J. T. Trevors, 1988, *Water, Air and Soil Pollution*, **39** 409-420.
10. Standards Australia, 1994, *Australian Standard 1336-1994, Recommended Practices for Eye Protection in the Industrial Environment*, Standards Association of Australia Publ., Sydney, Australia.
11. Standards Australia, Standards New Zealand, 1992, *Australian/New Zealand Standard 1337-1992, Eye Protectors for Industrial Applications*, Standards Association of Australia Publ., Sydney, Australia, Standards Association of New Zealand Publ. Wellington, New Zealand.
12. Standards Australia, 1987, *Australian Standard 2919 - 1987 Industrial Clothing*, Standards Association of Australia Publ., Sydney, Australia.
13. Standards Australia, 1990, *Australian Standard 3 765-1990 Clothing for Protection Against Chemical Hazards, Part I Protection Against General or Specific Chemicals, Part 2 Limited Protection Against Specific Chemicals*, Standards Association of Australia Publ., Sydney, Australia.
14. Standards Australia, 1978, *Australian Standard 2161-1978, Industrial Safety Gloves and Mittens (excluding Electrical and Medical Gloves)*, Standards Association of Australia Publ., Sydney, Australia.
15. Standards Australia, Standards New Zealand, 1994, *Australian/ New Zealand Standard 2210 - 1994 Occupational Protective Footwear, Part 1. ' Guide to Selection, Care and Use. Part 2: Specifications*, Standards Association of Australia Publ., Sydney, Australia, Standards Association of New Zealand Publ. Wellington, New Zealand.
16. National Occupational Health and Safety Commission, 1994, *Code of Practice for the Preparation of a Material Safety Data Sheets*, Australian Government Publishing Service, Canberra.



Shell

Cargo Handling Sheet

ShellSol 2325

Document Date: 31 May 2023
Revision 4

*Cargo Handling Sheets are for the use of vessels
chartered on behalf of Shell*

Product Details

Trade Name: ShellSol 2325
IMO Product Name: Kerosene
Chemical Family: Naphtha
Product Code: Q3351

SDS: <http://www.shell.com/business-customers/chemicals/safe-product-handling-and-transportation/safety-data-sheets.html>

Physical Properties

Density: 814 g/cm³ (20 °C / 68 °F)
Dynamic Viscosity: Data not available
Vapor Pressure: 0.01 Pa (20 °C / 68 °F)
Boiling Point: 215 - 250 °C / 419 - 482 °F
Pour Point: -30 °C / -22 °F
Flash Point: 89 °C / 192 °F
Appearance: Colourless

Note 1: Physical Properties are for reference only and valid as of date of this revision; see loading terminal for specific properties.

Note 2: Hazard Identification: Static accumulator; See SDS for full list of hazards and precautions.

Transhipments

Prior to arranging transhipment Charterer must agree to Owner's proposed plan. When arranged by the Owner, Owner must ensure that all transhipment vessels comply with the requirements of this cargo handling sheet.

Marpol Details

Marpol Annex: I
IMO Ship Type: Double hull vessel with carriage of oil certification
Inland Barge: Double Hull
IMO Pollution Category: Annex I
IBC 16.2.6: Not Applicable

IBC 16.2.9: Not Applicable
Pre-Wash Required: Not Applicable; wash/disposal as per Annex I
Compatibility Group: USCG Compatibility group 33

Cargo Handling Requirements

N2 Purge Cargo Tanks Prior Loading: No
N2 Blanket Required: No
Adjacent Space Purge: No
Loading Temperature Range: Ambient
Transit Temperature Range: Ambient - 40 °C / 104 °F
Unloading Temperature Range: Ambient - 40 °C / 104 °F
Maximum Heating Coil Temperature: Blanked off
Maximum Adjacent Temperature: 55 °C / 131 °F

Regional Requirements

None

Tank Acceptance Requirements

All nominated shipboard cargo handling systems are to be presented clean (residual free), dry, odour free, rust free, with good gaskets, fit to load this cargo.

Maintenance of heating coils is to be verified in the ship's log. If product is to be heated, heating coils are to be confirmed leak free. If product is not heated, heating coils are to be blown clear and dried with N2, and blanked off.

Stainless Steel or Coated Tank: Either, carrier to verify suitability of coating for product
Banned Prior Cargo: No
Wall Wash Required: No

Safety Information and Incident Reporting.

Safety Information: Refer the SDS (Safety Data Sheet) or e-SDS.

Incident Reporting: All incidents should be reported in accordance with regulations and charter party requirements.

For additional marine cargo handling advice or information, contact the regional Chemical Marine Technical Advisor.



Shell Chemical LP

PO Box 4407

Houston

Texas 77210 USA

Disclaimer

The information contained in this publication is, to the best of our knowledge, true and accurate, but any recommendations or suggestions that may be made are without guarantee, since the conditions of use are beyond our control. Furthermore, nothing contained herein shall be construed as a recommendation to use any product in conflict with existing patents covering any material or its use.

Shell

The expression "Shell" refers to the companies of the Shell Group of companies that are engaged in the chemical businesses. Each of the companies that make up the Shell Group of companies is an independent entity and has its own separate identity.

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

Version 7.1

Revision Date 11.02.2025

Print Date 21.03.2025

GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SECTION 1: Identification of the substance/mixture and of the company/undertaking**1.1 Product identifiers**

Product name : Sodium hydroxide

Product Number : S8045

Brand : SIGALD

Index-No. : 011-002-00-6

REACH No. : 01-2119457892-27-XXXX

CAS-No. : 1310-73-2

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Merck Life Science (Pty) Ltd.
1 Friesland Drive
Longmeadow Business Estate
MODDERFONTEIN
1609
SOUTH AFRICA

Telephone : +27 +27 (0) 8600 63725

Fax : +27 +27 (0) 860 522 329

E-mail address : Melissa.byrne@merckgroup.com

1.4 Emergency telephone

Emergency Phone # : 0-800-983-611

SECTION 2: Hazards identification**2.1 Classification of the substance or mixture**

Corrosive to Metals, (Category 1) H290: May be corrosive to metals.

Skin corrosion, (Sub-category 1A) H314: Causes severe skin burns and eye damage.

Serious eye damage, (Category 1) H318: Causes serious eye damage.



2.2 Label elements

Labelling according Regulation (EC) No 1272/2008

Pictogram



Signal Word

Danger

Hazard Statements

H290

May be corrosive to metals.

H314

Causes severe skin burns and eye damage.

Precautionary Statements

P234

Keep only in original packaging.

P260

Do not breathe dust.

P280

Wear protective gloves/ protective clothing/ eye protection/ face protection.

P303 + P361 + P353

IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.

P304 + P340 + P310

IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/ doctor.

P305 + P351 + P338

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard Statements

none

Reduced Labeling (<= 125 ml)

Pictogram



Signal Word

Danger

Hazard Statements

H314

Causes severe skin burns and eye damage.

Precautionary Statements

P260

Do not breathe dust.

P280

Wear protective gloves/ protective clothing/ eye protection/ face protection.

P303 + P361 + P353

IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.

P304 + P340 + P310

IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/ doctor.

P305 + P351 + P338

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard Statements

none

2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

Ecological information:



The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

Toxicological information:

The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

SECTION 3: Composition/information on ingredients

3.1 Substances

Synonyms : Caustic soda

Formula : NaOH

Molecular weight : 40,00 g/mol

CAS-No. : 1310-73-2

EC-No. : 215-185-5

Index-No. : 011-002-00-6

Component		Classification	Concentration
sodium hydroxide			
CAS-No.	1310-73-2	Met. Corr. 1; Skin Corr. 1A; Eye Dam. 1; H290, H314, H318 Concentration limits: >= 5 %: Skin Corr. 1A, H314; 2 - < 5 %: Skin Corr. 1B, H314; 0,5 - < 2 %: Skin Irrit. 2, H315; 0,5 - < 2 %: Eye Irrit. 2, H319; >= 0,4 %: Met. Corr. 1, H290;	<= 100 %
EC-No.	215-185-5		
Index-No.	011-002-00-6		

For the full text of the H-Statements mentioned in this Section, see Section 16.

SECTION 4: First aid measures

4.1 Description of first-aid measures

General advice

First aiders need to protect themselves. Show this material safety data sheet to the doctor in attendance.

If inhaled

After inhalation: fresh air. Call in physician.

In case of skin contact

In case of skin contact: Take off immediately all contaminated clothing. Rinse skin with water/ shower. Call a physician immediately.

In case of eye contact

After eye contact: rinse out with plenty of water. Immediately call in ophthalmologist. Remove contact lenses.



If swallowed

After swallowing: make victim drink water (two glasses at most), avoid vomiting (risk of perforation). Call a physician immediately. Do not attempt to neutralise.

4.2 Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed

No data available

SECTION 5: Firefighting measures**5.1 Extinguishing media****Suitable extinguishing media**

Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.

Unsuitable extinguishing media

For this substance/mixture no limitations of extinguishing agents are given.

5.2 Special hazards arising from the substance or mixture

Sodium oxides

Not combustible.

Ambient fire may liberate hazardous vapours.

5.3 Advice for firefighters

Stay in danger area only with self-contained breathing apparatus. Prevent skin contact by keeping a safe distance or by wearing suitable protective clothing.

5.4 Further information

Suppress (knock down) gases/vapors/mists with a water spray jet. Prevent fire extinguishing water from contaminating surface water or the ground water system.

SECTION 6: Accidental release measures**6.1 Personal precautions, protective equipment and emergency procedures**

Advice for non-emergency personnel: Avoid inhalation of dusts. Avoid substance contact. Ensure adequate ventilation. Evacuate the danger area, observe emergency procedures, consult an expert.

For personal protection see section 8.

6.2 Environmental precautions

Do not let product enter drains.

6.3 Methods and materials for containment and cleaning up

Cover drains. Collect, bind, and pump off spills. Observe possible material restrictions (see sections 7 and 10). Take up dry. Dispose of properly. Clean up affected area. Avoid generation of dusts.

6.4 Reference to other sections

For disposal see section 13.

SECTION 7: Handling and storage**7.1 Precautions for safe handling**

For precautions see section 2.2.



7.2 Conditions for safe storage, including any incompatibilities

Storage conditions

No metal containers.
Tightly closed. Dry.

Storage class

Storage class (TRGS 510): 8B: Non-combustible, corrosive hazardous materials

7.3 Specific end use(s)

Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

SECTION 8: Exposure controls/personal protection

8.1 Control parameters

Ingredients with workplace control parameters

8.2 Exposure controls

Personal protective equipment

Eye/face protection

Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU). Tightly fitting safety goggles

Skin protection

This recommendation applies only to the product stated in the safety data sheet, supplied by us and for the designated use. When dissolving in or mixing with other substances and under conditions deviating from those stated in EN 16523-1 please contact the supplier of CE-approved gloves (e.g. KCL GmbH, D-36124 Eichenzell, Internet: www.kcl.de).

Full contact

Material: Nitrile rubber

Minimum layer thickness: 0,11 mm

Break through time: 480 min

Material tested: KCL 741 Dermatrill® L

This recommendation applies only to the product stated in the safety data sheet, supplied by us and for the designated use. When dissolving in or mixing with other substances and under conditions deviating from those stated in EN 16523-1 please contact the supplier of CE-approved gloves (e.g. KCL GmbH, D-36124 Eichenzell, Internet: www.kcl.de).

Splash contact

Material: Nitrile rubber

Minimum layer thickness: 0,11 mm

Break through time: 480 min

Material tested: KCL 741 Dermatrill® L

Body Protection

protective clothing

Respiratory protection

required when dusts are generated.



Our recommendations on filtering respiratory protection are based on the following standards: DIN EN 143, DIN 14387 and other accompanying standards relating to the used respiratory protection system.

Recommended Filter type: Filter type P2

The entrepreneur has to ensure that maintenance, cleaning and testing of respiratory protective devices are carried out according to the instructions of the producer. These measures have to be properly documented.

Control of environmental exposure

Do not let product enter drains.

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

a) Physical state	pellets
b) Color	white
c) Odor	odorless
d) Melting point/freezing point	Melting point/ range: 318 °C
e) Initial boiling point and boiling range	1.390 °C at 1.013 hPa
f) Flammability (solid, gas)	The product is not flammable.
g) Upper/lower flammability or explosive limits	No data available
h) Flash point	Not applicable
i) Autoignition temperature	No data available
j) Decomposition temperature	No data available
k) pH	ca.> 14 at 100 g/l at 20 °C
l) Viscosity	Viscosity, kinematic: No data available Viscosity, dynamic: No data available
m) Water solubility	1.090 g/l at 20 °C
n) Partition coefficient: n-octanol/water	Not applicable for inorganic substances
o) Vapor pressure	No data available
p) Density	2,13 g/cm ³ at 20 °C
Relative density	No data available
q) Relative vapor density	No data available
r) Particle characteristics	No data available



- s) Explosive properties Not classified as explosive.
t) Oxidizing properties none

9.2 Other safety information

Dissociation constant 14,8 at 25 °C

Relative vapor density 1,38 - (Air = 1.0)

SECTION 10: Stability and reactivity

10.1 Reactivity

No data available

10.2 Chemical stability

The product is chemically stable under standard ambient conditions (room temperature) .

10.3 Possibility of hazardous reactions

Violent reactions possible with:

Acetone

Chlorine

Ethylene oxide

Fluorine

Hydrogen halides

Hydrazine hydrate

hydroxylamine

Acid anhydrides

Acrolein

Acid chlorides

Acids

sulfuric acid

Chloroform

Water

hydrogen peroxide

anhydrides

phosphides

halogen-halogen compounds

trichloroethene

can decompose violently in contact with:

Organic Substances

hydrogen sulphide

Risk of ignition or formation of inflammable gases or vapours with:

powdered aluminium

Ammonium salts

persulfates

Sodium borohydride

phosphorus

Oxides of phosphorus

Halogenated hydrocarbon

Light metals

Metals

Risk of explosion/exothermic reaction with:

Bromine



Calcium
in powder form
furfuryl alcohol
Nitromethane
Peroxides
organic nitro compounds
Nitriles
Acrylic monomers
Chloroform
with
Acetone
Nitrobenzene
with
Methanol
Nitrobenzene
with
salts
magnesium
Zinc
and
Tin
(in the presence of atmospheric oxygen and/or moisture)

10.4 Conditions to avoid

no information available

10.5 Incompatible materials

No data available

10.6 Hazardous decomposition products

In the event of fire: see section 5

SECTION 11: Toxicological information

11.1 Information on toxicological effects

Acute toxicity

Symptoms: If ingested, severe burns of the mouth and throat, as well as a danger of perforation of the esophagus and the stomach.

Symptoms: burns of mucous membranes, Cough, Shortness of breath, Possible damages:, damage of respiratory tract

Dermal: No data available

Skin corrosion/irritation

Skin - Rabbit

Result: Causes burns.

Remarks: (Regulation (EC) No 1272/2008, Annex VI)

Serious eye damage/eye irritation

Eyes - Rabbit

Result: Causes serious eye damage.

(OECD Test Guideline 405)

Remarks: (Regulation (EC) No 1272/2008, Annex VI)

Remarks: Causes serious eye damage.

Respiratory or skin sensitization

Patch test: - In vitro study



Result: negative
Remarks: (ECHA)

Germ cell mutagenicity

No data available

Carcinogenicity

No data available

Reproductive toxicity

No data available

Specific target organ toxicity - single exposure

No data available

Specific target organ toxicity - repeated exposure

No data available

Aspiration hazard

No data available

11.2 Additional Information

Endocrine disrupting properties

Product:

Assessment

The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

RTECS: WB4900000

burning sensation, Cough, wheezing, laryngitis, Shortness of breath, spasm, inflammation and edema of the larynx, spasm, inflammation and edema of the bronchi, pneumonitis, pulmonary edema, Material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes, and skin., To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Other dangerous properties can not be excluded.

Handle in accordance with good industrial hygiene and safety practice.

SECTION 12: Ecological information

12.1 Toxicity

Toxicity to fish	LC50 - Gambusia affinis (Mosquito fish) - 125 mg/l - 96 h Remarks: (ECOTOX Database)
Toxicity to daphnia and other aquatic invertebrates	EC50 - Ceriodaphnia (water flea) - 40,4 mg/l - 48 h Remarks: (ECHA)
Toxicity to bacteria	EC50 - Photobacterium phosphoreum - 22 mg/l - 15 min Remarks: (External MSDS)



12.2 Persistence and degradability

The methods for determining the biological degradability are not applicable to inorganic substances.

12.3 Bioaccumulative potential

No data available

12.4 Mobility in soil

No data available

12.5 Results of PBT and vPvB assessment

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

12.6 Endocrine disrupting properties

Product:

Assessment : The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

12.7 Other adverse effects

Harmful effect due to pH shift.
Forms corrosive mixtures with water even if diluted.
Neutralisation possible in waste water treatment plants.
Discharge into the environment must be avoided.

SECTION 13: Disposal considerations

13.1 Waste treatment methods

No data available

SECTION 14: Transport information

14.1 UN number

ADR/RID: 1823 IMDG: 1823 IATA: 1823

14.2 UN proper shipping name

ADR/RID: SODIUM HYDROXIDE, SOLID
IMDG: SODIUM HYDROXIDE, SOLID
IATA: Sodium hydroxide, solid

14.3 Transport hazard class(es)

ADR/RID: 8 IMDG: 8 IATA: 8

14.4 Packaging group

ADR/RID: II IMDG: II IATA: II

14.5 Environmental hazards

ADR/RID: no IMDG Marine pollutant: no IATA: no



14.6 Special precautions for user

Tunnel restriction code : (E)

Further information : No data available

14.7 Maritime transport in bulk according to IMO instruments

Not applicable for product as supplied.

SECTION 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

This material safety data sheet complies with the requirements of Regulation (EC) No. 1907/2006.

Other regulations

Take note of Dir 94/33/EC on the protection of young people at work.

15.2 Chemical Safety Assessment

A Chemical Safety Assessment has been carried out for this substance.

SECTION 16: Other information

Full text of H-Statements

H290	May be corrosive to metals.
H314	Causes severe skin burns and eye damage.
H315	Causes skin irritation.



Full text of other abbreviations

ADN - European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways; ADR - Agreement concerning the International Carriage of Dangerous Goods by Road; AIIC - Australian Inventory of Industrial Chemicals; ASTM - American Society for the Testing of Materials; bw - Body weight; CMR - Carcinogen, Mutagen or Reproductive Toxicant; DIN - Standard of the German Institute for Standardisation; DSL - Domestic Substances List (Canada); ECx - Concentration associated with x% response; ELx - Loading rate associated with x% response; EmS - Emergency Schedule; ENCS - Existing and New Chemical Substances (Japan); ErCx - Concentration associated with x% growth rate response; GHS - Globally Harmonized System; GLP - Good Laboratory Practice; IARC - International Agency for Research on Cancer; IATA - International Air Transport Association; IBC - International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk; IC50 - Half maximal inhibitory concentration; ICAO - International Civil Aviation Organization; IECSC - Inventory of Existing Chemical Substances in China; IMDG - International Maritime Dangerous Goods; IMO - International Maritime Organization; ISHL - Industrial Safety and Health Law (Japan); ISO - International Organisation for Standardization; KECI - Korea Existing Chemicals Inventory; LC50 - Lethal Concentration to 50 % of a test population; LD50 - Lethal Dose to 50% of a test population (Median Lethal Dose); MARPOL - International Convention for the Prevention of Pollution from Ships; n.o.s. - Not Otherwise Specified; NO(A)EC - No Observed (Adverse) Effect Concentration; NO(A)EL - No Observed (Adverse) Effect Level; NOELR - No Observable Effect Loading Rate; NZIoC - New Zealand Inventory of Chemicals; OECD - Organization for Economic Co-operation and Development; OPPTS - Office of Chemical Safety and Pollution Prevention; PBT - Persistent, Bioaccumulative and Toxic substance; PICCS - Philippines Inventory of Chemicals and Chemical Substances; (Q)SAR - (Quantitative) Structure Activity Relationship; REACH - Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals; RID - Regulations concerning the International Carriage of Dangerous Goods by Rail; SADT - Self-Accelerating Decomposition Temperature; SDS - Safety Data Sheet; TCSI - Taiwan Chemical Substance Inventory; TECI - Thailand Existing Chemicals Inventory; TSCA - Toxic Substances Control Act (United States); UN - United Nations; UNRTDG - United Nations Recommendations on the Transport of Dangerous Goods; vPvB - Very Persistent and Very Bioaccumulative

Further information

The information is believed to be correct but is not exhaustive and will be used solely as a guideline, which is based on current knowledge of the chemical substance or mixture and is applicable to appropriate safety precautions for the product. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.

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SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

Version 6.16

Revision Date 06.03.2024

Print Date 21.03.2025

GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SECTION 1: Identification of the substance/mixture and of the company/undertaking**1.1 Product identifiers**

Product name : Sulfuric acid

Product Number : 339741

Brand : Aldrich

Index-No. : 016-020-00-8

REACH No. : 01-2119458838-20-XXXX

CAS-No. : 7664-93-9

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Merck Life Science (Pty) Ltd.
1 Friesland Drive
Longmeadow Business Estate
MODDERFONTEIN
1609
SOUTH AFRICA

Telephone : +27 +27 (0) 8600 63725

Fax : +27 +27 (0) 860 522 329

E-mail address : Melissa.byrne@merckgroup.com

1.4 Emergency telephone

Emergency Phone # : 0-800-983-611

SECTION 2: Hazards identification**2.1 Classification of the substance or mixture**

Corrosive to Metals, (Category 1) H290: May be corrosive to metals.

Skin corrosion, (Sub-category 1A) H314: Causes severe skin burns and eye damage.

Serious eye damage, (Category) H318: Causes serious eye damage.



1)

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008

Pictogram



Signal Word

Danger

Hazard Statements

H290

May be corrosive to metals.

H314

Causes severe skin burns and eye damage.

Precautionary Statements

P234

Keep only in original packaging.

P280

Wear protective gloves/ protective clothing/ eye protection/ face protection.

P303 + P361 + P353

IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.

P304 + P340 + P310

IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/ doctor.

P305 + P351 + P338

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

P363

Wash contaminated clothing before reuse.

Supplemental Hazard Statements

none

Reduced Labeling (<= 125 ml)

Pictogram



Signal Word

Danger

Hazard Statements

H314

Causes severe skin burns and eye damage.

Precautionary Statements

P280

Wear protective gloves/ protective clothing/ eye protection/ face protection.

P303 + P361 + P353

IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.

P304 + P340 + P310

IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/ doctor.

P305 + P351 + P338

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

P363

Wash contaminated clothing before reuse.

Supplemental Hazard Statements

none



2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

Ecological information:

The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

Toxicological information:

The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

SECTION 3: Composition/information on ingredients

3.1 Substances

Formula : $\text{H}_2\text{O}_4\text{S}$
Molecular weight : 98,08 g/mol
CAS-No. : 7664-93-9
EC-No. : 231-639-5
Index-No. : 016-020-00-8

Component		Classification	Concentration
sulphuric acid			
CAS-No.	7664-93-9	Met. Corr. 1; Skin Corr. 1A; Eye Dam. 1; H290, H314, H318 Concentration limits: >= 15 %: Skin Corr. 1A, H314; 5 - < 15 %: Skin Irrit. 2, H315; 5 - < 15 %: Eye Irrit. 2, H319; >= 0,3 %: Met. Corr. 1, H290;	<= 100 %
EC-No.	231-639-5		
Index-No.	016-020-00-8		

For the full text of the H-Statements mentioned in this Section, see Section 16.

SECTION 4: First aid measures

4.1 Description of first-aid measures

General advice

First aiders need to protect themselves. Show this material safety data sheet to the doctor in attendance.

If inhaled

After inhalation: fresh air. Call in physician.

In case of skin contact

In case of skin contact: Take off immediately all contaminated clothing. Rinse skin with water/ shower. Call a physician immediately.



In case of eye contact

After eye contact: rinse out with plenty of water. Immediately call in ophthalmologist.
Remove contact lenses.

If swallowed

After swallowing: make victim drink water (two glasses at most), avoid vomiting (risk of perforation). Call a physician immediately. Do not attempt to neutralise.

4.2 Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed

No data available

SECTION 5: Firefighting measures**5.1 Extinguishing media****Suitable extinguishing media**

Use extinguishing measures that are appropriate to local circumstances and the surrounding environment.

Unsuitable extinguishing media

For this substance/mixture no limitations of extinguishing agents are given.

5.2 Special hazards arising from the substance or mixture

Sulfur oxides

Not combustible.

Ambient fire may liberate hazardous vapours.

5.3 Advice for firefighters

Stay in danger area only with self-contained breathing apparatus. Prevent skin contact by keeping a safe distance or by wearing suitable protective clothing.

5.4 Further information

Suppress (knock down) gases/vapors/mists with a water spray jet. Prevent fire extinguishing water from contaminating surface water or the ground water system.

SECTION 6: Accidental release measures**6.1 Personal precautions, protective equipment and emergency procedures**

Advice for non-emergency personnel: Do not breathe vapors, aerosols. Avoid substance contact. Ensure adequate ventilation. Evacuate the danger area, observe emergency procedures, consult an expert.

For personal protection see section 8.

6.2 Environmental precautions

Do not let product enter drains.

6.3 Methods and materials for containment and cleaning up

Cover drains. Collect, bind, and pump off spills. Observe possible material restrictions (see sections 7 and 10). Take up with liquid-absorbent and neutralising material (e.g. Chemizorb® H⁺, Merck Art. No. 101595). Dispose of properly. Clean up affected area.



6.4 Reference to other sections

For disposal see section 13.

SECTION 7: Handling and storage

7.1 Precautions for safe handling

For precautions see section 2.2.

7.2 Conditions for safe storage, including any incompatibilities

Storage conditions

No metal containers.

Tightly closed.

Storage class

Storage class (TRGS 510): 8B: Non-combustible, corrosive hazardous materials

7.3 Specific end use(s)

Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

SECTION 8: Exposure controls/personal protection

8.1 Control parameters

Ingredients with workplace control parameters

8.2 Exposure controls

Personal protective equipment

Eye/face protection

Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU). Tightly fitting safety goggles

Skin protection

This recommendation applies only to the product stated in the safety data sheet, supplied by us and for the designated use. When dissolving in or mixing with other substances and under conditions deviating from those stated in EN 16523-1 please contact the supplier of CE-approved gloves (e.g. KCL GmbH, D-36124 Eichenzell, Internet: www.kcl.de).

Full contact

Material: Viton®

Minimum layer thickness: 0,7 mm

Break through time: 480 min

Material tested: Vitoject® (KCL 890 / Aldrich Z677698, Size M)

This recommendation applies only to the product stated in the safety data sheet, supplied by us and for the designated use. When dissolving in or mixing with other substances and under conditions deviating from those stated in EN 16523-1 please contact the supplier of CE-approved gloves (e.g. KCL GmbH, D-36124 Eichenzell, Internet: www.kcl.de).



Splash contact
Material: butyl-rubber
Minimum layer thickness: 0,7 mm
Break through time: 120 min
Material tested: Butoject® (KCL 898)

Body Protection

Acid-resistant protective clothing

Respiratory protection

Recommended Filter type: Filter type P2

The entrepreneur has to ensure that maintenance, cleaning and testing of respiratory protective devices are carried out according to the instructions of the producer. These measures have to be properly documented.

Control of environmental exposure

Do not let product enter drains.

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

- | | |
|---|--|
| a) Physical state | clear, liquid |
| b) Color | colorless |
| c) Odor | odorless |
| d) Melting point/freezing point | Melting point: 10,31 °C |
| e) Initial boiling point and boiling range | 290 °C - lit. |
| f) Flammability (solid, gas) | No data available |
| g) Upper/lower flammability or explosive limits | No data available |
| h) Flash point | No data available |
| i) Autoignition temperature | No data available |
| j) Decomposition temperature | No data available |
| k) pH | 1,2 at 5 g/l |
| l) Viscosity | Viscosity, kinematic: No data available
Viscosity, dynamic: 23 mPa.s at 20 °C |
| m) Water solubility | soluble |
| n) Partition coefficient: n-octanol/water | Not applicable for inorganic substances |



- | | |
|-----------------------------|--|
| o) Vapor pressure | 1,33 hPa at 145,8 °C |
| p) Density | 1,84 g/cm ³ at 25 °C - lit. |
| Relative density | No data available |
| q) Relative vapor density | No data available |
| r) Particle characteristics | No data available |
| | |
| s) Explosive properties | No data available |
| t) Oxidizing properties | none |

9.2 Other safety information

- | | |
|------------------------|--------------------|
| Surface tension | 55,1 mN/m at 20 °C |
| Relative vapor density | 3,39 - (Air = 1.0) |

SECTION 10: Stability and reactivity

10.1 Reactivity

No data available

10.2 Chemical stability

The product is chemically stable under standard ambient conditions (room temperature) .

10.3 Possibility of hazardous reactions

A risk of explosion and/or of toxic gas formation exists with the following substances:

Water
 Alkali metals
 alkali compounds
 Ammonia
 Aldehydes
 acetonitrile
 Alkaline earth metals
 alkalines
 Acids
 alkaline earth compounds
 Metals
 metal alloys
 Oxides of phosphorus
 phosphorus
 hydrides
 halogen-halogen compounds
 oxyhalogenic compounds
 permanganates
 nitrates
 carbides
 combustible substances



organic solvent
acetylidene
Nitriles
organic nitro compounds
anilines
Peroxides
picrates
nitrides
lithium silicide
iron(III) compounds
bromates
chlorates
Amines
perchlorates
hydrogen peroxide

10.4 Conditions to avoid

no information available

10.5 Incompatible materials

animal/vegetable tissues Contact with metals liberates hydrogen gas.

10.6 Hazardous decomposition products

In the event of fire: see section 5

SECTION 11: Toxicological information

11.1 Information on toxicological effects

Acute toxicity

LD50 Oral - Rat - male and female - 2.140 mg/kg

Remarks: (ECHA)

Inhalation: No data available

Dermal: No data available

Skin corrosion/irritation

Skin - Rabbit

Result: Extremely corrosive and destructive to tissue.

Remarks: (IUCLID)

Serious eye damage/eye irritation

Remarks: Causes serious eye damage.

Respiratory or skin sensitization

No data available

Germ cell mutagenicity

Test Type: Ames test

Test system: Salmonella typhimurium

Result: negative

Remarks: (HSDB)

Carcinogenicity

No data available



Reproductive toxicity

No data available

Specific target organ toxicity - single exposure

No data available

Specific target organ toxicity - repeated exposure

No data available

Aspiration hazard

No data available

11.2 Additional Information**Endocrine disrupting properties****Product:**

Assessment

The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

RTECS: WS5600000

Material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes, and skin., spasm, inflammation and edema of the larynx, spasm, inflammation and edema of the bronchi, pneumonitis, pulmonary edema, burning sensation, Cough, wheezing, laryngitis, Shortness of breath, Headache, Nausea, Vomiting, Pulmonary edema. Effects may be delayed.

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

After inhalation of aerosols: damage to the affected mucous membranes. After skin contact: severe burns with formation of scabs. After eye contact: burns, corneal lesions. After swallowing: severe pain (risk of perforation!), nausea, vomiting and diarrhoea. After a latency period of several weeks possibly pyloric stenosis.

Other dangerous properties can not be excluded.

Handle in accordance with good industrial hygiene and safety practice.

SECTION 12: Ecological information**12.1 Toxicity**

Toxicity to daphnia and other aquatic invertebrates	static test EC50 - Daphnia magna (Water flea) - > 100 mg/l - 48 h (OECD Test Guideline 202)
Toxicity to algae	static test ErC50 - Desmodesmus subspicatus (green algae) - > 100 mg/l - 72 h (OECD Test Guideline 201)



12.2 Persistence and degradability

The methods for determining the biological degradability are not applicable to inorganic substances.

12.3 Bioaccumulative potential

No data available

12.4 Mobility in soil

No data available

12.5 Results of PBT and vPvB assessment

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

12.6 Endocrine disrupting properties

Product:

Assessment : The substance/mixture does not contain components considered to have endocrine disrupting properties according to REACH Article 57(f) or Commission Delegated regulation (EU) 2017/2100 or Commission Regulation (EU) 2018/605 at levels of 0.1% or higher.

12.7 Other adverse effects

Biological effects:

Harmful effect due to pH shift.

Caustic even in diluted form.

Does not cause biological oxygen deficit.

Endangers drinking-water supplies if allowed to enter soil and/or waters in large quantities.

Neutralisation possible in waste water treatment plants.

Discharge into the environment must be avoided.

SECTION 13: Disposal considerations

13.1 Waste treatment methods

No data available

SECTION 14: Transport information

14.1 UN number

ADR/RID: 1830

IMDG: 1830

IATA: 1830

14.2 UN proper shipping name

ADR/RID: SULPHURIC ACID

IMDG: SULPHURIC ACID

IATA: Sulphuric acid



14.3 Transport hazard class(es)

ADR/RID: 8

IMDG: 8

IATA: 8

14.4 Packaging group

ADR/RID: II

IMDG: II

IATA: II

14.5 Environmental hazards

ADR/RID: no

IMDG Marine pollutant: no

IATA: no

14.6 Special precautions for user

Tunnel restriction code : (E)

Further information : No data available

SECTION 15: Regulatory information**15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture**

This material safety data sheet complies with the requirements of Regulation (EC) No. 1907/2006.

Authorisations and/or restrictions on use

Regulation (EU) 2019/1148 on the marketing : sulphuric acid
and use of explosives precursors

Other regulations

Take note of Dir 94/33/EC on the protection of young people at work.

15.2 Chemical Safety Assessment

A Chemical Safety Assessment has been carried out for this substance.

SECTION 16: Other information**Full text of H-Statements**

H290 May be corrosive to metals.

H314 Causes severe skin burns and eye damage.

H315 Causes skin irritation.



Full text of other abbreviations

ADN - European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways; ADR - Agreement concerning the International Carriage of Dangerous Goods by Road; AIIC - Australian Inventory of Industrial Chemicals; ASTM - American Society for the Testing of Materials; bw - Body weight; CMR - Carcinogen, Mutagen or Reproductive Toxicant; DIN - Standard of the German Institute for Standardisation; DSL - Domestic Substances List (Canada); ECx - Concentration associated with x% response; ELx - Loading rate associated with x% response; EmS - Emergency Schedule; ENCS - Existing and New Chemical Substances (Japan); ErCx - Concentration associated with x% growth rate response; GHS - Globally Harmonized System; GLP - Good Laboratory Practice; IARC - International Agency for Research on Cancer; IATA - International Air Transport Association; IBC - International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk; IC50 - Half maximal inhibitory concentration; ICAO - International Civil Aviation Organization; IECSC - Inventory of Existing Chemical Substances in China; IMDG - International Maritime Dangerous Goods; IMO - International Maritime Organization; ISHL - Industrial Safety and Health Law (Japan); ISO - International Organisation for Standardization; KECI - Korea Existing Chemicals Inventory; LC50 - Lethal Concentration to 50 % of a test population; LD50 - Lethal Dose to 50% of a test population (Median Lethal Dose); MARPOL - International Convention for the Prevention of Pollution from Ships; n.o.s. - Not Otherwise Specified; NO(A)EC - No Observed (Adverse) Effect Concentration; NO(A)EL - No Observed (Adverse) Effect Level; NOELR - No Observable Effect Loading Rate; NZIoC - New Zealand Inventory of Chemicals; OECD - Organization for Economic Co-operation and Development; OPPTS - Office of Chemical Safety and Pollution Prevention; PBT - Persistent, Bioaccumulative and Toxic substance; PICCS - Philippines Inventory of Chemicals and Chemical Substances; (Q)SAR - (Quantitative) Structure Activity Relationship; REACH - Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals; RID - Regulations concerning the International Carriage of Dangerous Goods by Rail; SADT - Self-Accelerating Decomposition Temperature; SDS - Safety Data Sheet; TCSI - Taiwan Chemical Substance Inventory; TECI - Thailand Existing Chemicals Inventory; TSCA - Toxic Substances Control Act (United States); UN - United Nations; UNRTDG - United Nations Recommendations on the Transport of Dangerous Goods; vPvB - Very Persistent and Very Bioaccumulative

Further information

The information is believed to be correct but is not exhaustive and will be used solely as a guideline, which is based on current knowledge of the chemical substance or mixture and is applicable to appropriate safety precautions for the product. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.

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SAFETY DATA SHEET

Creation Date 22-Sep-2009

Revision Date 24-Dec-2021

Revision Number 5

1. Identification

Product Name Tributyl phosphate

Cat No. : AC169930000; AC169930010; AC169930025; AC169930050;
AC169930100; AC169932500

CAS No 126-73-8
Synonyms TBP

Recommended Use Laboratory chemicals.
Uses advised against Food, drug, pesticide or biocidal product use.

Details of the supplier of the safety data sheet

Company

Fisher Scientific Company
One Reagent Lane
Fair Lawn, NJ 07410
Tel: (201) 796-7100

Acros Organics
One Reagent Lane
Fair Lawn, NJ 07410

Emergency Telephone Number For information **US** call: 001-800-ACROS-01 / **Europe** call: +32 14 57 52 11
Emergency Number **US**:001-201-796-7100 / **Europe**: +32 14 57 52 99
CHEMTREC Tel. No.**US**:001-800-424-9300 / **Europe**:001-703-527-3887

2. Hazard(s) identification

Classification

This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

Acute oral toxicity	Category 4
Skin Corrosion/Irritation	Category 2
Serious Eye Damage/Eye Irritation	Category 2
Carcinogenicity	Category 2

Label Elements

Signal Word
Warning

Hazard Statements
Harmful if swallowed

Causes skin irritation
Causes serious eye irritation
Suspected of causing cancer

**Precautionary Statements****Prevention**

Obtain special instructions before use
Do not handle until all safety precautions have been read and understood
Use personal protective equipment as required
Wash face, hands and any exposed skin thoroughly after handling
Do not eat, drink or smoke when using this product
Wear eye/face protection

Response

IF exposed or concerned: Get medical attention/advice

Skin

IF ON SKIN: Wash with plenty of soap and water
If skin irritation occurs: Get medical advice/attention
Take off contaminated clothing and wash before reuse

Eyes

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing
If eye irritation persists: Get medical advice/attention

Ingestion

IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell
Rinse mouth

Storage

Store locked up

Disposal

Dispose of contents/container to an approved waste disposal plant

Hazards not otherwise classified (HNOC)

Harmful to aquatic life with long lasting effects

3. Composition/Information on Ingredients

Component	CAS No	Weight %
Tributyl phosphate	126-73-8	>95

4. First-aid measures

General Advice

If symptoms persist, call a physician.

Eye Contact

Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Get medical attention.

Skin Contact

Wash off immediately with plenty of water for at least 15 minutes. If skin irritation persists, call a physician.

Inhalation

Remove to fresh air. If not breathing, give artificial respiration. Get medical attention if symptoms occur.

Ingestion	Clean mouth with water and drink afterwards plenty of water.
Most important symptoms and effects	None reasonably foreseeable.
Notes to Physician	Treat symptomatically

5. Fire-fighting measures

Suitable Extinguishing Media	Water spray, carbon dioxide (CO ₂), dry chemical, alcohol-resistant foam.
Unsuitable Extinguishing Media	No information available
Flash Point	146 - °C / 294.8 - 329 °F
Method -	No information available
Autoignition Temperature	400 °C / 752 °F
Explosion Limits	
Upper	No data available
Lower	No data available
Sensitivity to Mechanical Impact	Not impact sensitive
Sensitivity to Static Discharge	No information available

Specific Hazards Arising from the Chemical

Keep product and empty container away from heat and sources of ignition.

Hazardous Combustion Products

Carbon monoxide (CO). Carbon dioxide (CO₂). Oxides of phosphorus. Phosphorus trihydride (phosphine).

Protective Equipment and Precautions for Firefighters

As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.

NFPA

Health	Flammability	Instability	Physical hazards
3	1	0	N/A

6. Accidental release measures

Personal Precautions	Use personal protective equipment as required. Ensure adequate ventilation.
Environmental Precautions	Should not be released into the environment. Do not flush into surface water or sanitary sewer system.

Methods for Containment and Clean Up Keep in suitable, closed containers for disposal. Soak up with inert absorbent material.

7. Handling and storage

Handling	Wear personal protective equipment/face protection. Ensure adequate ventilation. Avoid ingestion and inhalation. Do not get in eyes, on skin, or on clothing.
Storage.	Keep in a dry, cool and well-ventilated place. Keep container tightly closed. Keep in properly labeled containers. Protect from direct sunlight. Keep away from oxidizing agents. Incompatible Materials. Strong oxidizing agents. Bases.

8. Exposure controls / personal protection

Exposure Guidelines

Component	ACGIH TLV	OSHA PEL	NIOSH IDLH	Mexico OEL (TWA)
Tributyl phosphate	TWA: 5 mg/m ³	(Vacated) TWA: 0.2 ppm (Vacated) TWA: 2.5 mg/m ³ TWA: 5 mg/m ³	IDLH: 30 ppm TWA: 0.2 ppm TWA: 2.5 mg/m ³	TWA: 0.2 ppm

Legend

ACGIH - American Conference of Governmental Industrial Hygienists

OSHA - Occupational Safety and Health Administration

NIOSH IDLH: NIOSH - National Institute for Occupational Safety and Health

Engineering Measures

Ensure adequate ventilation, especially in confined areas. Ensure that eyewash stations and safety showers are close to the workstation location.

Personal Protective Equipment**Eye/face Protection**

Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA's eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166.

Skin and body protection

Wear appropriate protective gloves and clothing to prevent skin exposure.

Respiratory Protection

Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.

Hygiene Measures

Handle in accordance with good industrial hygiene and safety practice.

9. Physical and chemical properties

Physical State	Liquid
Appearance	Colorless
Odor	Odorless
Odor Threshold	No information available
pH	No information available
Melting Point/Range	-79 °C / -110.2 °F
Boiling Point/Range	289 °C / 552.2 °F
Flash Point	146 - °C / 294.8 - 329 °F
Evaporation Rate	No information available
Flammability (solid,gas)	Not applicable
Flammability or explosive limits	
Upper	No data available
Lower	No data available
Vapor Pressure	No information available
Vapor Density	No information available
Specific Gravity	0.979
Solubility	No information available
Partition coefficient; n-octanol/water	No data available
Autoignition Temperature	400 °C / 752 °F
Decomposition Temperature	177 °C
Viscosity	No information available
Molecular Formula	C ₁₂ H ₂₇ O ₄ P
Molecular Weight	266.32

10. Stability and reactivity

Reactive Hazard

None known, based on information available

Stability

Stable under normal conditions.

Conditions to Avoid	Temperatures above 146°C. Incompatible products. Protect from water.
Incompatible Materials	Strong oxidizing agents, Bases
Hazardous Decomposition Products	Carbon monoxide (CO), Carbon dioxide (CO ₂), Oxides of phosphorus, Phosphorus trihydride (phosphine)
Hazardous Polymerization	No information available.
Hazardous Reactions	None under normal processing.

11. Toxicological information

Acute Toxicity

Product Information Component Information

Component	LD50 Oral	LD50 Dermal	LC50 Inhalation
Tributyl phosphate	LD50 = 1390 mg/kg (Rat)	LD50 > 10000 mg/kg (Rabbit)	LC50 = 1.359 mg/L (Rat) 4 h

Toxicologically Synergistic Products No information available

Delayed and immediate effects as well as chronic effects from short and long-term exposure

Irritation	Irritating to eyes and skin
Sensitization	No information available
Carcinogenicity	Limited evidence of a carcinogenic effect.

Component	CAS No	IARC	NTP	ACGIH	OSHA	Mexico
Tributyl phosphate	126-73-8	Not listed	Not listed	A3	Not listed	Not listed

ACGIH: (American Conference of Governmental Industrial Hygienists)

A1 - Known Human Carcinogen
A2 - Suspected Human Carcinogen
A3 - Animal Carcinogen
ACGIH: (American Conference of Governmental Industrial Hygienists)

Mutagenic Effects Not mutagenic in AMES Test

Reproductive Effects No information available.

Developmental Effects No information available.

Teratogenicity No information available.

STOT - single exposure None known
STOT - repeated exposure None known

Aspiration hazard No information available

Symptoms / effects, both acute and delayed No information available

Endocrine Disruptor Information No information available

Other Adverse Effects The toxicological properties have not been fully investigated. Inhalation of high vapor concentrations may cause symptoms like headache, dizziness, tiredness, nausea and vomiting. May cause respiratory irritation. May be harmful if swallowed.

12. Ecological information

Ecotoxicity

Do not empty into drains. Do not flush into surface water or sanitary sewer system. The product contains following substances which are hazardous for the environment. Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Contains a substance which is: Toxic to aquatic organisms.

Component	Freshwater Algae	Freshwater Fish	Microtox	Water Flea
Tributyl phosphate	EC50: = 4.4 mg/L, 96h (Pseudokirchneriella subcapitata) EC50: = 1.1 mg/L, 72h (Desmodesmus subspicatus)	LC50: = 8.18 mg/L, 96h (Pimephales promelas) LC50: = 4.5 mg/L, 96h (Oryzias latipes) LC50: = 9.6 mg/L, 96h static (Oryzias latipes) LC50: 1.0 - 10.0 mg/L, 96h static (Pimephales promelas) LC50: = 4.2 mg/L, 96h static (Oncorhynchus mykiss) LC50: = 13 mg/L, 96h flow-through (Oncorhynchus mykiss) LC50: 7.66 - 8.74 mg/L, 96h flow-through (Pimephales promelas)	Not listed	EC50: 1.58 - 8.43 mg/L, 48h Static (Daphnia magna)

Persistence and Degradability No information available

Bioaccumulation/ Accumulation No information available.

Mobility .

Component	log Pow
Tributyl phosphate	2.5

13. Disposal considerations

Waste Disposal Methods Chemical waste generators must determine whether a discarded chemical is classified as a hazardous waste. Chemical waste generators must also consult local, regional, and national hazardous waste regulations to ensure complete and accurate classification.

14. Transport information

DOT Not regulated
TDG Not regulated
IATA Not regulated
IMDG/IMO Not regulated

15. Regulatory information

United States of America Inventory

Component	CAS No	TSCA	TSCA Inventory notification - Active-Inactive	TSCA - EPA Regulatory Flags
Tributyl phosphate	126-73-8	X	ACTIVE	-

Legend:

TSCA US EPA (TSCA) - Toxic Substances Control Act, (40 CFR Part 710)

X - Listed

'-' - Not Listed

TSCA 12(b) - Notices of Export Not applicable

International Inventories

Canada (DSL/NDL), Europe (EINECS/ELINCS/NLP), Philippines (PICCS), Japan (ENCS), Japan (ISHL), Australia (AICS), China (IECSC), Korea (KECL).

Component	CAS No	DSL	NDSL	EINECS	PICCS	ENCS	ISHL	AICS	IECSC	KECL
Tributyl phosphate	126-73-8	X	-	204-800-2	X	X	X	X	X	KE-34036

KECL - NIER number or KE number (<http://ncis.nier.go.kr/en/main.do>)

U.S. Federal Regulations

SARA 313	Not applicable
SARA 311/312 Hazard Categories	See section 2 for more information
CWA (Clean Water Act)	Not applicable
Clean Air Act	Not applicable
OSHA - Occupational Safety and Health Administration	Not applicable
CERCLA	Not applicable

California Proposition 65 This product does not contain any Proposition 65 chemicals.

U.S. State Right-to-Know Regulations

Component	Massachusetts	New Jersey	Pennsylvania	Illinois	Rhode Island
Tributyl phosphate	X	X	X	X	X

U.S. Department of Transportation

Reportable Quantity (RQ):	N
DOT Marine Pollutant	N
DOT Severe Marine Pollutant	N

U.S. Department of Homeland Security This product does not contain any DHS chemicals.

Other International Regulations

Mexico - Grade No information available

Authorisation/Restrictions according to EU REACH

Component	REACH (1907/2006) - Annex XIV - Substances Subject to Authorization	REACH (1907/2006) - Annex XVII - Restrictions on Certain Dangerous Substances	REACH Regulation (EC 1907/2006) article 59 - Candidate List of Substances of Very High Concern (SVHC)
Tributyl phosphate	-	Use restricted. See item 75. (see link for restriction details)	-

<https://echa.europa.eu/substances-restricted-under-reach>

Safety, health and environmental regulations/legislation specific for the substance or mixture

Component	CAS No	OECD HPV	Persistent Organic Pollutant	Ozone Depletion Potential	Restriction of Hazardous Substances (RoHS)
Tributyl phosphate	126-73-8	Listed	Not applicable	Not applicable	Not applicable

Component	CAS No	Seveso III Directive (2012/18/EC) -	Seveso III Directive (2012/18/EC) -	Rotterdam Convention (PIC)	Basel Convention (Hazardous Waste)
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		Qualifying Quantities for Major Accident Notification	Qualifying Quantities for Safety Report Requirements		
Tributyl phosphate	126-73-8	Not applicable	Not applicable	Not applicable	Not applicable

16. Other information

Prepared By Regulatory Affairs
Thermo Fisher Scientific
Email: EMSDS.RA@thermofisher.com

Creation Date 22-Sep-2009
Revision Date 24-Dec-2021
Print Date 24-Dec-2021
Revision Summary This document has been updated to comply with the US OSHA HazCom 2012 Standard replacing the current legislation under 29 CFR 1910.1200 to align with the Globally Harmonized System of Classification and Labeling of Chemicals (GHS).

Disclaimer

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text

End of SDS

APPENDIX B

This section provides the guidelines from Rydberg et al that was followed to size the settler.

Agreeing than no mass is lost in the extraction step, one can assume a complete mass balance as presented in Equation (B-1) and elaborated in Equation (B-2).

$$m_{in} = m_{out} \quad (B-1)$$

$$m_{i,f} = m_{i,Org} + m_{i,Raff} \quad (B-2)$$

Where m refers to mass (g), i the specified metal, F the feed, Org the organic phase and $Raff$ the aqueous phase after extraction took place. Relating mass to concentration, C (g/L) and volume, V (L) as provided in Equation (B-3), Equation (B-2) can be rewritten as Equation (B-4).

$$C_i = \frac{m_i}{V_{tot}} \quad (B-3)$$

$$C_F V_F = C_{Org} V_{Org} + C_{Raff} V_{Raff} \quad (B-4)$$

The ICP EOS machinery allows measurement of metals dissolved in aqueous phases and not organic phases. The organic concentration will therefore typically be unknown and can be calculated by manipulation of Equation (B-4) as presented in Equation (B-5).

$$C_{Org} V_{Org} = C_F V_F - C_{Raff} V_{Raff} \quad (B-5)$$

The percentage of targeted metal extracted to the organic phase is conventionally utilised to define the separation efficiency obtained from the extraction at specified conditions. To calculate the percentage extraction E (%), Equation (B-6) is provided.

$$E = \frac{m_{i,Org}}{m_{i,F}} \times 100 \quad (B-6)$$

Where that $m_{i,Org}$ and $m_{i,F}$ refers to the mass of the specified metal in the organic phase and in the feed stream.

Substitution of Equation (B-3) results in Equation (B-7).

$$E = \frac{C_{i,Org} V_{Org}}{C_{i,F} V_F} \times 100 \quad (B-7)$$

Substituting in Equation (B-5) Equation (B-8) is obtained.

$$E = \frac{C_{i,F}V_F - C_{i,Raff}V_{Raff}}{C_{i,F}V_F} \times 100$$

$$= \left(1 - \frac{C_{i,Raff}V_{Raff}}{C_{i,F}V_F}\right) \times 100 \quad (B-8)$$

When assuming no loss of the feed solution ($V_F = V_{Raff}$), Equation (B-9) can be used.

$$E = \left(1 - \frac{C_{i,Raff}}{C_{i,F}}\right) \times 100 \quad (B-9)$$

Furthermore, an organic to aqueous ratio, P_R is defined in Equation (B-10).

$$P_R = \frac{V_{Org}}{V_F} = \frac{V_{Org}}{V_{Raff}} \quad (B-10)$$

Another term very much known in the SX field is the *distribution coefficient* D , which is also referred to as the equilibrium constant K_d is defined in Equation (B-11). The distribution coefficient provides an indication of which phase the metal will favour and consequently speaks to the efficiency of extraction that can be expected. While a value $D > 1$ indicates that the metal favours the organic phase, a value $D < 1$ indicates that the metal favours the aqueous phase.

$$K_d = D = \frac{C_{i,Org}}{C_{i,Raff}} \quad (B-11)$$

Expression of E in terms of D

With further manipulation of Equation (B-7) by substitution of equations (B-4), (B-10) and (B-11), Equation (B-12) can be obtained.

$$E = \left(\frac{P_R D}{P_R D + 1}\right) \times 100 \quad (B-12)$$

Hereafter Equation (B-12) and (B-7) can be set equal to each other and Equation (B-8) and (B-7) are set equal to each other as expressed in Equation (B-13) and (B-14) respectively.

$$E = \frac{C_{i,Org}V_{Org}}{C_{i,F}V_F} \times 100 = \left(\frac{P_R D}{P_R D + 1}\right) \times 100 \quad (B-13)$$

$$E = \frac{C_{i,Org}V_{Org}}{C_{i,F}V_F} \times 100 = \left(1 - \frac{C_{i,Raff}V_{Raff}}{C_{i,F}V_F}\right) \times 100 \quad (B-14)$$

These equations then result in two expressions after substitution of Equation (B-10) as presented by Equation (B-15) and Equation (B-16).

$$C_{i,Org} = C_{i,F} \left(\frac{D}{1 + P_R D} \right) \quad (B-15)$$

$$C_{i,Raff} = C_{i,F} \left(\frac{1}{1 + P_R D} \right) \quad (B-16)$$

Addition of Equation (B-15) and Equation (B-16) results in Equation (B-17).

$$C_{i,Org} + C_{i,Raff} = C_{i,F} \left(\frac{1 + D}{1 + P_R D} \right) \quad (B-17)$$

It is then clear, when using a $P_R = 1$ Equation (B-18) can be used.

$$C_{i,Org} + C_{i,Raff} = C_{i,F} \quad (B-18)$$

Finally, the separation factor β as defined in Equation (B-19) acts an indication of the extractant selectiveness towards the targeted metal.

$$\beta = \frac{D_T}{D_I} \quad (B-19)$$

Where D_T and D_I refers to the distribution coefficient of the target and impurity (unwanted) metal respectively.

APPENDIX C

This Appendix provides the technical datasheets of the membranes used in this study.

3M™ Liqui-Cel™ EXF-2.5×8 Series Membrane Contactor

Typical Properties

Membrane Characteristics	
Cartridge Configuration	Extra-Flow with Center Baffle
Liquid Flow Guidelines	0.1 – 0.7 m ³ /hr (0.5 – 3.0 gpm)
Membrane Type	X50 Fiber
	Recommended for CO ₂ removal from liquid and other gas transfer applications
	X40 Fiber
	Recommended for O ₂ removal from liquid and other gas transfer applications
Membrane/Potting Material	Polypropylene / Polyethylene
Priming Volume (approximate)	
Shellside	0.40 L (0.11 gal)
Lumenside	0.15 L (0.04 gal)

Pressure Guidelines*	
	X50 or X40 Fiber
Maximum Shellside <u>LIQUID</u> Working Temperature/ Pressure	5–40°C, 7.2 barg (41–104°F, 105 psig) 70°C, 2.1 barg (158°F, 30 psig)
If no vacuum is used, 1 barg (15 psig) can be added to pressures above.	
Maximum Applied Gas Pressure	4.8 barg at 25°C (70 psig at 77°F)
Maximum applied gas pressure is for integrity testing at ambient temperatures. Normal operating pressures are typically lower.	
Maximum Lumenside Liquid Temperature/Pressure of Semibody Contactor	5°C, 6.2 barg (41°F, 90 psig) 15–25°C, 4.8 barg (59–77°F, 70 psig) 70°C, 1.0 barg (158°F, 15 psig)
* See Operating Guide for complete temp/pressure limits for housings and membrane.	
Note: Liquid pressure should always exceed gas pressure, including during start-up and shut-down procedures.	

Housing Options and Characteristics	
Material	Polypropylene
Flange Connections	
Shellside (Liquid Inlet/Outlet)	¼ inch NPT female ⅜ inch Flaretek® (nut included)** ½ inch Flaretek® (nut included)**
Lumenside	¼ inch NPT female

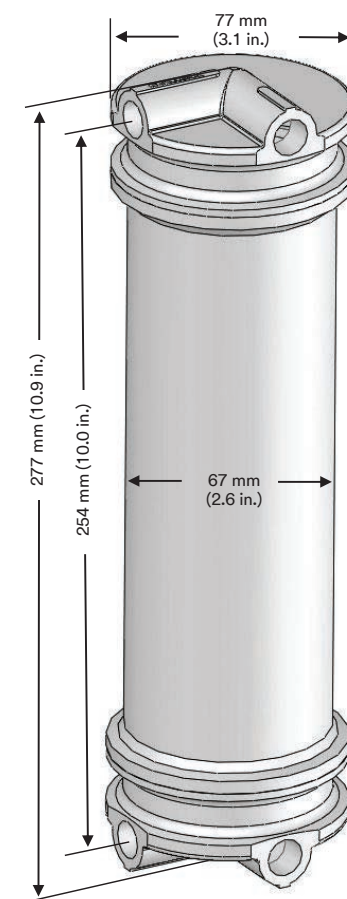
** Only available with FKM seal option with welded end caps.

Seal Material Options	Applications
FKM	General Purpose
FFKM (K - UPW)***	Ultra Pure Water
FFKM (K - EXT)****	Chemical Extraction

***Only available with welded end caps with NPT connections and X40 fiber.

****Only available with clamped end caps and NPT connections.

Weight (approximate)	
Dry	0.5 kg (1.1 lbs)
Water-filled (shellside)	0.9 kg (2.0 lbs)



Welded end caps with NPT connections

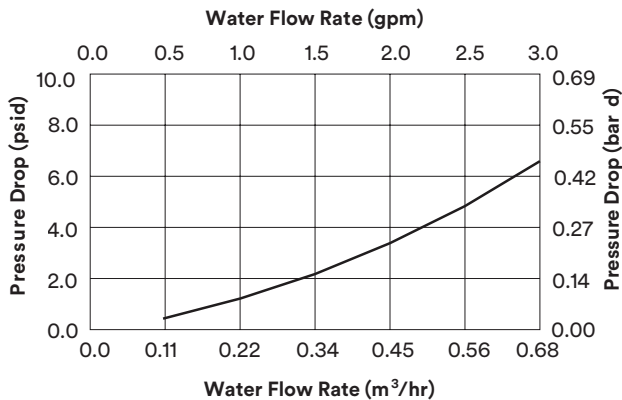
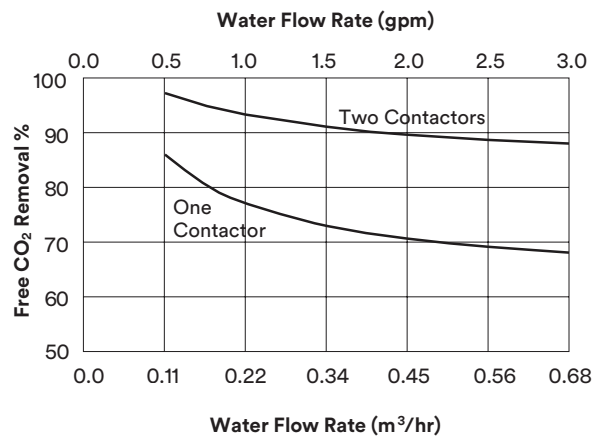
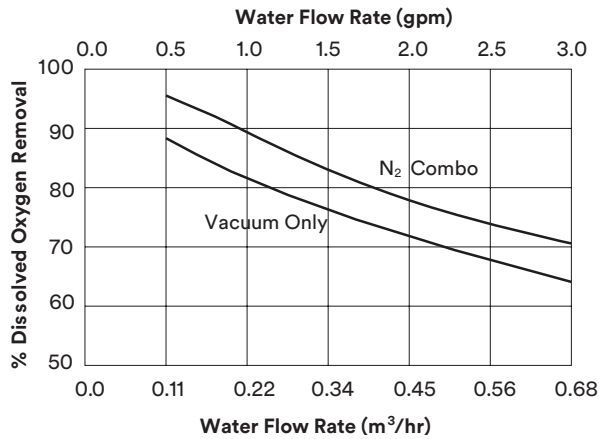
All dimensions are nominal values for contactors with NPT connections. Overall length with Flaretek® connections increases. See full housing drawing on 3M.com/Liqui-Cel for additional details.

Not for consumer sale or use.

3M™ Liqui-Cel™ EXF-2.5×8 Series Membrane Contactor

Regulatory

Complies with the limits as set by (EU) 2015/863 amending Annex II to the Restriction on Hazardous Substances (RoHS) Directive (2011/65/EU). 3M™ Liqui-Cel™ EXF-2.5×8 Series Membrane Contactors with FKM seals are constructed of FDA Title 21 CFR § 170-190 compliant materials for wetted parts only at ambient temperatures. 3M™ Liqui-Cel™ EXF-2.5×8 Series Membrane Contactors with FFKM (K-UPW) or FFKM (K-EXT) seals **are not** constructed of FDA Title 21 CFR § 170-190 compliant materials.



Curves represent nominal values. Characteristics may change under different operating conditions.

Test condition O₂ Removal with X40 membrane 20°C: N₂ vacuum combo mode, N₂ sweep flow rate: 0.05 scfm and 50 mm Hg vacuum Vacuum mode: 50 mm Hg

Test condition CO₂ Removal with X50 membranes 25°C: Air-combo, vacuum 150 mm Hg, air sweep G/L 0.5.

Pressure drop curves using NPT connection. Flaretek® connection will have lower pressure drop.

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3M.com/Liqui-Cel

3M™ Liqui-Cel™ EXF-8×80 Series Membrane Contactor

Typical Properties

Membrane Characteristics	
Cartridge Configuration	Extra-Flow with Center Baffle
Liquid Flow Guidelines	7 – 28 m³/hr (30 – 125 gpm)
Membrane Type	X40 Fiber
	Recommended for high pressure O₂ removal and other gas transfer applications
Membrane/Potting Material	Polypropylene / Epoxy
Priming Volume (approximate)	
Shellside	30.3 L (8.0 gal)
Lumenside	19.7 L (5.2 gal)

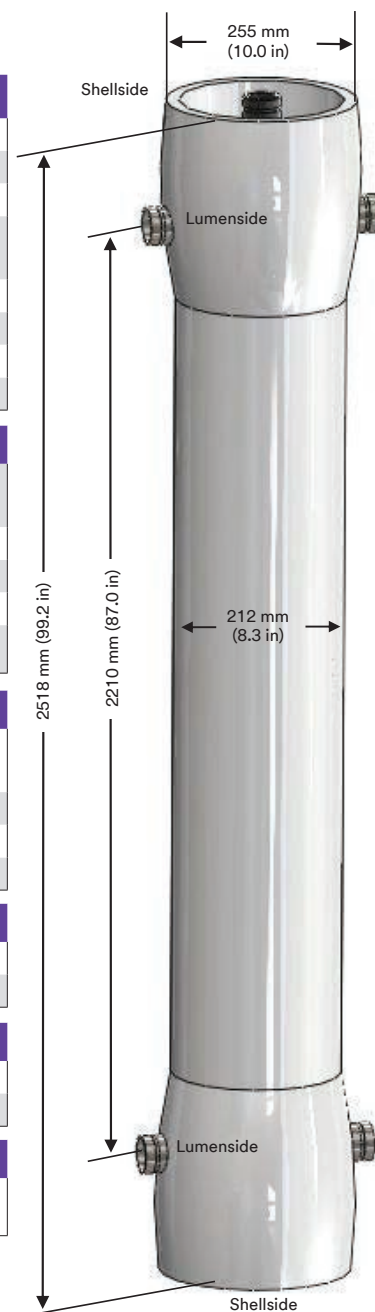
Pressure Guidelines*	
Maximum Shellside LIQUID Working Temperature/ Pressure	5-25°C, 19.7 barg (41-86°F, 285 psig) 60°C, 12.0 barg (140°F, 175 psig)
If no vacuum is used, 1.0 barg (15 psig) can be added to pressures above.	
Maximum Applied Gas Pressure	2.1 barg at 25°C (30 psig at 77°F)
Maximum applied gas pressure is for integrity testing at ambient temperatures. Normal operating pressures are typically lower.	
* See Operating Guide for complete temp/pressure limits for housings and membrane.	
Note: Liquid pressure should always exceed gas pressure.	

Housing Characteristics	
Material	Fiber Reinforced Plastic (FRP) FRP Vessel Code-rated to ASME BPVC Section X
Connections	
Shellside (Liquid Inlet/Outlet)	1.5 Inch Grooved pipe fitting
Lumenside	1.5 Inch Grooved pipe fitting

Seal Options	
Material	Applications
EPDM	All Purpose

Weight (approximate)	
Dry	52 kg (115 lbs)
Water-filled (shellside)	89 kg (196 lbs)

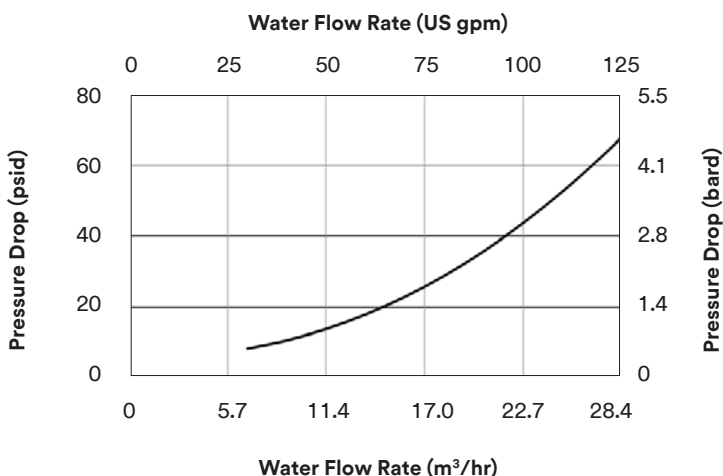
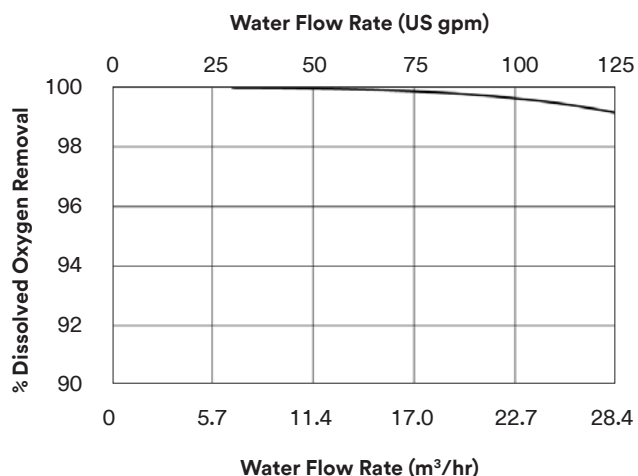
Regulatory	
Complies with the limits as set by (EU) 2015/863 amending Annex II to the Restriction on Hazardous Substances (RoHS) Directive (2011/65/EU).	



All dimensions are nominal values.
See full housing drawing on
3M.com/Liqui-Cel for
additional details.

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3M™ Liqui-Cel™ EXF-8×80 Series Membrane Contactor



Curves represent nominal values with FRP vessel using water at 20° C. Characteristics may change under different operating conditions.
Test condition O2 Removal with X40 membrane: N2-vacuum combo mode, vacuum: 50 mm Hg N2 sweep: 0.5 SCFM.

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3M.com/Liqui-Cel

3M™ Liqui-Cel™ EXF-10×28 Industrial Series Membrane Contactor

Typical Properties

Membrane Characteristics	
Cartridge Configuration	Industrial Use Extra-Flow with Center Baffle
Liquid Flow Guidelines	10 – 48 m ³ /hr (44 – 210 gpm)
Membrane Type	X-IND Fiber
Membrane/Potting Material	Polypropylene / Epoxy
Priming Volume (approximate)	
Shellside	26.1 L (6.9 gal)
Lumenside	10.6 L (2.8 gal)

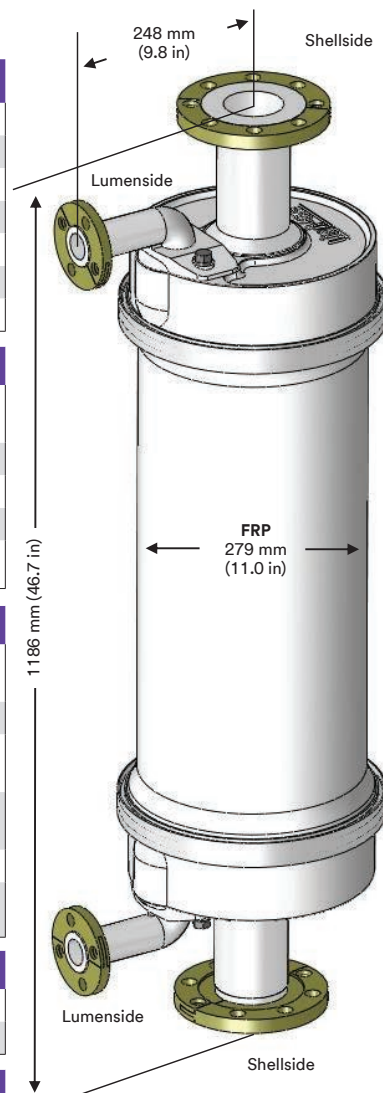
Pressure Guidelines*	
Maximum Shellside <u>LIQUID</u> Working Temperature/ Pressure	5-50°C, 4.1 barg (41-122°F, 60 psig)
If no vacuum is used, 1.0 barg (15 psig) can be added to pressures above.	
Maximum Applied Gas Pressure	4.1 barg at 25°C (60 psig at 77°F)
Maximum applied gas pressure is for integrity testing at ambient temperatures. Normal operating pressures are typically lower.	
* See Operating Guide for complete temp/pressure limits for housings and membrane.	
Note: Liquid pressure should always exceed gas pressure.	

Housing Characteristics	
Material	Fiber Reinforced Plastic (FRP) for Industrial Use Exterior finish is gray
Flange Connections	
Shellside (Liquid Inlet/Outlet)	3 inch class 150 raised face flange per ANSI B16.5 80A at 10K flat face flange per JIS B2238
Lumenside	1 inch class 150 raised face flange per ANSI B16.5 50A at 10K flat face flange per JIS B2238
Mounting Kit	
A Mounting Kit with 2 cradles and 2 straps is available and sold separately. It will hold the contactor horizontally or vertically.	

Seal Options	
Material	Applications
EPDM	General Purpose

Weight (approximate)	
Dry	33 kg (73 lbs)
Water-filled (shellside)	57 kg (125 lbs)
Cartridge only – dry	10 kg (23 lbs)

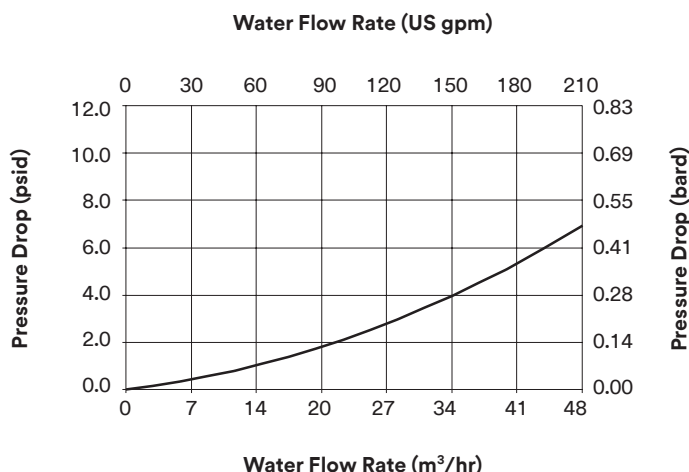
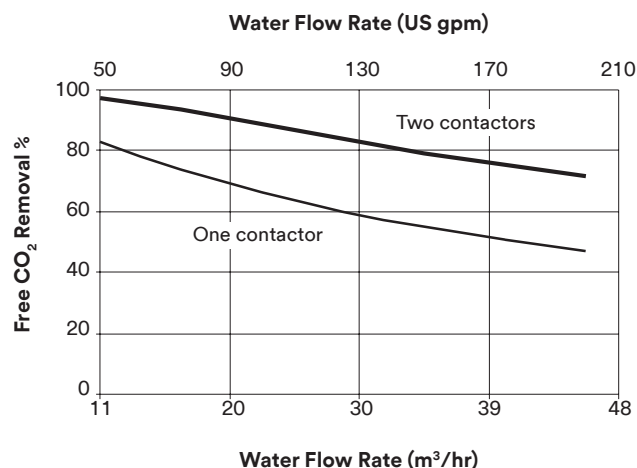
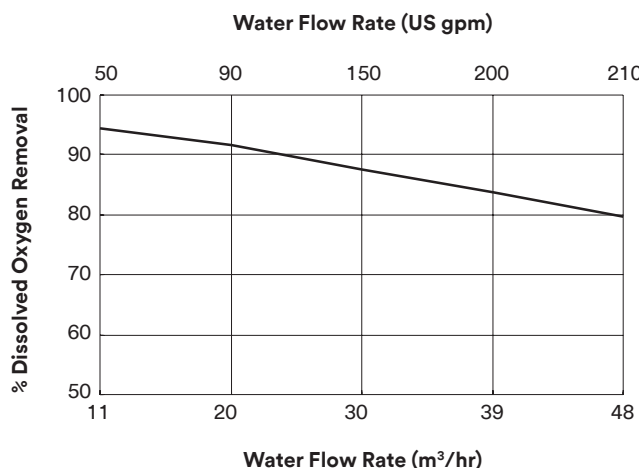
Regulatory	
Complies with the limits as set by (EU) 2015/863 amending Annex II to the Restriction on Hazardous Substances (RoHS) Directive (2011/65/EU).	



All dimensions are nominal values. See full housing drawing on 3M.com/Liqui-Cel for additional details.

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3M™ Liqui-Cel™ EXF-10×28 Industrial Series Membrane Contactor



Curves represent nominal values, generated using water at 20°C. Characteristics may change under different operating conditions.

Test condition O₂ Removal: N₂-vacuum combo mode, vacuum: 50 mm Hg N₂ sweep: 0.25 scfm at 20°C.

Test condition CO₂ Removal: Air vacuum combo mode, vacuum: 75 mm Hg, air sweep: 1 scfm at 25°C.

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3M™ Liqui-Cel™ EXF-14×28 Series Membrane Contactor

Typical Properties

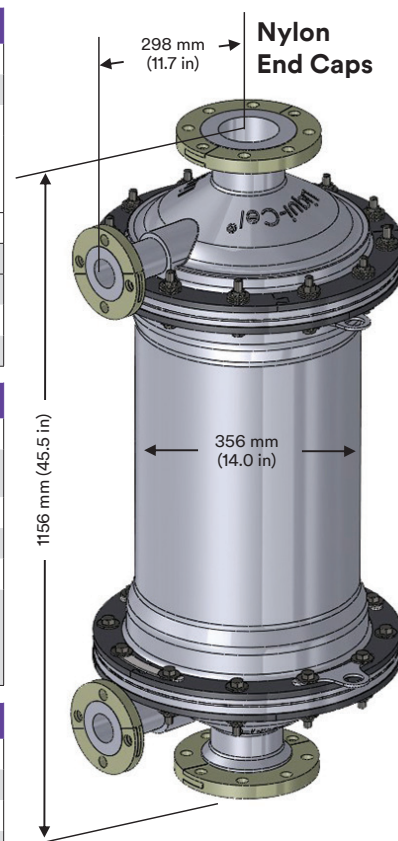
Membrane Characteristics				
Cartridge Configuration	Extra-Flow with Center Baffle			
Liquid Flow Guidelines	16 – 91 m³/hr (70 – 400 gpm)			
Membrane Type	X50 Fiber		X40 Fiber	
	Recommended for CO ₂ removal from liquid and other gas transfer applications		Recommended for O ₂ removal from liquid and other gas transfer applications	
Membrane/Potting Material	Polypropylene / Epoxy			
	With Nylon End Caps		With Engineered Thermoplastic End Caps	
Priming Volume (approximate)	X50 Fiber	X40 Fiber	X50 Fiber	X40 Fiber
Shellside	33.5 L (8.8 gal)	35.5 L (9.3 gal)	35.4 L (9.3 gal)	37.3 L (9.9 gal)
Lumenside	21.7 L (5.7 gal)	20.9 L (5.5 gal)	23.8 L (6.3 gal)	23.0 L (6.1 gal)

Pressure Guidelines*	
Maximum Shellside LIQUID Working Temperature/ Pressure	X50 or X40 Fiber 5-25°C, 7.2 barg (41-77°F, 105 psig) 50°C, 2.1 barg (122°F, 30 psig)
If no vacuum is used, 1.0 barg (15 psig) can be added to pressures above.	
Maximum Applied Gas Pressure	4.1 barg at 25°C (60 psig at 77°F)
Maximum applied gas pressure is for integrity testing at ambient temperatures. Normal operating pressures are typically lower.	
*Pressures are based on fluid group 2 (other) liquids and gases per the European Union Pressure Equipment Directive 2014/68/EU. See Operating Guide for pressure limits in the European Union with fluid group 1 (hazardous) liquids and gases. See Operating Guide for complete listing of temp/pressure limits for housings and membrane.	
Note: Liquid pressure should always exceed gas pressure.	

Housing Characteristics	
Material	PVC Vessel with Engineered Thermoplastic or Nylon End Caps
Flange Backing Rings	SMC (Sheet Molded Compound)
Flange Connections	
Shellside (Liquid Inlet/Outlet)	4 inch class 150 raised face flange per ANSI B16.5 100A 10K raised face flange per JIS B2238
Lumenside	2 inch class 150 raised face flange per ANSI B16.5 50A 10K flat face flange per JIS B2238
Mounting Kit	
A Mounting Kit with 2 cradles and 2 straps is available and sold separately. It will hold the contactor horizontally or vertically.	

Seal Options	
Material	
EPDM	
FKM**	Only available with Engineered Thermoplastic End Caps
**3M™ Liqui-Cel™ EXF-14×28 Membrane Contactors with FKM o-rings are NOT tested and certified by WQA against NSF/ANSI 61.	

Weight (approximate)		
End Cap Material	With Nylon End Caps	With Engineered Thermoplastic Caps
Dry	62 kg (136 lbs)	54 kg (118 lbs)
Water-filled (shellside)	97 kg (213 lbs)	89 kg (196 lbs)



NOTE: Overall length with engineered thermoplastic end caps is 1158 mm (45.6 in). All dimensions are nominal values.

See full housing drawings on 3M.com/Liqui-Cel for additional details.

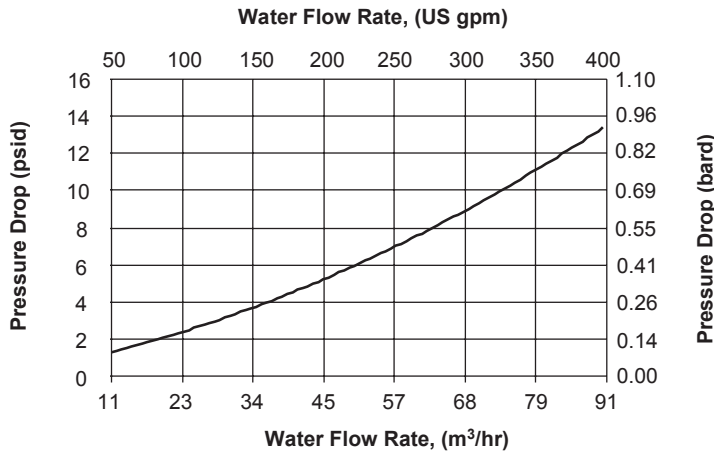
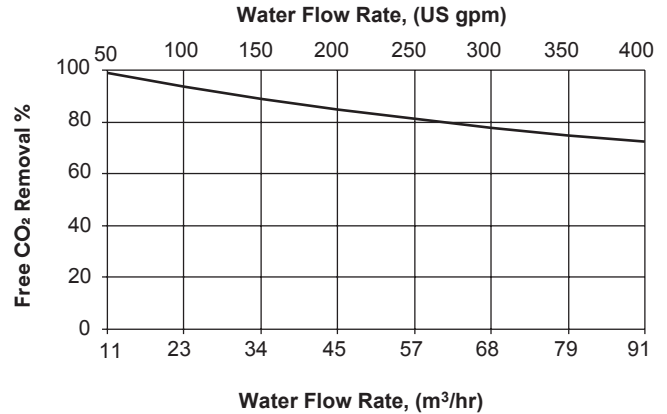
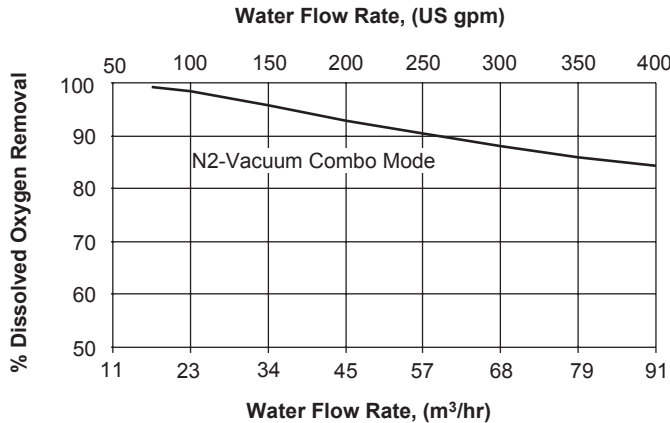
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3M™ Liqui-Cel™ EXF-14x28 Series Membrane Contactor

Typical Properties

Regulatory

Complies with the limits as set by (EU) 2015/863 amending Annex II to the Restriction on Hazardous Substances (RoHS) Directive (2011/65/EU).



Note: Performance can be improved by adjusting the sweep rate.

Curves represent nominal values, generated using water at 20°C. Characteristics may change under different operating conditions.

Test condition O₂ Removal: X40 membrane, N₂-vacuum combo mode, vacuum: 75 mm Hg, N₂ Sweep 0.25 scfm.

Test condition CO₂ Removal: X50 membrane, Air vacuum combo mode, vacuum: 150 mm Hg, air sweep 8 scfm.

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3M™ Liqui-Cel™ EXF-14x28
 Series Membrane Contactors
 with EPDM seals are tested
 and certified by WQA against
 NSF/ANSI 61.

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 Rev. 04/2021

3M.com/Liqui-Cel

3M™ Liqui-Cel™ EXF-14×40 Series Membrane Contactor

Typical Properties

Membrane Characteristics		
Cartridge Configuration	Extra-Flow with Center Baffle	
Liquid Flow Guidelines	16 – 125 m ³ /hr (70 – 550 gpm)	
Membrane Type	X40 Fiber	
	Recommended for O ₂ removal from liquid and other gas transfer applications	
Membrane/Potting Material	Polypropylene / Epoxy	
Priming Volume (approximate)		
	With Nylon End Caps	With Engineered Thermoplastic End Caps
Shellside	51.3 L (13.5 gal)	53.2 L (14.1 gal)
Lumenside	23.8 L (6.3 gal)	25.9 L (6.9 gal)

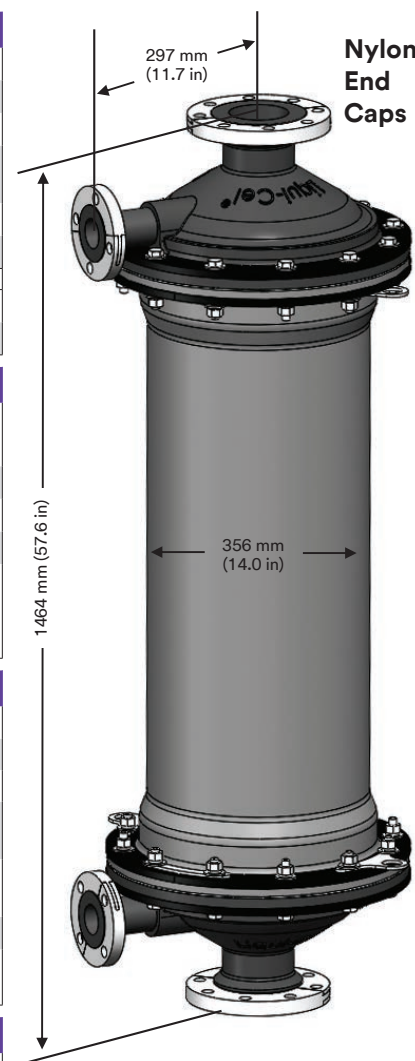
Pressure Guidelines*	
Maximum Shellside <u>LIQUID</u> Working Temperature/ Pressure	5-25°C, 7.2 barg (41-77°F, 105 psig) 50°C, 2.1 barg (122°F, 30 psig)
If no vacuum is used, 1.0 barg (15 psig) can be added to pressures above.	
Maximum Applied Gas Pressure	4.1 barg at 25°C (60 psig at 77°F)
Maximum applied gas pressure is for integrity testing at ambient temperatures. Normal operating pressures are typically lower.	
*Pressures are based on fluid group 2 (other) liquids and gases per the European Union Pressure Equipment Directive 2014/68/EU. See Operating Guide for pressure limits in the European Union with fluid group 1 (hazardous) liquids and gases. Also, see Operating Guide for complete temp/pressure limits for housings and membrane.	
Note: Liquid pressure should always exceed gas pressure.	

Housing Characteristics	
Housing Material	PVC Vessel with Engineered Thermoplastic or Nylon End Caps
Flange Backing Rings	SMC (Sheet Molded Compound)
Flange Connections	
Shellside (Liquid Inlet/Outlet)	4 inch class 150 raised face flange per ANSI B16.5 100A at 10K raised face flange per JIS B2238
Lumenside	2 inch class 150 raised face flange per ANSI B16.5 50A at 10K flat face flange per JIS B2238
Mounting Kit	
A Mounting Kit with 2 cradles and 2 straps is available and sold separately. It will hold the contactor horizontally or vertically.	

Seal Options	
Material	Applications
EPDM (ANSI / NSF 61)	General Purpose

Weight (approximate)		
	With Nylon End Caps	With Engineered Thermoplastic End Caps
Dry	72 kg (160 lbs)	64 kg (141 lbs)
Water-filled	124 kg (273 lbs)	116 kg (256 lbs)

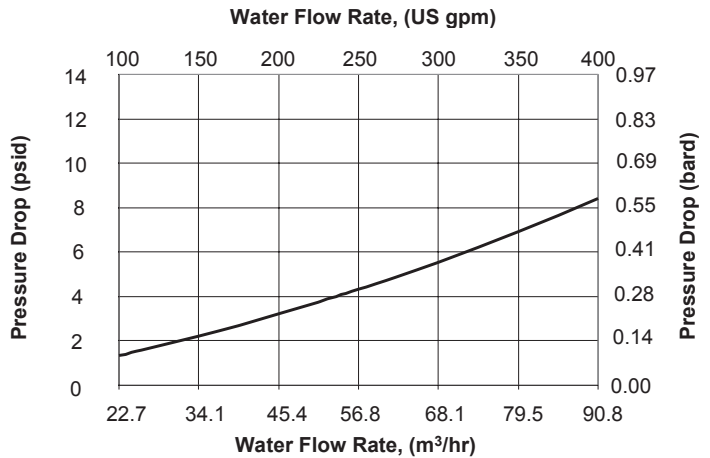
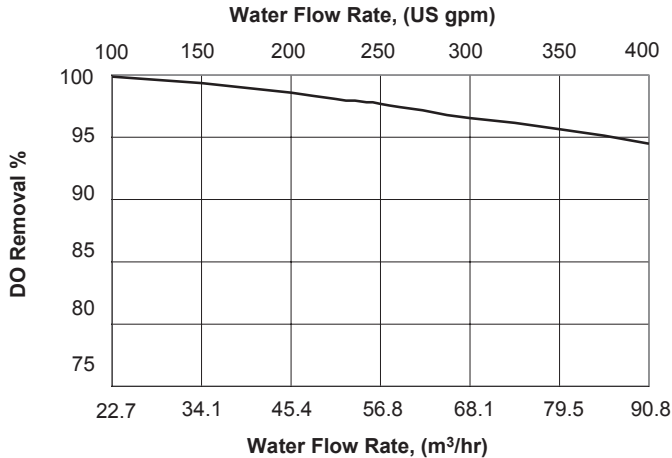
Regulatory
Complies with the limits as set by (EU) 2015/863 amending Annex II to the Restriction on Hazardous Substances (RoHS) Directive (2011/65/EU).



NOTE: Overall length with engineered thermoplastic end caps is 1466 mm (57.7 in). All dimensions are nominal values. See full housing drawings on 3M.com/Liqui-Cel for additional details.

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3M™ Liqui-Cel™ EXF-14×40 Series Membrane Contactor



Curves represent nominal values, generated using water at 20°C.

Test condition O₂ Removal: X40 membrane, N₂-vacuum combo mode, Vacuum: 50 torr, N₂: 0.8 scfm.

Characteristics may change under different operating conditions.

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