Fedor Vasilyev

MODEL-BASED DESIGN AND OPTIMISATION OF HYDROMETALLURGICAL LIQUID–LIQUID EXTRACTION PROCESSES
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Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium 2303 at Lappeenranta University of Technology, Lappeenranta, Finland on the 12th of November, 2018, at 14 o’clock.

Acta Universitatis
Lappeenrantaensis 818
Supervisors
Professor Tuomo Sainio
LUT School of Engineering Science
Lappeenranta University of Technology
Finland

D.Sc. Sami Virolainen
LUT School of Engineering Science
Lappeenranta University of Technology
Finland

Reviewers
Professor Marcelo Borges Mansur
Department of Metallurgical and Materials Engineering
Federal University of Rio de Janeiro
Brazil

Associate Professor Mark Foreman
Department of Nuclear Chemistry / Industrial Materials Recycling
Chalmers University of Technology
Sweden

Opponents
Professor Marcelo Borges Mansur
Department of Metallurgical and Materials Engineering
Federal University of Rio de Janeiro
Brazil

Professor Ville Alopaeus
Department of Chemical and Metallurgical Engineering
Aalto University
Finland
Abstract

Fedor Vasilyev

Model-based design and optimisation of hydrometallurgical liquid–liquid extraction processes

Lappeenranta 2018
119 pages

Acta Universitatis Lappeenraensis 818
Diss. Lappeenranta University of Technology

ISBN 978-952-335-281-0 (PDF)
ISSN-L 1456-4491
ISSN 1456-4491

Hydrometallurgical methods are suitable for the treatment of primary, secondary, high- and low-grade raw materials enabling the production of metals essential to modern society, in an environmentally and economically sustainable way. Among other methods, liquid–liquid extraction is widely used in the processing of various base, precious and other metals due to the development of stable selective extractants that effectively recover valuable metals from complex raw materials. The increasing demands for pure metals and environmentally sustainable processes further promote the development of liquid–liquid extraction as a separation technique.

The purpose of the studies presented in this thesis is to develop tools, which can help to decrease costs and improve the efficiency of process development in hydrometallurgy. Since modelling and simulation can be used effectively in the development of processes for production of metals, the application of modelling and simulation tools to hydrometallurgical process development is explored in the current thesis. The fields: model formulation, efficient solution of model equations, simulation of counter-current liquid–liquid extraction cascades as well as automated process synthesis in hydrometallurgy are studied. Mechanistic modelling is applied to simulate liquid–liquid extraction processes, whereas a metaheuristic algorithm is implemented in order to perform the efficient automated synthesis of the hydrometallurgical processes.

Mechanistic models are based on the chemistry of the separation processes and provide detailed information on their thermodynamic and kinetic limitations. Also they can serve as a tool for determining the optimal configuration of a metal’s recovery process. The research on mechanistic modelling and process simulation was focused on two cases, for which the equilibrium models were developed. The first one was the efficiency improvement of copper liquid–liquid extraction by studying the factors affecting the copper extraction and the fate of iron as the main impurity in the process. New experimental data on the extraction equilibrium of copper and iron in the extraction and
stripping steps were collected. The data were used to validate the developed model. It was found that the high copper loading of the organic phase in the extraction stages leads to decreased iron co-extraction and, consequently, higher process efficiency. The developed simulation tool helps quantify the effect.

The second case was devoted to the analysis of the operation and performance of a liquid–liquid extraction process for fractionation of cobalt, nickel, and lithium from Li–ion battery leachates of different composition. The process model was developed and validated using data taken from literature. A simple and effective process flowsheet, in which cobalt and nickel were first selectively extracted, yielding pure lithium raffinate, and then separated as pure products in the stripping steps, was thoroughly studied and optimized using numerical simulation. The process was found to be able to separate cobalt, nickel, and lithium from leachates of different composition in a single extraction circuit. Furthermore, the operation of the process is rather flexible, and pure fractions (>99%) of lithium, nickel, and cobalt may be produced with high yield.

Advanced mathematical and statistical methods were employed to ensure confidence in the modelling and simulation results. The mechanistic models of extraction equilibrium were solved by the rate-based approach, which provides fast calculations with controlled accuracy. Nonlinear regression analysis was used to estimate the values of the model parameters. A Markov chain Monte Carlo algorithm was used to assess the reliability of the modelling results. The sequential-modular approach was used for simulation of counter-current operation of the liquid–liquid extraction processes.

A method for the automated synthesis of hydrometallurgical processes using limited amounts of experimental data was developed. The method allows the selection and sequencing of the most effective process step options (e.g., leaching, liquid–liquid extraction, and precipitation) and simultaneously optimising their performance. An algorithm based on the Ant colony optimisation technique was used to generate promising process alternatives and identify the most economic one in an iterative manner. Key performance indicators were employed to compare the process alternatives. The applicability of the method was studied by investigating zinc recovery from argon oxygen decarburisation dust and the recovery of lanthanides from nickel metal hydride batteries. The processes for the recovery of the valuable components were successfully synthesised, and recommendations for further improvements of the processes were given.

Keywords: hydrometallurgy, process development, process synthesis, liquid–liquid extraction, solvent extraction, equilibrium, key performance indicators, ant colony optimisation, modelling, parameter estimation, simulation.
Acknowledgements

This thesis is based on the research work that was carried out in the School of Engineering Science at Lappeenranta University of Technology, Finland, between 2014 and 2018.

I express my deepest gratitude to my supervisors, Professor Tuomo Sainio and Dr. Sami Virolainen, for giving me the support and freedom to perform the research, test new ideas and methods. I thank them for their invaluable advice and guidance throughout the studies. Professor Tuomo Sainio is also acknowledged for his efforts in providing financial support for the research.

I gratefully thank the reviewers of this thesis, Professor Marcelo Borges Mansur and Associate Professor Mark Foreman, for their inspiring comments and questions, which made it possible to improve the thesis. I especially thank Associate Professor Mark Foreman, who made me look at the topic of my thesis from a different perspective: broader, yet more precisely and prudently.

Business Finland and the Finnish metals refining companies who participated in System Integrated Metals Processing program (SIMP) are acknowledged for funding. Alike, The Finnish Chemical Society Foundation is acknowledged for financial support through a personal grant.

I wish to thank The Graduate School of Chemical Engineering for organising the courses and workshops, during which we had fascinating scientific discussions in the broad field of chemical engineering. The aspiration of Mr. Peter Jones for the development of the academic writing skill in his students is acknowledged. I acknowledge the CSC - IT Center for Science Ltd. for computational resources they provide for scientific research.

All my colleagues from the Chemical Separation Methods group and the School of Engineering Science deserve my warmest thanks for the enjoyable moments of work and coffee breaks we had together. I wish to thank Professor Jari Hämäläinen for foundation of the informal seminars, where we broaden our awareness of the research at the school in a relaxed atmosphere.

Many thanks to my parents, who always encourage me in every undertaking. I wish also say thanks to all my relatives. It would be unfair to omit expressing my thanks to many of my friends and peers, whom I met during the courses, conferences and vacations, for the unforgettable moments we shared.

Finally, my deepest gratitude goes to my amazing wife Maria and our playful son Stepan for casting sparks of joy on everything we have around us.

Fedor Vasilyev
October 2018
Lappeenranta, Finland
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Publications
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This thesis is based on the following journal publications, which are referred to in the text by Roman numbers I-IV. The rights have been granted by publishers to include the papers in the dissertation.


Author's contribution in the publications

I. The author planned the experiments together with the co-authors, carried out all the experiments and analysed the data with the co-authors. The author developed the model and analysed the modelling results. The author made the main contribution to the writing of the paper.

II. The author planned and carried out all the experiments and analysed the data. The author also developed the model, analysed the modelling results and performed the simulations. The author made the main contribution to the writing of the paper.

III. The author developed the model, analysed the modelling results and performed the simulations. The paper was written together with the co-authors.

IV. The author developed the method together with the co-authors. The author collected the data from literature sources, implemented the algorithm and performed all the calculations. The author made the main contribution to the writing of the paper.
Related conference presentations


Vasilyev F., Virolainen S., Sainio T., Dynamic modelling of a mixer-settler in copper solvent extraction process, Topical issues of rational use of natural resources, April 22-24, 2015, St. Petersburg, Russia. Oral presentation.

Nomenclature

Latin alphabet

A  deprotonated cation exchange extractant
B  parameter
a  activity
c  molar concentration  mol/L
E  extent of extraction  %
F  flowrate  L/s
HA protonated cation exchange extractant
I  ionic strength  mol
k  reaction rate constant
K  equilibrium constant
M  extractable cations
P  purity
r  generation rate of an individual species  mol/(Ls)
Y  yield

Greek alphabet

α  parameter
γ  activity coefficient
φ  holdup
ϑ  stoichiometric coefficient of the species
σ  standard deviation of the parameter estimates

Letter-like symbols

â the distance of the closest approach of ions in the extended
铑 rate of an elementary reaction  mol/(Ls)

Superscripts

exp measured experimental data
mod data calculated with model

Subscripts

Aq aqueous phase
C complex
D distribution
DH Debye–Hückel
Dim dimerisation
Nomenclature

f forward
l number of a process step
Org organic phase
pur purification
r reverse
tot total

Abbreviations

ACO ant colony optimization
BO barren organic
cv constructive variables
DoE design of experiments
EoL End-of-life goods
esv equipment state variables
irv inlet regime variables
LLX liquid–liquid extraction
LE lean electrolyte
LO loaded organic
MCMC Markov chain Monte Carlo
orv outlet regime variable
PLS pregnant leach solution
PNO pre-neutralised organic
PPI purification performance index
RE rich electrolyte
SCI separation cost indicator
SE standard error
SSR sum of the squared residuals
1 Introduction

Background

In this thesis, the term liquid–liquid extraction refers to the distribution of a solute between two immiscible liquid phases that are in contact with each other. Usually, one of the phases is an aqueous solution and the other, generally, an organic solvent (Figure 1a). The distribution of a solute between the phases may be caused by a difference in its solubility, in nonreactive systems, or by chemical reactions producing species that preferentially distribute into one of the phases. The former is referred to as nonreactive extraction, and the latter as reactive extraction.

![Figure 1. A schematic representation of liquid–liquid extraction. a) The initial state of the aqueous and organic phases; the solute M is usually dissolved in only one of the two liquids; b) Mixing of the phases with the formation of a dispersion, in which the solute redistributes between the phases until equilibrium is reached; c) The phases separate, when the mixing is stopped.](image)

In industrial applications, the transfer of a solute from one phase to another occurs in a dispersion formed when the phases are vigorously mixed (Figure 1b). The phases have different densities, causing them to separate when the mixing is stopped (Figure 1c). The change in colour of the phases in Figure 1 from a) to b) indicates that a solute, M, is redistributed between the phases, and that phase equilibrium is reached during the mixing.

The industrial use of liquid–liquid extraction largely began in the 1940s and 1950s, with its application to uranium production and for the reprocessing of irradiated nuclear materials in the U.S. Manhattan Project (Rydberg et al., 2004). In the following decades, the technology was developed extensively and introduced as a separation and purification process in a large number of chemical and metallurgical industries. In the present day, liquid–liquid extraction is a widely employed separation method for the refining of a range of elements and chemicals in diverse applications, for example in extractive
metallurgy, biotechnology, the food industry and in the production of pharmaceuticals, industrial chemicals and petrochemicals.

Hydrometallurgy is technology, within the field of extractive metallurgy, involving the use of aqueous chemistry for the recovery of metals from ores, concentrates and recycled or residual materials at ordinary temperatures\(^1\). In hydrometallurgy, liquid–liquid extraction is frequently referred to as *solvent extraction* and is used for the processing of a variety of base and precious metals (Ritcey, 2006a; Sole, 2008). Demands for higher product purity, less pollution, and the need for the recovery of valuable metals from complex matrices and lower grade resources, together with the efficiency and high selectivity of liquid–liquid extraction are the driving forces behind its use in hydrometallurgy (Ryberg *et al.*, 2004).

Due to its high selectivity, and ability to treat large volumes, liquid–liquid extraction is commonly used in hydrometallurgy for separation and purification in large-scale processes for the production of metals from primary raw materials. High-purity copper, for instance, is produced through a combination of the leaching of oxidized copper ore, or sulfide copper concentrate in sulfuric acid, followed by concentration and purification by liquid–liquid extraction with a hydroxyoxime extractant and, finally, recovery of copper by electrowinning (Kordosky, 2002; Molnar and Verbaan, 2003). This process is the most widely used application of liquid–liquid extraction in the metallurgical industry (Kordosky, 2002; Tamminen, Sainio & Paatero, 2013). Another major application of liquid–liquid extraction in hydrometallurgy is the separation of nickel and cobalt (Flett, 2005). Plants using the technology in these applications process solutions resulting from ores, concentrates, precipitates mattes, various scrap materials, and waste effluents with organophosphorus acid extractants (Ritcey, 2006a). Other major applications of liquid–liquid extraction are the recovery of uranium (Zhu, Pranolo & Cheng, 2016), separation of rare earth elements (Innocenzi *et al.*, 2018) and precious metals (Cieszynska and Wieczorek, 2018).

The demand for metals used in new energy technologies, and the production of portable electronic devices, is increasing due to the world’s increasing population and continuing technological development (Reuter *et al.*, 2013). At the same time, high-quality ores are being depleted, and there is an overall decrease in ore-grades (Reuter *et al.*, 2013). It is important to note that almost all metals used in new energy technologies, and the production of portable electronic devices, are by-products from the production of base metals, with the exception of the rare-earth elements and lithium (Reuter *et al.*, 2013; Technology Metals Research, 2018). However, the stocks of metals in use by society are increasing, and at the end of their use, this metal stock becomes an increasingly valuable resource contained in End-of-life (EoL) goods (Reuter *et al.*, 2013; Graedel *et al.*, 2011). It is of increasing importance to ensure that technologically valuable metals do not

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\(^1\) In contrast to pyrometallurgy where high temperatures are used that causes solid materials to melt.
disappear together with the EoL goods into landfill, or into processes that cannot fully recover the most valuable and scarce elements.

Liquid–liquid extraction is well suited to the recovery of metals from low grade, mixed metal ores and can be adapted to the recovery of metals from secondary sources (Wilson et al., 2014; Forsén and Aromaa, 2013). Secondary raw materials are often characterised by high complexity and may contain combinations of elements that do not occur in primary raw materials (Forsén and Aromaa, 2013; Reuter et al., 2013). Due to its high selectivity, and wide range of available extractants, liquid–liquid extraction is especially suitable for these purposes and is often successfully included in process flowsheets for the recovery of valuable metals from secondary raw materials. Numerous examples of recycling Li-ion battery wastes (Granata et al., 2012; Mantuano et al., 2006), spent catalysts (Zhao et al., 2017; Paiva et al., 2017), and discarded LCD panel glass (J. Yang, Retegan & Ekberg, 2013; Virolainen, Ibana & Paatero, 2011) are found in the scientific literature. Thus, the key characteristics of liquid–liquid extraction – flexibility, the ability to separate elements with similar physical properties from both concentrated and dilute solutions, high extraction efficiency and low emissions – assure it a promising and important role, not only in primary metals production but also in metals recycling.

Process simulation in chemical engineering is the representation of a chemical process by a mathematical model, which is then solved to obtain information about the performance of the process (Motard, Shacham & Rosen, 1975). As discussed by Reuter et al. (2013), advanced modelling and simulation tools play an important role in metal recycling. Mechanistic models are based on the physics and chemistry that lie beneath separation processes and provide detailed information on their thermodynamic and kinetic limitations. These mechanistic models are a tool that can be used in determining the optimal combination and arrangement of recycling processes. Mechanistic modelling allows the prediction of complex nonlinear behaviour within the extraction processes. It facilitates the testing of different process options and configurations as well as assessing the performance of the processes for various raw material qualities. Equilibrium-based simulation of separation processes gives an estimate of the steady-state of a process under given operating conditions. Dynamic simulation can aid in the design of process and control system, in order to ensure that the process can operate and meet product specifications when the process deviates from steady-state operation (Komulainen et al., 2006; Komulainen et al., 2009; Moreno, Pérez-Correa & Otero, 2009).

Mechanistic modelling of a liquid–liquid extraction system depends upon the availability of information on the extraction mechanism, such as the reaction path, stoichiometry of the extraction reactions, and distribution equilibria. Slope analysis is a technique frequently used in liquid–liquid extraction studies to deduce a stoichiometry of the extraction reactions from equilibrium experiments in dilute aqueous and organic solutions (Batchu, Sonu & Lee, 2014; Mansur, Slater & Bicaia, 2002; Guimarães and Mansur, 2017; Lum, Stevens & Kentish, 2012; Geist et al., 2006). The stoichiometry is determined using the linearization of the mass action law equation of an extraction reaction. Slope analysis can only be used with a very low metal concentration in both phases, and with...
changes to the liquid phases that are very small and do not cause the activity coefficients of the species involved in the liquid–liquid extraction to change.

During the development of a liquid–liquid extraction process, McCabe-Thiele analysis is employed in flowsheet design to estimate the number of theoretical stages required to obtain a specified level of process performance and for evaluating the performance of an operating circuit (Rydberg et al., 2004; Thomas, 2010). McCabe-Thiele analysis of a counter-current cascade (Figure 2) involves the graphical construction of an isotherm, an operating line, and the stepwise evaluation of the number of stages (Rydberg et al., 2004). The extraction and stripping isotherms define the capabilities of the extractant in both the extraction and striping sections of the plant (Rydberg et al., 2004; Thomas, 2010). The data for the isotherms can be collected experimentally using one of two methods. The first employs variation of the phase ratio of the aqueous and organic phases; the second involves recontacting the organic phase with fresh aqueous phase until the saturation loading of the extractant is reached. Generally, the first method is recommended due to its ease of implementation (Rydberg et al., 2004).

![McCabe-Thiele diagrams for a counter-current cascade](image)

**Figure 2.** McCabe-Thiele diagrams for a counter-current cascade. a) Loading step; b) Stripping step. Blue lines – extraction and strip isotherms; red lines – operating lines; black lines – lines used to determine the number of process stages.

The extraction isotherm defines the maximum amount of a solute that may be extracted from the pregnant leach solution for each organic-to-aqueous volumetric ratio. According to the first method of data collection, the organic phase is mixed with the leachate at various phase ratios until equilibrium is obtained (the equilibrium pH of the aqueous solution must be the same in every point on the isotherm). The organic and aqueous phase are separated, and the solute concentration in each phase analysed. The data are plotted on the diagram (Figure 2a), with organic solute concentration on the y-axis and aqueous on the x-axis. The position and shape of the isotherm are primarily affected by the solute
concentration in the leachate, the acidity in the leachate, the choice of extractant, and the extractant concentration.

The stripping isotherm (Figure 2b) defines the maximum amount of a solute that may be removed from the loaded organic for each phase ratio. The loaded organic phase is mixed with stripping aqueous solution at various phase ratios until equilibrium is reached. The organic and aqueous phase are separated, and the solute concentration in each phase analysed. The data are plotted (Figure 2b), with the aqueous solute concentration on the y-axes and organic concentration on the x-axis.

The number of stages in an extraction step for a given extraction isotherm and leachate concentration is determined in the following way. First, a vertical line, AB, is drawn starting from point A, which corresponds to the solute concentration in the leachate, until it crosses the operating line. Then, a horizontal line, BC, is drawn until it crosses the isotherm. The point C indicates the equilibrium concentration of a solute in the aqueous and organic phases after the first loading stage. Then, a vertical line, CD, is drawn until it crosses the operating line. Again, a horizontal line, DE, is drawn. The point E indicates the equilibrium concentration of a solute in the aqueous and organic phases after the second loading stage. The point G indicates the solute concentration in the raffinate. The two-stage extraction provides \(\frac{1.2^{-0.1}}{1.2} \cdot 100\% \approx 92\%\) recovery of the solute. Only two stages are considered here; more stages can be, however, considered to achieve higher solute recovery. The slope of the operating line shows the phase ratio, while its position is determined by the concentrations of the organic and aqueous streams that enter and leave the extraction. The same procedure is applied for the stripping step (Figure 2b); however, the starting point is the concentration of a solute in the loaded organic phase.

This simple graphical method found wide application in liquid–liquid extraction. For example, McCabe-Thiele diagrams were used to analyse different process configurations in coupled multistage extraction and stripping circuits in an extraction process by Gálvez et al. (2004). However, the method heavily relies on equilibrium data in the form of extraction and stripping isotherms, which can vary depending upon the extractants used, their concentrations, and acidity in the aqueous phase. Quite small changes in aqueous phase composition or in phase ratio can change the isotherms and cause dramatic effects on the performance of a counter-current cascade (Rydberg et al., 2004). Moreover, McCabe-Thiele analysis does not give a good indication of the transfer of impurities in the process.

The application of modern computational techniques has made the use of McCabe-Thiele diagrams largely redundant (Rydberg et al., 2004). It is often easier, and more accurate, to calculate the cascade directly using numerical models. For example, an empirical modelling approach, relying on response surface methodology, has been used to design a separation process for a system with competing extraction reactions by Olivier, Dorfling & Eksteen (2012) and Bourget et al. (2011). The method allows for the transfer of impurities to be assessed. However, it requires large variations in the experimental data to accurately predict process performance in a wide range of operating conditions. On the
other hand, the mechanistic modelling offers higher flexibility and accuracy in process design.

Mechanistic models are based on the laws of chemistry and, therefore, are able to predict complex process behaviour in systems with competitive extraction. In the mechanistic modelling of an extraction equilibrium, a set of reaction equations, which is thought to describe the actual extraction mechanism is assumed (Whewell and Hughes, 1979; Bart and Rousselle, 1999; Agarwal et al., 2012; Lum et al., 2012). The stoichiometry of the extraction reactions, determined using the slope analysis, is essential information for the subsequent mechanistic modelling. A set of nonlinear mass action and mass balance equations, corresponding to the set of reaction equations, is solved in order to calculate the speciation in both aqueous and organic phase. Models developed in this way give an opportunity to investigate the extraction performance in a wide range of conditions and elucidate the limitations of the process. However, validation of the models with a reasonable amount of experimental data is still required.

When the kinetics of an extraction process is studied, dynamic models are developed to help infer the extraction mechanism, the limiting step of the extraction, and estimate the rate at which the extraction equilibrium is approached (Lyon, Utgikar & Greenhalgh, 2017; Flett, Okuhara & Spink, 1973; Bart and Rousselle, 1999; Torkaman et al., 2014). Reactor modelling aims to assess the extraction performance depending on the interplay of hydrodynamics and mass transfer in different contactors (mixing tanks, settlers or columns). For that purpose, such computationally intensive modelling tools as computational fluid dynamics (Hlawitschka et al., 2017; Lane et al., 2016; Ye et al., 2016) and particle population balance modelling (Fang et al., 2017; Alzyod, Attarakih & Bart, 2016; Korb and Bart, 2017) are used.

Rintala, Lillkung & Aromaa (2011) discussed the development of a method that could support the synthesis of an entire hydrometallurgical process, consisting of various subprocesses. The method would be required to enable automated process synthesis, by selecting and sequencing unit operations within a process to produce products of a certain quality from a specified raw material. The method could employ either the available experimental data on the performance of process options or the established process models or both at the same time. An example of such a task is the design of a process consisting of multiple liquid–liquid extraction circuits with different extractants employed in each of them to produce pure solutions of valuable metals from a leachate containing a complex mixture of the metals. To synthesise a complete hydrometallurgical process, leaching, solution purification and product recovery are required to be considered for all the target metals from a raw material. It is a complex combinatorial problem that is currently solved manually based on previous experience (Rintala et al., 2011; Gálvez et al., 2004; Zhang et al., 1998). There are examples of automated synthesis of chemical processes (Shafiee et al., 2017; Schuldt and Schembecker, 2013; Cziner et al., 2005). However to the author’s knowledge, the automated synthesis of hydrometallurgical processes has not been studied.
Although numerical models of separation systems and contactors continue to be developed and improved all the time in liquid–liquid extraction, they are often under-utilised (Ritcey, 2006a). The explanation for this under-utilization of the models can be found in the fact that deep knowledge of extraction phenomena and computing skills are often required, not only for development of the models but also for their fruitful utilisation. Conventionally, the mathematical models usually presented in the scientific literature, for example the models presented by Whewell and Hughes (1979) and Agarwal et al. (2012), are used to explain the extraction of a single metal in a single phase contact and in a rather narrow range of conditions. However, the models applicable to simulation of counter-current separation of a multicomponent mixture have high industrial relevance (Bourget et al., 2011). In addition, the solution of the sophisticated numerical models requires considerable computing power and consumes time. Nonetheless, the utilization of numerical models and process simulation tools is advantageous in process analysis, optimization, and control.

Research gaps and motivation

As has been discussed above, modelling and simulation can play an important role in the development of hydrometallurgical processes, both in general and in liquid–liquid extraction in particular. With rare exceptions, the liquid–liquid extraction of only single metals in a single phase contact is usually modelled. However, simulating a competitive extraction of multiple metals can lead to a better understanding of process behaviour and, consequently, to higher performance efficiency. Although simulation of new counter-current processes for the separation of several metals can reveal insights into challenges encountered in pilot scale experiments, it is rarely done. The development of simulation tools has significant industrial relevance, since the tools can be used in process analysis, optimization, and control. In addition, typically no computer-aided methods are used in the early stages of hydrometallurgical process development, when a promising process route has to be synthesised (Rintala et al., 2011). Therefore, the motivation for the current research was found in the need to decrease the costs and improve the efficiency of hydrometallurgical process development.

Research problems

The purpose of the current research was to decrease the cost and improve the efficiency of hydrometallurgical process development. The application of process simulation tools in hydrometallurgical process development was chosen as a mean to achieve this purpose. Therefore, the aim of the research was to develop simulation tools applicable to the development of liquid–liquid extraction processes and for the automation of hydrometallurgical processes. To achieve this aim, the following research problems were identified and respective objectives were formulated.

1. Mechanistic modelling of liquid–liquid extraction of metals
The objective was to develop numerical models to simulate the equilibrium of liquid–liquid extraction of metals. These mechanistic mathematical models for the liquid–liquid
extraction of metals provide an opportunity to investigate the extraction performance in a wide range of conditions by numerical simulation, and to elucidate the limitations of the process. The application of mathematical modelling and simulation can decrease the costs encountered during process development.

2. **Numerical methods for mechanistic modelling and simulation**

In the current research, the objective was to test different numerical methods that could enable mechanistic modelling of liquid–liquid extraction equilibrium of metals. The mathematical and statistical methods applicable for analysing the reliability of the modelling results had to be checked. Such information is important for the development of a general approach to the modelling and simulation of liquid–liquid extraction processes.

3. **Automated process synthesis**

The objective was to develop a method for the automated synthesis of hydrometallurgical processes to enable exploration of new process alternatives. In the initial stages of hydrometallurgical process development, the synthesis of possible process routes and comparison of process alternatives is traditionally done based on previous experience, as well as on extensive experimentation. Computational power is rarely used to support the decisions.

**Scope and limitations**

The main focus of the current research is on methods to enhance hydrometallurgical process development using computer aids. Mathematical modelling and simulation is seen here as a tool for fast and efficient process development. Although significant effort is needed to develop process models, the results of the process simulation can decrease costs in further process development stages. In this study, the leaching and product metal recovery steps are merely considered as process boundary conditions in the design of liquid–liquid extraction processes, whereas all the hydrometallurgical process steps are considered in the method developed for automated process synthesis. The original feature of the research presented in this thesis is that the numerical methods applicable to modelling, simulation, and process development are studied along with chemistry and engineering aspects of the extraction processes under consideration. In addition, the mechanistic models of the liquid–liquid extraction processes developed in the current thesis allow more in-depth study of these processes.

**Structure of thesis**

This thesis comprises two main parts: a summary and four papers published in international scientific journals, given as appendices. The summary consists of six chapters. The introduction, Chapter 1, presents the research background, explains the motivation for the research and sets-out the objectives of the studies. The description of liquid–liquid extraction of metals and its place in hydrometallurgy, extraction mechanisms, reactor design considerations, and optimisation of process performance are
given in Chapter 2. The approaches to modelling extraction equilibrium and simulation of liquid–liquid extraction cascades developed in this study are presented in Chapter 3. Two case studies: copper extraction and separation of cobalt, nickel, and lithium are also introduced. Chapter 4 contains descriptions of the methods developed for process synthesis and process design in hydrometallurgy. The main results obtained in the current thesis work are presented and discussed in Chapter 5. The conclusions and outlook for future research based on the presented results are given in Chapter 6.
2 Liquid–Liquid Extraction of Metals

Hydrometallurgical metal recovery typically consists of leaching, solution concentration and/or purification, and, finally, product metal recovery. Liquid–liquid extraction is frequently employed for the concentration and/or purification operations. A scheme of a hydrometallurgical process, in which liquid–liquid extraction is involved, is illustrated in Figure 3. The aqueous feed stream, pregnant leach solution, which requires concentration and/or purification, is contacted with the stripped organic phase in an extraction circuit. By means of chemical reactions of metal ions from the aqueous phase and extractant molecules from the organic phase, hydrophobic complexes are formed. These hydrophobic complexes may then enter the organic phase. The loaded organic phase is then contacted with the strip liquor in the stripping circuit, and the extracted metal is transferred back into another aqueous phase. The concentrated and purified metal in the loaded strip liquor is suitable for the product metal recovery stage. The organic phase is recycled between the extraction and stripping circuits in the process.

Figure 3. A hydrometallurgical process to recover metals from raw materials, where liquid–liquid extraction is responsible for solution concentration and purification.

As will be discussed in Section 2.2, depending on the properties of the metal species present in the pregnant leach solution, the extractants of different types (acting according to different extraction mechanisms) can be employed in liquid–liquid extraction processes. Along with an extractant, the organic phase can contain phase modifiers (to enhance phase separation or to increase the solubility of certain species), antioxidants (to retard or prevent degradation of components of the organic phase), phase-transfer catalysts (to improve the reaction kinetics) and synergistic extractant (to improve extraction or separation factors) dissolved in an inexpensive hydrocarbon diluent (to decrease the viscosity of the organic phase) (Sole, 2008).
Control of the extraction and stripping steps can be realized by changing acidity (pH-swing), counteranion concentration (anion-swing) or temperature in the process steps, depending on the type of extractant. In addition, special techniques such as redox stripping or stripping with complexing agents are sometimes needed to increase stripping efficiency. For example, reductive stripping under vacuum of iron(III) from di-(2-ethylhexyl)phosphoric acid (D2EHPA), using zinc powder as a reducing agent, was suggested (Lupi and Pilone, 2000). Efficient stripping of actinides from the loaded organic phase (extractant CyMe4-BTBP) with sodium glycolate solution as a complexing agent was shown to be possible (Geist et al., 2006; Andersson et al., 2009).

A generalised liquid–liquid extraction circuit is illustrated in Figure 4. Commercial processes are usually operated counter-currently, with the aqueous and organic streams flowing in opposite directions in order to maximise extraction (or stripping) and separation efficiencies (Sole, 2008). A scrub and wash steps may be included in the extraction circuit, depending on a particular application. Washing is used for the physical removal of impurities from the organic phase. A wash step may be included to minimise the loss of organic phase by entrainment in the aqueous phase, or to minimise carry-over of contaminants into the loaded strip liquor. The wash step may also be located after the scrub, strip, or regeneration steps, depending on the process chemistry or the purity requirements of the product. For example, in the extraction of copper from cuprous chloride solution, using a liquid ion exchange reagent, the copper-loaded organic solution must be washed with copper sulfate electrolyte to prevent the transfer of excess chloride to the electrowinning step (Lu and Dreisinger, 2014).

Figure 4. Generalised liquid–liquid extraction circuit.

The extraction process is rarely specific so that impurities may be co-extracted with the target metal. A scrub step is sometimes used between the extraction and stripping steps
for the chemical removal of impurities from the organic phase. An aqueous scrub liquor is introduced to remove unwanted co-extracted species from the loaded organic phase by displacing the impurities with the more strongly complexed target metal. For example, zirconium nitrate was used as a scrubbing agent in the process for recovery and separation of zirconium and hafnium from raffinate stream of zirconium purification plant with Mixed Alkyl Phosphine Oxide as the extractant (Pandey et al., 2016). In the scrubbing step, co-extracted hafnium was displaced from the organic phase by zirconium in the scrub solution.

Some processes also include an extractant regeneration step. A regeneration step is employed to convert the extractant to the appropriate chemical form required for extraction. For instance, stripping with strong acid may convert an extractant to its protonated form. However, extraction may require the extractant in the ammonium form to facilitate pH control. In that case, a regeneration step could be employed for the conversion of the protonated form of the extractant to the ammonium salt form. The separation of cobalt and nickel from other impurities in the leachate of spent Li-ion batteries with Cyanex 272 is an example of such a process (Virolainen et al., 2017).

2.1 Equipment design under mass transfer

There are three fundamental phenomena (Figure 5) that determine the performance of a liquid–liquid extraction of metals: chemical reactions, mass transfer between the dispersed and continuous phases, and the hydrodynamics in the contactor (Bart, 2002). Although a few metal compounds are sufficiently covalent to be extracted into an inert organic phase (e.g. RuO₄, OsO₄, GeCl₄, AsCl₃, SbCl₅, and HgCl₂), for a number of reasons, such as their ease of hydrolysis, this type of compound is unlikely to feature in a commercial extraction process (Rydberg et al., 2004). In general, metal salts exist in aqueous solutions as hydrated species and, as such, are incompatible with nonpolar organic solutions typically used in hydrometallurgy. Therefore, species must be reacted with an organic compound to make them more hydrophobic (see Section 2.2 for more details) to achieve extraction. Thus, the extraction reactions are usually the core of an extraction process. The extraction reactions normally encountered in the liquid–liquid extraction of metals are usually reversible, and the equilibrium of the reactions largely determine the extraction performance. The kinetics of extraction is a function of both the various chemical reactions occurring in the system and the rates of diffusion of the various species involved in the extraction process. The mass transfer rate determines the transport of the reactants to the interface and the products of the reactions from the interface. In turn, the rate of mass transfer is strongly influenced by hydrodynamics in a contactor. Hydrodynamics can affect the drop size distribution and dispersed phase holdup, which, in turn, determine interfacial area and droplet residence time and, thus, extraction efficiency (Korb and Bart, 2017; Darmana et al., 2007).
Adequate contact between the two phases is necessary to ensure that good mass transfer of the extracted and stripped species across the organic-aqueous interface occurs. Depending on various physical and chemical factors, inherent in the extraction system, different contact systems may be appropriate. Continuous counter-current extraction can be performed in stagewise or differential contactors.

A typical contactor for stagewise extraction is a mixer-settler (Figure 6a). This comprises some means for mixing the two phases and an adjoining means for separating them. The mixer provides adequate interfacial area for the extraction to take place, without creating such small droplets that they will not then settle efficiently and, provided there is sufficient residence time, for the desired degree of extraction to take place. Settlers typically comprise a relatively large shallow tank, rectangular in shape, which provides sufficient residence time for the mixed phases to separate while they flow from an inlet at one end to the two outlets for the separated phases at the other. Mixer-settlers are assembled in mixer-settler cascades to enable continuous stagewise extraction.

Figure 6. A schematic representation of a mixer–settler and column.
Mixer-settlers are usually preferred for systems that exhibit poor phase disengagement, slow kinetics, and thus require a considerable settling area. Stage efficiencies in this configuration are high, meaning that a close approach to equilibrium is achieved. Mixer-settler circuits are usually employed when a small number of extraction stages (2-4) is required. However, the separation of rare earth elements that requires a large number of equilibrium stages is usually performed in mixer-settler circuits, due to slow kinetics (Ryu et al., 2013; Belova, 2017).

Differential extraction in a column (Figure 6b) allows contact between the two phases to be continuous and, therefore, permit a large number of possible theoretical stages, thereby maximising mass-transfer. They are useful for processing low flow rates and for systems that exhibit a tendency to form emulsions. Another important advantage of columns is that the extraction and stripping processes occur in a fully enclosed system. This is critical for systems in which toxicity is an issue. Columns take up very little floor space but require considerable headroom; mixer-settler requirements are the opposite (Sole, 2008). Also, there are examples of processes in which both mixer-settlers and columns are employed for different tasks. For example, in THORP design, pulsed columns are used in the highly active and plutonium purification cycles to allow critically safe operation with the high plutonium concentrations, while mixer-settlers are used in a uranium purification cycle (Phillips, 1993). Centrifugal contactors, characterised by very short contact time, found very limited application in liquid–liquid extraction in hydrometallurgy (Sole, 2008; Rydberg et al., 2004).

2.2 **Optimal operation of liquid–liquid extraction**

The optimization of separation processes aims to produce the purest possible product at the highest yield and lowest possible cost, and under the most favourable environmental and safety conditions. Liquid–liquid extraction in hydrometallurgy is a complex operation involving multicomponent extraction, where target metals are separated from impurities present in the feed solution (Pinto et al., 2009). The feed from upstream leaching usually contains several metals leached from the raw material, and the extractants used are never absolutely selective. Thus, impurities are always co-extracted with the target metals. The equilibrium distribution and kinetics of extraction of different species determine selectivity in an extraction process.

The International Union of Pure and Applied Chemistry (IUPAC) (Rice, Irving & Leonard, 1993) gave the recommendations on the definitions of the quantitative description of liquid–liquid extraction systems. The same definitions are used throughout this thesis.
The partitioning between the two phase of a particular solute, $M_i$, (usually measured at equilibrium) is described by distribution ratio, which is defined as “the ratio of the total analytical concentration of a solute in the extract (regardless of its chemical form) to its total analytical concentration in the other phase”, Eq. (1). Several solutes are usually involved in the extraction in the separation systems, the distribution ratio for the various solutes are indicated by $D_{M1}$, $D_{M2}$, etc. Since the solute partitions differently, depending on extraction conditions, the value of the distribution ratio depends on the extraction conditions.

$$D_i = \frac{[M_i]}{[M_i]} \quad (1)$$

The solutes can be separated from each other by liquid–liquid extraction with a particular extractant only if the distribution ratio of the solutes are different. Therefore, the ability of the solutes to be separated is described by the separation factor, Eq. (2), defined as the ratio of the respective distribution ratios of two solutes measured under the same conditions. By convention, the solutes designated to $M_1$ and $M_2$ are chosen so as to make $\alpha_{M_1/M_2} > 1$.

$$\alpha_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}} \quad (2)$$

In industrial applications, it is more practical to use the fraction extracted $E$ (recovery) defined as the fraction of the total quantity of a substance extracted by the extractant under specified conditions, Eq. (3), where $[M_i]_0$ and $[M_i]$ denote the concentrations of a solute at the start and after the extraction, respectively, under the assumption that the extractant did not contain the solute initially.

$$E_i = 1 - \frac{[M_i]}{[M_i]_0} \quad (3)$$

If the solute from the aqueous phase is extracted with $n$ successive portions of organic phase, the phase volume ratio (organic/aqueous) being $V_{org}/V_{aq}$, the fraction extracted is
given by Eq. (4). Eq. (4) is valid only with the assumption that the distribution ratio is constant in all the successive phase contacts. This assumption is not always valid in industrial applications, where pH variation can be observed in the process stages.

\[ E_i = 1 - \left( \frac{V_{\text{org}}}{V_{\text{aq}}} D_i + 1 \right)^{-n} \]  

\[ (4) \]

The fraction extracted for a solute in a continuous counter-current extraction process with \( n \) steps and phase ratio \( \frac{V_{\text{org}}}{V_{\text{aq}}} \) in each step is given by Eq. (5). Again, Eq. (5) is only valid if the distribution ratio is constant.

\[ E_i = 1 - \frac{V_{\text{org}}}{V_{\text{aq}}} D_i - 1 \left( \frac{V_{\text{org}}}{V_{\text{aq}}} D_i \right)^{n+1} - 1 \]  

\[ (5) \]

Purity of the target element in the product stream is an important measure of extraction performance in industrial applications, since product purity directly affects the product price. Purity of the target species in the product streams is defined by Eq. (6).

\[ P = \frac{\text{mass of species } j \text{ in the product}}{\sum \text{mass of all species in the extract}} \]  

\[ (6) \]

As has been discussed above, the primary objective of a liquid–liquid extraction plant in hydrometallurgy is typically to achieve as high a recovery of a target metal as possible (minimising losses of the target metal to raffinate) while minimising the co-extraction of impurities (producing the highest quality metal product, thereby reducing further purification costs). A multistage operation inevitably becomes necessary in order to achieve the required separation performance, giving rise to complex circuits with several loading, scrubbing, and stripping stages. The optimal operation of an extraction circuit is achieved by means of a careful choice of operating conditions. The efficiency of the extraction of a target metal can be increased by adding extraction and stripping stages to
the circuit, increasing the extractant concentration, adjusting contact time(s) and mixing conditions or changing the relative organic and aqueous flowrates (the O/A ratio). Industrial liquid–liquid extraction circuits are easily controlled and forgiving, allowing a consistent product stream composition (Schlesinger *et al.*, 2011a).

### 2.3 Metal extraction mechanisms

As discussed in Section 2.1, metal salts normally exist in the aqueous phase as hydrated species, which are hydrophilic and thus do not transfer into nonpolar organic solvents typically used in hydrometallurgy. A hydrophilic inorganic solute must therefore be rendered hydrophobic and lipophilic in order to enter the organic phase (Ryberg *et al.*, 2004). In general, three metal extraction mechanisms are known:

- Reaction of the metal cation, with suitable anions, to produce a neutral complex that is preferentially dissolved in the organic phase;
- Formation of an ion pair that is preferentially dissolved in the organic phase;
- Replacement of hydrated water molecules by an organic solvating reagent.

Reagents that are capable of such reactions are termed acidic, basic (or ion pair) or solvating. Therefore, a commercial metal-extracting reagent used in reactive liquid–liquid extraction is selected depending on the nature of the extractable metal species present in the aqueous solution. Wilson *et al.* (2014) based their classifications of the metal extraction mechanisms on the coordination chemistry and distinguished the extraction mechanisms as the extraction of metal cations, the extraction of metalate ions, and metal salt extraction.

Some extractants can, however, change their extraction mechanism under extreme conditions, or depending on the metal being extracted. The extraction of actinides from nitric acid with di(2-ethylhexyl)phosphoric acid (DEHPA) exemplifies the change of the extraction mechanism (Svantesson *et al.*, 1980). The distribution coefficient of curium(III) and americium(III) first gradually decreases as the concentration of the nitric acid increases, but with exceptionally high nitric acid concentration, starts to go up again as the nitric acid concentration increases. On the other hand, the distribution coefficient of neptunium(III) first increases as the concentration of nitric acid increases, but then at extremely high nitric acid concentration, starts to go down as the nitric acid concentration increases.

**Metal cation extraction**

The extraction of a metal cation from an aqueous phase containing a weak inner sphere ligand (for example sulfate ion) is realized by the generation of a charge-neutral complex, $\text{MA}_2$, that is preferably dissolved in the organic phase by combining anionic ligand $\text{A}^-$.
with the metal cation $M^{z+}$, as in Eq. (7). The pH-dependence of the equilibrium makes it possible to control the loading and stripping steps by varying the pH of the aqueous phase with which the organic phase is in contact.

$$z\text{HA} + M^{z+} \rightleftharpoons \text{MA}_z^- + z\text{H}^+ \quad (7)$$

This extraction mechanism was considered in the extraction of copper and iron through the use of a hydroxyoxime-type extractant Acorga M5640 in Publications I and II. The same mechanism explains the extraction of base metals by organophosphorus extractants (phosphinic, phosphonic and phosphoric acids). However, the stoichiometry $\text{MA}_2(\text{HA})_2$ of the complexes with divalent metal cations is usually observed when the extractant is present in excess due to self-adduct formation. This extraction mechanism was considered in the extraction of cobalt, nickel, and lithium by Cyanex 272 in Publication III.

**Metalate extraction**

At high concentration of a strong inner sphere ligand (for example, chloride ion), metalate ions, $\text{M}X_{2}^{b-}$, are very likely to be present in the aqueous solution. The metalates can be transferred to the organic phase by the formation of outer sphere ion pairs. This can be achieved in two ways. Mixing a solution of a neutral extractant, $\text{A}^-$, with an acidic aqueous solution can lead to protonation of the extractant and the “pH-swing” process, Eq. (8). Loading is favoured by lowering the pH of the aqueous phase and stripping by raising the pH.

$$b\text{A}^- + b\text{H}^+ + \text{M}X_{2}^{b-} \rightleftharpoons (\text{AH})_b\text{M}X_{z}^- \quad (8)$$

Alternatively, an extractant that carries a permanent positive charge, $\text{A}^+$, can be employed in an anion exchange process, Eq. (9). In this case, loading and stripping are influenced by variation of the concentration of the counteranion $Y^-$ in an “anion-swing” process.

$$b\text{A}^+ + \text{M}X_{2}^{b-} \rightleftharpoons (\text{A})_b\text{M}X_{z}^- + bY^- \quad (9)$$
For example, the extraction of Pt(IV) from chloride solution by Aliquat 336 was studied by (Fontàs, Salvadó & Hidalgo, 1999), and the extraction mechanism was found to be

\[
2R_4N\text{Cl} + [PtCl}_4]^{2-} \rightleftharpoons (R_4N)_2[PtCl}_4] + 2Cl^-
\] (10)

The structure of assemblies formed in metalate extraction processes are not fully understood (Wilson et al., 2014). They involve electrostatic, hydrogen bonding, and other supramolecular interactions.

**Metal salt extraction**

It is possible to generate charge-neutral complexes $\text{MX}_z(A)_b$ that are preferably dissolved in the organic phase by using a neutral reagent $\text{A}$, which effectively solvates the metal salt, $\text{MX}_z$, according to Eq. (11). The solvation extractant molecules may be coordinated in the inner or outer sphere, or both. The metal salt extraction operates on an “anion-swing” mechanism.

\[
b\overline{\text{A}} + \text{MX}_z \rightleftharpoons \text{MX}_z(A)_b
\] (11)

In the PUREX process, first developed for the recovery of plutonium and uranium, the metal salt extraction mechanism is used in the extraction of an uranyl cation, with two molecules of tri-n-butylphosphate (TBP), Eq. (12) (Irish and Reas, 1957; Wilson et al., 2014; Rydberg et al., 2004). The extraction and stripping are controlled by variation of the concentration of nitric acid in the aqueous phase.

\[
\text{UO}_2^{2+} + 2\text{NO}_3^- + 2\text{TBP} \rightleftharpoons \text{UO}_2(\text{NO}_3)_2(\text{TBP})_2
\] (12)

### 2.4 Liquid–liquid extraction equilibria

Reactive extraction of metals from aqueous solutions into organic solvents can be achieved through three different extraction mechanisms, depending on the properties of the metals (see Section 2.3). However, the extraction usually occurs through a number of elementary steps. The subdivision of an extraction reaction into its elementary steps is
useful for understanding how the distribution ratio varies as a function of the type and concentration of the reagents.

The chemical reaction equilibria in one or both liquid phase(s) and the distribution between the phases of different species involved in the reactions affect the value of the distribution ratio. The distribution of the species can be measured, and the distribution constant can be defined as the ratio of the concentration of a substance in a single definite form, $S$, in the organic phase to its concentration in the same form in the aqueous phase at equilibrium:

$$K_{DS} = [S]_o/[S]$$

For a chemical reaction, for example Eq. (14), involved in the metal extraction mechanism, the extraction (equilibrium) constant, Eq. (15), can be expressed as the equilibrium constant of the reaction in terms of the reacting species.

$$M^{z+} + zHR \rightleftharpoons MR_z^{z+} + zH^+$$

$$K_{ex} = \frac{[MA_z][H^+]^z}{[M^{z+}][HA]^z}$$

When the thermodynamics of extraction processes is considered, an assumption is made that equilibrium has been established. The extraction chemical reactions can occur at the interface, in the organic phase, and in the aqueous phase (Rydberg et al., 2004; Szymanowski, 1993). However, regardless of the number of stages, or steps, of an extraction process, the total enthalpy change for the extraction is the sum of all changes, according to Hess’s law. Therefore, regardless of a chosen reaction site or the reaction path taken from the initial to the final state, the same prediction, in terms of thermodynamics, of the distribution ratio value can be obtained.

The values of the extraction constants for the elementary reactions and the distribution constants for the species involved in a thermodynamically-consistent extraction process affect the value of the distribution ratio. In the following sections, the mechanisms that usually occur in the extraction of metals are discussed, following the methodology given by (Rydberg et al., 2004). The distribution ratios are defined for each of the mechanisms.
2.4.1 Extraction of inert metal compounds

A small number of almost purely covalent inorganic compounds can be extracted by nonsolvating organic solvents (Figure 7). These stable molecular compounds (e.g. RuO₄, OsO₄, GeCl₄, AsCl₃, SbCl₃, and HgCl₂) are nonelectrolytes, and can be considered inert solutes. However, for a number of reasons, such as their ease of hydrolysis, this type of compound is unlikely to feature in a commercial extraction process (Rydberg et al., 2004).

![Table: Extraction of inert metal compounds]

<table>
<thead>
<tr>
<th>Solute S extracted into organic phase</th>
<th>$\bar{S}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonelectrolyte solute S in aqueous phase</td>
<td>$\uparrow\downarrow$</td>
</tr>
</tbody>
</table>

Figure 7. Liquid–liquid extraction equilibrium of inert metal compounds.

The distribution of the inert solute S (Figure 7), which does not undergo any reaction, either in aqueous, or in organic solutions, except for solubility, follows the Nernst distribution law, and the equilibrium extraction can be described either by a distribution constant $K_{D,S}$, or an equilibrium extraction constant $K_{ex}$:

$$S \rightleftharpoons \bar{S}; \quad K_{D,S} = K_{ex} = \frac{[\bar{S}]}{[S]} \quad \text{(16)}$$

2.4.2 Extraction of coordinatively saturated metal chelates

Chelating organic extractants are able to complex a metal ion through two or more binding sites of “basic” atoms, such as O, N, or S, to form metal chelates. Chelating provides extra stability to the metal complex.

![Table: Coordinationally saturated metal adducts]

<table>
<thead>
<tr>
<th>Coordinationally saturated metal adduct complex in organic phase</th>
<th>$\overline{MA_z}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal ion $M^{z+}$ is complexed by $zA^-$ ligands to form neutral $MA_z$</td>
<td>$\rightleftharpoons M^{z+} + zA^- \overset{\text{complex}}{\rightleftharpoons} MA_z$</td>
</tr>
</tbody>
</table>

Figure 8. Liquid–liquid extraction equilibrium of coordinatively saturated metal chelate type complexes.
An uncharged metal complex $\text{MA}_z$ is formed from a metal ion $\text{M}^{z+}$ (central atom) through a stepwise reaction with the anion $\text{A}^-$ (ligand) of a monobasic organic acid, HA, defining a stepwise formation constant $K_n$, Eqs. (17) and (18), and an overall formation constant $K_{\text{tot}}$, Eq. (19).

$$\text{M}^{z+} + \text{A}^- \rightleftharpoons \text{MA}^{z-1}_1; K_1 = \frac{[\text{MA}^{z-1}_1]}{[\text{M}^{z+}] [\text{A}^-]} \quad (17)$$

$$\text{MA}^{z-1}_1 + \text{A}^- \rightleftharpoons \text{MA}^{z-2}_2; K_2 = \frac{[\text{MA}^{z-2}_2]}{[\text{MA}^{z-1}_1] [\text{A}^-]} \quad (18)$$

$$\text{M}^{z+} + n\text{A}^- \rightleftharpoons \text{MA}^{z-n}_n; K_{\text{tot}} = \frac{[\text{MA}^{z-n}_n]}{[\text{M}^{z+}] [\text{A}^-]^n} \quad (19)$$

The $\text{MA}_z$ complex is lipophilic and dissolves in organic solvents and the distribution constant $K_{D,C}$ of the complex is defined as:

$$\text{MA}_z \rightleftharpoons \text{MA}^-_z; K_{D,C} = \frac{[\text{MA}^-_z]}{[\text{MA}_z]} \quad (20)$$

Taking all metal species in the aqueous phase into account, the distribution of the metal can be written in the form of Eq. (21), which shows that the distribution ratio depends only on the free ligand concentration.

$$D_M = \frac{[\text{MA}_z]}{\sum [\text{MA}^{z-n}_n]} = \frac{K_{D,C}K_{\text{tot}}[\text{A}^-]^z}{\sum K_n [\text{A}^-]^n} \quad (21)$$

However, for practical reasons, it is simpler to use the extraction constant $K_{ex}$ for the reaction

$$\text{M}^{z+} + z\text{HA} \rightleftharpoons \text{MA}^-_z + z\text{H}^+ \quad (22)$$
in which case the $MA_n^{z-n}$ complexes in the aqueous phase are neglected. The relevant equations for the extraction constant and distribution ratio are

$$K_{ex} = \frac{[MA_x][H^+]^x}{[M^{z+}][HA]^z}$$  \hspace{1cm} (23)

and

$$D'_M = K_{ex} \frac{[HA]^x}{[H^+]^z}$$  \hspace{1cm} (24)

Thus only one constant, $K_{ex}$, is needed to predict the metal extraction for given concentrations of protons and extractant molecules. Eq. (24) is valid only when the complexes $MA_n^{z-n}$ can be neglected in the aqueous phase.

As discussed in Section 2.5.1, copper is extracted with hydroxyoxime extractants according to the chelation mechanism. Furthermore, phenolic oximes like LIX 84 can be used to separate palladium(II) and platinum(IV) from chloride solutions (Rane and Venugopal, 2006). Hydroxyoxime forms an extractable 2:1 chelate complex with palladium(II) ($PdA_2$) in acidic solutions, Eq. (25), whilst platinum(IV) is not extracted below pH 8.

$$PdCl_4^{2-} + 2HA \rightleftharpoons PdA_2 + 4Cl^- + 2H^+$$  \hspace{1cm} (25)

An aliphatic extractant LIX63 in a mixture of Solvent 70 and decanol was found to be able to extract copper, cobalt, and nickel from a deep eutectic solvent (formed from choline chloride and lactic acid into mixtures of either Aliquat 336 or DEHPA diluted with hydrocarbons) (Albler et al., 2017). However, the very slow kinetics of nickel extraction from the deep eutectic solvent makes this reagent unsuitable for mixer-settlers.
2.4.3 Extraction of metal complexes as adducts

A coordinatively saturated neutral metal complex forms \( MA_z(H_2O)_x \) in the aqueous phase, where \( 2z+x \) equals the maximum coordination number of the metal. In the absence of a solvating organic solvent, this complex preferentially distributes into the aqueous phase. A more lipophilic adduct complex \( MA_zB_b \) may be formed if the water of hydration is replaced by organic molecules, B (Figure 9).

<table>
<thead>
<tr>
<th>Coordinatively saturated metal adduct complex in organic phase (and B)</th>
<th>( B )</th>
<th>( MA_zB_b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation of neutral complex coordinatively saturated by adduct former ( B )</td>
<td>( \uparrow \uparrow )</td>
<td>( M^{z+} + bB + zA^- \rightleftharpoons MA_zB_b )</td>
</tr>
</tbody>
</table>

Figure 9. Liquid–liquid extraction equilibrium of inert metal compounds.

Depending on the ligand, several types of such adducts exist:

- type \( MA_zB_b \), where A and B are different organic structures;
- type \( MX_zB_b \), where \( MX_z \) is a neutral inorganic compound (salt);
- type \( MA_z(HA)_b \), where A and HA are the basic and neutral variant of the same molecule (self-adducts).

2.4.3.1 Type \( MA_zB_b \)

The extraction of the metal complex adduct can be written

\[
M^{z+} + zHA + bB \rightleftharpoons MA_zB_b + zH^+ \tag{26}
\]

The extraction constant for the reaction is defined by

\[
K_{ex} = \frac{[MA_zB_b][H^+]^z}{[M^{z+}][HA]^z[B]^b} \tag{27}
\]
or

\[ K_{ex} = D_M \frac{[H^+]^z}{[HA]^z[B]^b} \]  

(28)

Thus the distribution of the metal, \( D_M \), depends on the concentrations of \( H^+ \) and \( HA \) to the power \( z \) of the charge of the metal ion, and on the concentration of \( B \) to the power of \( b \).

It can be shown that

\[ K_{ex} = \frac{K_a^z K_{n} K_{DC} K_{ad,bb}}{K_{DR}^z} \]  

(29)

where \( K_a = [H^+][A^-]/[HA] \) is the acid dissociation constant, \( K_{DR} = [HA]/[HA] \) is the distribution constant for the undissociated acid \( HA \), and \( K_{ad,bb} = [MA_x B_y]/[B]^b[MA_z] \) is the formation constant for the adduct \( MA_x B_y \) in the organic phase. The five parameters \( K_a, K_n, K_{DC}, K_{ad,bb}, \) and \( K_{DR} \) are, in general, unrelated, even though it may not always be possible to change one without affecting the others, as each molecular species may take part in several equilibria. Without considering the independent parameters, it is often difficult to understand why \( K_{ex} \) varies in the way observed, and it may be impossible to predict improvement of the system.

### 2.4.3.2 Type MX\(_2\)B\(_b\)

Mineral salts and mineral acids can be extracted by the adduct formation mechanism (Rydberg et al., 2004). Metal salts with monodentate univalent anions like \( \text{Cl}^- \), \( \text{ClO}_4^- \), \( \text{SCN}^- \), and \( \text{NO}_3^- \) are strongly hydrated in the aqueous phase and have quite limited solubility in inert solvents. In order to extract acids of these anions, they must either form an adduct with a strongly basic extractant, like tri-n-butyl phosphate (TBP), or trioctylphosphine oxide (TOPO) or be in solvating solvents such as ethers, ketones, alcohols, or esters. Monomeric metal hydroxides can also be extracted in the form of the adducts by strong donor molecules.

For example, the extraction of americium(III), europium(III), and curium(III) with 6,6′-bis(5,6-dialkyl-[1,2,4]triazin-3-yl)-[2,2′] bipyridines (BTBP) proceeds via a solvating mechanism (Geist et al., 2006)
The extraction of nickel with some of the BTBP-class ligands is an example of complex extraction behaviour, when a solvating extraction is employed (Ekberg et al., 2007). It was shown that the BTBPs are capable of forming both 1:1 and 1:2 complexes with nickel(II). When the BTBP concentration is low, the nickel distribution ratio is governed by the formation of the nickel/BTB complex while at higher BTBP concentrations the partitioning of the nickel complex between the two phases dictates the nickel distribution ratio.

The BTBP can distribute between the organic and the aqueous phases

\[
K_{D,BTBP} = \frac{[BTBP]}{[BTBP]} \tag{31}
\]

At excess of the extractant molecules, the 1:2 complex with nickel(II) is formed:

\[
K_{Ni(BTBP)_2} = \frac{[Ni(BTBP)_2]}{[Ni^{2+}][BTBP]^2} \tag{32}
\]

When the organic phase is deficient in extractant molecules, in comparison to the available amount of nickel(II), the 1:1 complex is formed

\[
K_{NiBTBP} = \frac{[NiBTBP]}{[Ni^{2+}][BTBP]} \tag{33}
\]

Both 1:1 and 1:2 complexes can enter the organic phase with the distribution ratios

\[
K_{D,NiBTBP} = \frac{[NiBTBP]}{[NiBTBP]} \tag{34}
\]
Taking all nickel species in the aqueous and organic phases into account, the distribution of nickel can be written in the form of Eq. (36), in which shows that the distribution ratio depends only on the free ligand concentration.

\[
D_{D_{\text{Ni}}} = \frac{[\text{Ni}^{2+}] + [\text{Ni}(\text{BTBP})] + [\text{Ni}(\text{BTBP})_2]}{1 + K_{\text{NiBTBP}}[\text{BTBP}] + K_{\text{Ni}(\text{BTBP})}[\text{BTBP}]^2}
\]  

(36)

In comparison to copper(II) extraction, Eq. (24), the equation for the distribution ratio of the nickel extraction with BTBP, Eq. (36), cannot be further simplified because the extraction of both 1:1 and 1:2 complexes is significant, and both complexes are able to enter the organic phase.

2.4.3.3 Type MAz(HA)_b

Hydration only occurs in neutral complexes that are coordinatively unsaturated by the organic ligand. The hydrate water reduces the extractability of the complex. In the absence of strong donor molecules, which can replace this hydrate water, there is still a chance for the undisassociated acid to replace the water, leading to a self-adduct according to the reaction:

\[
MA_z(H_2O)_w + bHA \rightleftharpoons MA_z(HA)_b + wH_2O
\]  

(37)

This competition between the formation of an adduct with HA, or with H_2O, is observed as an increasing extraction, with increasing HA concentration (Rydberg et al., 2004) and as an increasing viscosity with increasing loading (Thomas, 2010). Existence of similar adducts, like MAzB_b, supports the existence of self-adducts. Self-adducts are rather common, and have been identified for complexes of calcium, barium, nickel, cobalt, cadmium, and uranium(IV) with acetylacetone, theoyltrifluoroacetone, tropolone, oxine,
and organophosphinic acid (Rydberg et al., 2004; Thomas, 2010; Lindell et al., 2000). Self-adducts of cobalt, nickel, and lithium complexes in the extraction with Cyanex 272 extractant were modelled in Publication III.

2.4.4 Metal extraction by liquid anion exchangers

Metals that react with inorganic ligands to form negatively charged complexes can be extracted by extractants with large organic cations by liquid anion exchange (Rydberg et al., 2004). The extraction mechanism is depicted in Figure 10.

![Figure 10. Liquid–liquid extraction equilibrium of inert metal compounds.](image)

The amines form strong adducts with hydrogen ions. The adducts are so strong that they remain protonated while exchanging the anion. A classic example is the formation of the ammonium ion NH$_4^+$ when NH$_3$ is dissolved in water. The organic amines (the amine base RN) have a nitrogen atom attached to a large organic molecule R, usually containing more than 7 aliphatic or aromatic carbon atoms. They are highly soluble in organic diluents and almost insoluble in water. In contact with an aqueous phase containing HX, the amine base RN reacts with the acid HX to form RNH$^+$X$^-$, but with an excess amount of acid HX into the organic phase, and also with additional water. The formation of the ion pair salt can be written

$$\text{RN} + H^+ + X^- \rightleftharpoons RNH^+X^-$$  \hspace{1cm} (38)

Four types of organic ammonium cations exist: primary amines RNH$_3^+$, secondary amines R$_2$NH$_2^+$, tertiary amines R$_3$NH$^+$, and quaternary ammonium cations R$_4$N$^+$. In general the amines extract metal complexes in the order tertiary $>$ secondary $>$ primary. Only long-chain tertiary and, less frequently, quaternary ammonium cations are used in industrial applications, due to their suitable physical properties. Trioctylamine (TOA) is the most frequently used. In practice, there is a difficulty related to the need to use high
ligand concentrations, \([X^-]\), in the aqueous phase in order to obtain the negatively charged complexes.

In general, the metal \(M^{z+}\) reactions with a monobasic anion \(X^-\) can be written

\[
M^{z+} + nX^- \rightleftharpoons MX_n^{z-n}; \beta_n = \frac{[MX_n^{z-n}]}{[M^{z+}][X^-]^n}
\]  

(39)

When \(z-n=p<0\), a negatively charged metal complex has been formed, which can be then extracted

\[
MX_n^{-p} + pRNH^+X^- \rightleftharpoons \frac{(RNH^+)_p^{+p}MX_n^{-p}}{[RNH]^p[X^-]^p} + pX^- \]  

(40)

With the extraction constant written as

\[
K_{ex} = \frac{[\frac{(RNH^+)_p^{+p}MX_n^{-p}}{[RNH]^p[X^-]^p}]}{[MX_n^{-p}][RNH^+X^-]^p}
\]  

(41)

With the assumption that all the stepwise complexes \(MX_n^{-p}\) are in the aqueous phase, the distribution ratio is defined as

\[
D_M = \frac{\frac{(RNH^+)_p^{+p}MX_n^{-p}}{\sum[MX_n^{z-n}]} = K_{ex} \beta_p[X^-]^p[RNH]^p}{1 + \sum \beta_p[X^-]^p}
\]  

(42)

The distribution of a metal, \(M\), depends on both the free amine salt concentration in the organic phase and the concentration of free \(X^-\) in the aqueous phase until all metal in the aqueous phase is bound in the \(MX_n^{-p}\) complex.
2.5 Selected commercial extractants used for the extraction of base metals

The extractants used in the publications included in this thesis are briefly characterised in this section. Only the liquid–liquid extraction with hydroxyoxime and organophosphorus extractants was investigated. The extraction and separation of copper and iron with hydroxyoxime extractant Acorga M5640 was considered in Publications I and II. The liquid–liquid extraction separation of cobalt, nickel, and lithium with organophosphorus extractant Cyanex 272 was simulated in Publication III. The liquid–liquid extraction with D2EHPA was included in both hydrometallurgical processes synthesised in Publication IV.

2.5.1 Hydroxyoxime extractants

Hydroxyoxime extractants belong to the class of chelating acidic extractants. Chelating extractants contain donor groups capable of forming bidentate complexes with metal ions that provide extra stability to the metal complex. The mechanism involved in the extraction with hydroxyoxime extractants is discussed in Section 2.4.2. These extractants are widely used for the separation of different base metals from both acidic and alkaline solutions. The best known application of hydroxyoxime extractants is copper extraction.

LIX 63, an aliphatic α-hydroxyoxime, was the first commercial extractant developed for copper extraction (Sole, 2008). Although it was very selective for copper, it could operate only at pH from 5 to 8. Since most leach solutions were at pH between 0.7 and 2.2, there was a need for the development of an extractant that could operate at higher acidities. The introduction of aromatic rings into the oxime structure in LIX 65 increased the acidity of the exchangeable proton and thus enabled copper extraction at higher acidity, compared with LIX 63. The further developed extractant LIX 84 has demonstrated a higher ability to extract copper from acidic sulfate solutions and a higher rate of extraction. The first commercial extractants were all based on ketoxime functionality, did not allow the extraction of copper at pH below 1.8 and still had slow extraction kinetics. The second-generation aldoxime extractants were developed to overcome these limitations of the ketoximes. Aldoxime extractants demonstrate very fast extraction kinetics, high selectivity over iron, and high loading capacity. Because aldoximes extract copper at high acidity, stripping of the copper is difficult. Aldoxime extractants are therefore modified with polar organic compounds to enhance stripping at the common acid strength of spent electrolyte from electrowinning tankhouses (160-180 g/L H₂SO₄) (Schlesinger et al., 2011a; Sole, 2008).

The different blends mixtures of aldoximes and ketoximes are used to achieve a better extraction and stripping performance through a combination of the properties of the different types of extractants. Today, aldoximes modified with nonylphenol, tridecanol or long-chain esters and aldoxime-ketoxime mixtures are the most widely used copper
extractant systems. The most sophisticated approach to extractant selection is based on customizing the extractant composition for each plant, depending on composition and concentration of leachate, concentration of solids, engineering limitations, and geological, climatic, or operational characteristics (Sole, 2008).

Table 1. Selected hydroxyoxime extractants used for copper extraction (Sastre and Szymanowski, 2004; Szymanowski, 1993).

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Type</th>
<th>Molecular structure</th>
<th>Modifier</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIX 63</td>
<td>α-hydroxyoxime</td>
<td>CH₃(CH₂)₆CH(C₆H₄)OH</td>
<td>-</td>
</tr>
<tr>
<td>5,8-diethyl-7-hydroxydodecan-6-oxime</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LIX 65N</td>
<td>Ketoxime</td>
<td>LIX 65N+LIX 63 44:1</td>
<td>LIX 63 to accelerate extraction</td>
</tr>
<tr>
<td>2-hydroxy-5-nonylbenzophenone oxime</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>LIX 64N</td>
<td>Ketoxime</td>
<td>LIX 63</td>
<td>-</td>
</tr>
<tr>
<td>2-hydroxy-5-nonylacetophenone oxime</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Acorga M5640</td>
<td>Aldoxime</td>
<td>Fatty esters</td>
<td></td>
</tr>
<tr>
<td>2-hydroxy-5-nonylsalicylaldoxime</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.5.2 **Organophosphorus extractants**

Acidic organophosphorus extractants include esters of orthophosphoric, phosphoric and phosphinic acids, and other compounds containing polyfunctional groups (Ritcey, 2006b). These have one ionisable proton, with the exception of phosphate monoesters, which have two. Their metal donor atom (O or S) can be varied to suit the hard-soft
properties of different metals. These extractants were developed for the separation of cobalt and nickel, though many other applications are now available (Thomas, 2010; Wilson et al., 2014; Ritecy, 2006b). The organophosphorus acid extractants form stable dimeric structures in non-polar solvents. When the extractant is present in excess, formation of a metal complex involves the retention of one of the hydrogen bonds in the dimer, whilst the other is broken to release a proton, which is released by the metal cation. Extraction of divalent metal cations of base metals by organophosphorus extractants usually gives complexes with 4:1 ligand:metal stoichiometry, \([MA_2(HA)_2]\) that correspond to the self-adduct formation extraction mechanism discussed in Section 2.4.3.3. With the increasing loading and decreasing number of extractant molecules available for metal complexation, the organophosphorus acid extractants are able to form polymeric structures with the average ligand:metal stoichiometry of 2:1. This can lead to increased viscosity and third phase formation. Modification of the extractants can decrease this effect. Organophosphorus acid extractants have been shown to be effective in the extraction of wide range of metals, particularly d- and f- block elements, the latter often in synergistic mixtures (Wilson et al., 2014).

Di-2-ethylhexyl phosphoric acid (D2EHPA) is a very versatile extractant that has been used commercially for the extraction of many metals including uranium, cobalt and nickel, rare earths, zinc, and vanadium (Ritecy and Ashbrook, 1984). Among the advantages offered by D2EHPA are its chemical stability, good kinetics of extraction, good loading and stripping characteristics as well as its low solubility in the aqueous phase. The selectivity series for several base metals from sulfate solution with D2EHPA is Fe(III)>Zn>Ca>Cu>Mg>Co>Ni.

Since D2EHPA demonstrates very low Co/Ni selectivity, an ester of a phosphonic acid (2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester) was developed for the effective separation of cobalt and nickel in sulfate medium (Ritecy and Ashbrook, 1984). Along with a good selectivity of Co over Ni, this extractant features the extraction of zinc at lower pH than normally occurs with D2EHPA. The selectivity series for several base metals from sulfate solution with phosphonic extractant is Fe(III)>Zn> Cu >Ca> Co> Mg>Ni.

A phosphinic acid extractant, bis-2,4,4-trimethyl pentyl phosphinic acid, was developed to further increase the Co/Ni selectivity in extraction from both chloride and sulfate solutions (Ritecy and Ashbrook, 1984). The phosphinic acid extractant possesses high selectivity (especially for cobalt over calcium and magnesium), low aqueous solubility, and high chemical stability (Thomas, 2010). The separation factor between cobalt and nickel is 10-100 times higher than other extractants. The selectivity series for several base metals from sulfate solution with phosphinic extractant is Fe(III)>Zn> Cu >Co> Mg> Ca>Ni. Besides Co/Ni separation, other commercial applications include iron and zinc removal and the purification and separation of the heavy rare earth elements.
The selectivity of Co/Ni separation shown by the organophosphorus acid extractants increases in the order phosphoric<phosphonic<phosphinic, under similar conditions (Ritcey and Ashbrook, 1984).

Table 2. Structure of the selected commercial organophosphorus extractants.

<table>
<thead>
<tr>
<th>Extractants</th>
<th>Structure of compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2EHPA</td>
<td>[\text{CaH}<em>{17} \text{O} \quad \text{P} \quad \text{O} \quad \text{CaH}</em>{17} \text{O} \quad \text{OH} ]</td>
</tr>
<tr>
<td>PC88A</td>
<td>[\text{CaH}<em>{17} \quad \text{P} \quad \text{O} \quad \text{CaH}</em>{17} \quad \text{OH} ]</td>
</tr>
<tr>
<td>Cyanex 272</td>
<td>[\text{CaH}<em>{17} \quad \text{P} \quad \text{O} \quad \text{CaH}</em>{17} \quad \text{OH} ]</td>
</tr>
<tr>
<td>TBP</td>
<td>[\text{CaH}<em>{9} \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{CaH}</em>{9} \quad \text{O} \quad \text{CaH}_{9} \quad \text{O} ]</td>
</tr>
</tbody>
</table>

As shown in Sections 2.4.3.2, the solvation of neutral inorganic molecules or complexes, by electron-donor containing extractants, is an important metal extraction mechanism. The solvation increases the solubility of inorganic species in the organic phase. The most well known, and most used, solvating extractant is tri-n-butyl phosphate (TBP). It is widely used in the nuclear field (Irish and Reas, 1957; Svanstsson et al., 1979; Rydberg et al., 2004; Wilson et al., 2014). In addition, TBP finds many applications in the processing of base metals as a synergistic solvating extractant or modifier, which enhances the extraction or prevents third phase formation (Suzuki et al., 2012).
3 Modelling Extraction Equilibrium

In the current study, two extraction systems were investigated: the extraction of copper with a hydroxyoxime extractant, in the presence of iron, and the separation of cobalt, nickel, and lithium using an organophosphorus extractant. The modern hydroxyoxime extractants used in hydrometallurgical copper recovery are very selective to copper over major impurities. However, some transfer of the impurities from the pregnant leach solution to the rich electrolyte has been reported (Molnar and Verbaan, 2003), especially for extraction from concentrated pregnant leach solutions. As iron(III) is the most critical impurity for copper electrowinning, and since chemical co-extraction contributes the most to its transfer from pregnant leach solution to rich electrolyte, the extraction equilibrium of iron(III) was studied in addition to that of copper. The extraction of cobalt, nickel, and lithium was studied since separation of these metals, and their production in a pure form, is critical for the recycling of spent Li-ion batteries. The employment of liquid–liquid extraction can offer a viable option for this separation task. A mechanistic modelling approach was utilised in modelling the extraction equilibrium of the systems. The aim of the mechanistic modelling was to develop a tool that could be used in process flowsheeting to explore different potential process configurations and operation parameters.

3.1 Extraction of copper in the presence of iron(III)

Hydroxyoxime extractants have been proven to be very selective towards copper (Szymanowski, 1993; Kabugo et al., 2017), which has resulted in their extensive exploitation in large industrial hydrometallurgical copper recovery plants. However, a slight transfer of iron(III) from the pregnant leach solution to rich electrolyte is inevitable (Gotfryd and Pietek, 2013; Molnar and Verbaan, 2003) and there is a problem for many processes that bleed to control iron levels in the strip liquor. Most of the iron(III) transfer is due to chemical extraction (Thomas, 2010). Mechanistic mathematical modelling of the competitive extraction of copper and iron(III) helps identify the process conditions for the most selective transfer of copper from pregnant leach solution to rich electrolyte and the lowest transfer of iron(III).

3.1.1 Extraction of copper(II) with hydroxyoxime extractant

As chelating extractants, hydroxyoxime reagents complex with copper(II) through two binding sites of nitrogen and oxygen atoms to form metal chelates, shown in Figure 11 (Flett et al., 1973; Szymanowski, 1993; Piotrowicz et al., 1989; Schlesinger et al., 2011a).
As discussed in Section 2.4.2, copper(II) can be extracted by a hydroxyoxime extractant by the chelation mechanism depicted in Figure 12.

Extractant molecules as a monobasic organic acid, HA, distribute between the organic and the aqueous phases. The distribution of the extractant follows the Nernst distribution law and the distribution is described by a distribution constant Eq. (43). Next the acidic extractant molecules dissociate in the aqueous phase with a dissociation constant $K_a$, Eq. (44).

$$ HA \rightleftharpoons HA^–; K_{D,HA} = \frac{[HA^–]}{[HA]} \quad (43) $$

$$ HA \rightleftharpoons H^+ + A^–; K_a = \frac{[H^+][A^–]}{[HA]} \quad (44) $$
An uncharged metal complex CuA$_2$ is formed from Cu$^{2+}$, through a stepwise reaction with the anion A$^-$ of a monobasic acidic extractant, HA, defining a stepwise formation constant $K_n$, Eqs. (45) and (46), and an overall formation constant $\beta_{\text{tot}}$, Eq. (47).

$$\text{Cu}^{2+} + A^- \rightleftharpoons \text{CuA}^+; \quad K_1 = \frac{[\text{CuA}^+]}{[\text{Cu}^{2+}][A^-]} \quad (45)$$

$$\text{CuA}^+ + A^- \rightleftharpoons \text{CuA}_2; \quad K_2 = \frac{[\text{CuA}_2]}{[\text{CuA}^+][A^-]} \quad (46)$$

$$\text{Cu}^{2+} + 2A^- \rightleftharpoons \text{CuA}_2; \quad \beta_{\text{tot}} = \frac{[\text{CuA}_2]}{[\text{Cu}^{2+}][A^-]^2} \quad (47)$$

The CuA$_2$ complex is lipophilic and dissolves in organic solvents; the distribution constant $K_{D,C}$ of the complex is defined:

$$\text{CuA}_2 \rightleftharpoons \overset{\text{CuA}_2}{\overset{\text{CuA}}{\text{Cu}}} ; \quad K_{D,C} = \frac{[\text{CuA}_2]}{[\text{CuA}]} \quad (48)$$

Taking all metal species in the aqueous phase (Cu$^{2+}$, CuA$^+$, and CuA$_2$) into account, the distribution of the metal can be written in the form of Eq. (49), in which shows that the distribution ratio depends only on the free ligand concentration.

$$D_{\text{Cu}} = \frac{[\text{CuA}_2]}{[\text{Cu}^{2+}] + [\text{CuA}^+] + [\text{CuA}_2]} = \frac{K_{D,C}\beta_{\text{tot}}[A^-]^2}{1 + K_1[A^-] + \beta_{\text{tot}}[A^-]^2} \quad (49)$$

where

$$[A^-] = \frac{K_a [HA]}{K_{D,HA} [H^+]} \quad (50)$$
is the expression for the free ligand concentration derived from the distribution of the extractant between the phases and its dissociation in the aqueous phase, which shows that the free ligand concentration and, consequently, the distribution ratio of copper(II) depends on the extractant concentration in the organic phase and acidity in the aqueous phase.

For practical reasons, it is simpler to use the extraction constant $K_{\text{ex,Cu}}$ for the extraction reaction

$$\text{Cu}^{2+} + 2HA \rightleftharpoons \text{CuA}_2 + 2H^+; K_{\text{ex,Cu}} = \frac{[\text{CuA}_2][H^+]^2}{[\text{Cu}^{2+}][HA]^2}$$  \hspace{1cm} (51)

Eq. (52), for the distribution ratio, can be derived from Eq. (49) under the assumption that the solubility of the species $\text{CuA}^+$ and $\text{CuA}_2$ are negligibly low. However, this assumption is not always true. There are examples of metals being extracted in several complexes soluble in the organic phase (Ekberg et al., 2007; Albler et al., 2017). The expression for the distribution ratio cannot be so significantly simplified in such cases.

$$D'_{\text{Cu}} = K_{\text{ex,Cu}} \frac{[HA]^2}{[H^+]^2}$$  \hspace{1cm} (52)

Thus only one constant, $K_{\text{ex,Cu}}$, is needed to predict the metal extraction for the given concentrations of protons and extractant under the assumption that the solubility of the metal complexes $\text{CuA}^+$ and $\text{CuA}_2$ in the aqueous phase is negligibly small. This assumption is valid for most modern commercial reagents used for copper extraction. Moreover, $D'_{\text{Cu}}$ can be easily measured in shaking experiments, enabling the mechanistic modelling of the copper extraction process using the $K_{\text{ex,Cu}}$ constant. This approach was used in Publications I and II as discussed in Section 3.1.3.

The extraction constant $K_{\text{ex,Cu}}$ can be expressed as the product of several equilibrium constants for other assumed equilibria in the net reaction

$$K_{\text{ex,Cu}} = K_{\text{DC}} \beta_{\text{tot}} K_a^2 K_{D,\text{HA}}^{-2}$$  \hspace{1cm} (53)
The extraction constant $K_{ex}$ determines the efficiency of an extraction process. It depends on the internal chemical parameters of the system, i.e. the chemical reactions and the concentration of reactants of both phases. In principle, the constants for all the steps in the described extraction mechanism can be measured with different measurement techniques (Rydberg et al., 2004).

Similar expressions for the steps of the extraction mechanism for iron(III) can be derived. Speciation of inorganic salts and acids in the aqueous solution affects the availability of both copper(II) and protons and must be considered, when the extraction from the concentrated solutions is modelled. Modelling the extraction of copper and iron using the extraction constants for the net extraction reactions and aqueous phase speciation is discussed in the next sections.

### 3.1.2 Speciation in the system CuSO$_4$–Fe$_2$(SO$_4$)$_3$–H$_2$SO$_4$–H$_2$O

The mechanism of copper and iron(III) extraction considered in the current study accounts for aqueous phase speciation and the interfacial ion exchange reactions of copper and iron(III), as depicted in Figure 13. In the system CuSO$_4$–Fe$_2$(SO$_4$)$_3$–H$_2$SO$_4$–H$_2$O, the aqueous solution contains ions that are products of the dissociation reactions of substances present in the solution: CuSO$_4$, Fe$_2$(SO$_4$)$_3$ and H$_2$SO$_4$. The pH of solutions in copper liquid–liquid extraction is usually below 2, as lower acidity leads to poorer extractant selectivity (Gotfryd and Pietek, 2013; Molnar and Verbaan, 2003; Ochromowicz and Chmielewski, 2013) and because a higher pH will lead to the formation of iron hydroxyl complexes and even iron precipitates (Yue et al., 2014). The hydrolysis of iron(III) was not considered in the present study, since copper extraction is usually performed at a pH lower than 2. A detailed description of aqueous phase speciation was presented in Publications I and II.

### 3.1.3 Interfacial and organic phase chemistry

The liquid–liquid extraction of a given metal ion by an acidic hydroxyoxime extractant is the ion transfer between the aqueous and organic phases according to an overall equilibrium reaction, Eq. (54), which leads to the expression of the extraction equilibrium constant, Eq. (55) (Flett et al., 1973; Ritcey and Ashbrook, 1984).

\[
M^{n+} + n\overline{HA} \rightleftharpoons M\overline{A}_n + nH^+ \quad (54)
\]
Modelling Extraction Equilibrium

\[ K_{LLX} = \frac{[MA_n^+] \cdot [H^+]^n}{[M^{n+}] \cdot [HA]^n} K_y \]  

(55)

The product of activity coefficients, \( K_y \), given in Eq. (56), accounts for the nonideality of the aqueous and organic phases. The activity coefficients for the aqueous phase species are calculated using an activity coefficient model for electrolyte solutions as discussed in Section 3.3. The application of the existing activity coefficient models for the organic phase (e.g. Scott-Hildebrandt, NTLR and UNIQUAC) is hindered by the lack of respective data and, consequently, values of the models parameters. In addition, the organic phase typically contains extractant molecules, modifier molecules and a solvent that increases the number of required parameters in the models and further complicates estimation of the values of the model’s parameters. Therefore, the activity coefficients for the organic phase species are usually assumed to be constant.

\[ K_y = \frac{\gamma_{MA_2} \gamma_{H}^+}{\gamma_{M^{n+}} \gamma_{HA}^n} \]  

(56)

Figure 13. Mechanism of liquid–liquid extraction of copper and iron(III) from a sulfate solution with an hydroxyoxime extractant in an aqueous/organic two-phase system. A stands for the deprotonated hydroxyoxime molecule.
The extraction equilibrium in diluted systems is usually obtained using a simple linear regression model, Eq. (57), derived from Eq. (55). The term $\log K_y$ vanishes since activity coefficients of all the species are assumed to be constant. However, the term $\log K_y$ may significantly deviate from zero nil in real solutions, as will be demonstrated later (Figure 22 in Section 5.1.1).

$$\log D = \log K_{llx} + z \cdot pH + z \cdot \log[HA]$$  \hfill (57)

As a divalent metal, copper is extracted with a hydroxyoxime-type extractant according to the overall extraction reaction, Eq. (58), which leads to the expression of the extraction equilibrium constant, Eq. (59), where activity coefficients of organic phase species are assumed to be constant.

$$Cu^{2+} + 2HA \rightleftharpoons CuA_2^+ + 2H^+ \hfill (58)$$

$$K_{llx}^{Cu} = \frac{[CuA_2^+] \cdot [H^+]^2 \cdot \gamma_{H^+} \gamma_{Cu^{2+}}}{[Cu^{2+}] \cdot [HA]^2}$$  \hfill (59)

As a trivalent metal, iron(III) is extracted according to the overall extraction reaction shown in Eq. (60), which leads to the expression of the extraction equilibrium constant, Eq. (61), where activity coefficients of the organic phase species are assumed to be constant.

$$Fe^{3+} + 3HA \rightleftharpoons FeA_3^- + 3H^+ \hfill (60)$$

$$K_{llx}^{Fe} = \frac{[FeA] \cdot [H^+]^3 \cdot \gamma_{H^+} \gamma_{Fe^{3+}}}{[Fe^{3+}] \cdot [HA]^3}$$  \hfill (61)

Speciation calculations presented in Publication II indicated that the predominant species containing iron in the aqueous solution were $FeSO_4^{+}$ and $Fe(SO_4)^2^-$. As a cation exchanger, oxime could also extract $FeSO_4^+$ along with $Fe^{3+}$. That is why the presence of sulfate ions in the iron-loaded organic phase was checked. The loaded organic phase was
stripped with hydrochloric acid and the resulting aqueous phase was analysed using ion chromatography. No sulfate ions were detected in the aqueous phase after stripping. If the FeSO$_4$ was the extractable species, SO$_4^{2-}$ would had been detected in the strip liquor. Therefore, it was inferred that ferric ion is the only extractable species.

It has been argued that the phenolic hydroxyoxime extractants are able to form dimers according to the reaction Eq. (62) (Szymanowski and Borowiak-Resterna, 1991). The strong interligand H-bonds between the oxime hydrogen and the phenolic oxygen atoms define a planar donor set, and a cavity that is a particularly good fit for copper (II), as shown in Figure 11 (Wilson et al., 2014). The dimerisation depends mainly on the diluent: it is more prominent in aliphatic hydrocarbon diluents, whereas it is small in aromatic hydrocarbon diluents (Sastre and Szymanowski, 2004; Szymanowski, 1993; Szymanowski and Borowiak-Resterna, 1991). The concentration-based equilibrium constant of dimerization is shown by Eq. (63). Polymerisation of the copper-oxime complex and solvation of the copper complex by hydroxyoxime molecules are unlikely (Szymanowski and Borowiak-Resterna, 1991). In addition, it has been shown, in Publication I, that there is no statistical proof of the phenomena existing when the reactive extraction equilibrium is analysed using the data collected in equilibrium shaking experiments.

$$2HA \rightleftharpoons (HA)_2$$ \hspace{1cm} (62)

$$K_{\text{Dim}} = \frac{[HA]^2}{[HA]^2}$$ \hspace{1cm} (63)

### 3.2 Extraction of Co, Ni, and Li with organophosphorus extractants

In the current study, the liquid–liquid extraction of cobalt, nickel and lithium is considered as an interphase extraction process (Figure 14). The extraction equilibrium is modelled with consideration for aqueous phase speciation, competing interfacial ion exchange extraction reactions of the cations and the formation of extracted cation-extractant complexes of different stoichiometry in the bulk organic phase.
Figure 14. Mechanism of liquid−liquid extraction of lithium, nickel and cobalt from a sulfate solution with saponified phosphinic acid in an aqueous/organic two-phase system. M stands for Co$^{2+}$, Ni$^{2+}$, Li$^+$ or NH$_4^+$; A stands for deprotonated phosphinic acid.

### 3.2.1 Extraction of metal cations with organophosphorus extractants

As discussed in Section 2.4.3.3, the undissociated acid can replace the hydrate water in the metal extractant complex leading to the formation of a self-adduct as depicted in the scheme in Figure 15.

![Figure 15. Liquid–liquid extraction of metal complexes with formation of self-adducts.](image)

The organophosphorus acid extractants form stable dimer complexes in the organic phase Eq. (64). Monomeric extractant molecules, HA, distribute between the organic and the aqueous phases. The distribution of the extractant follows the Nernst distribution law and the distribution is described by a distribution constant Eq. (65). Then the acidic extractant molecules dissociate in the aqueous phase with a dissociation constant $K_a$, Eq. (66).
The extractable self-adduct metal complex is formed in the aqueous phase according to the reaction in Eq. (67). An overall formation constant \( \beta_{\text{tot}} \) is represented by Eq. (68).

\[
M^{z+} + bHA + zA^- \rightleftharpoons MA_z(HA)_b
\]

\[
\beta_{\text{tot}} = \frac{[MA_z(HA)_b]}{[M^{z+}][A^-]^z[HA]^b}
\]

The \( MA_z(HA)_b \) complex is lipophilic and dissolves in organic solvents and the distribution constant \( K_{D,C} \) of the complex is defined:

\[
MA_z(HA)_b \rightleftharpoons MA_z(HA)_b; K_{D,C} = \frac{[MA_z(HA)_b]}{[MA_z(HA)_b]}
\]

Taking all metal species in the aqueous phase \( (M^{z+}, MA_z(HA)_b) \) into account, the distribution of the metal can be written in the form of Eq. (70), in which shows that the distribution ratio depends only on the free ligand concentration and acidity of the aqueous phase.

\[
D_{M, add} = \frac{[MA_z(HA)_b]}{[M^{z+}] + [MA_z(HA)_b]} = \frac{K_{D,C} \beta_{\text{tot}} [A^-]^z [HA]^b}{1 + \beta_{\text{tot}} [A^-]^z [HA]^b} = \frac{[H^+]^{z+} K_{D,HA}^{z+} + \beta_{\text{tot}} K_{D,A}[HA]^{z+}}{[H^+]^{z+} K_{D,HA}^{z+} + \beta_{\text{tot}} K_{D,A}[HA]^{z+}}
\]
As the concentration of protons in the aqueous phase decreases, the $[H^+]^z K_{D,HA}^{z+b}$ term also decreases and approaches zero. In that case, the distribution ratio becomes dependent only on the distribution coefficient of the metal complex: $D_{Cu} \approx K_{DC}$. On the other hand, under the assumption that the solubility of the $MA_z(HA)_b$ complex in the aqueous phase is negligibly small in comparison with the equilibrium concentration of metal cations

$$D'_{M,add} = \frac{MA_z(HA)_b}{[M^{z+}]} = K_{DC} \beta_{tot} [A^-]^z [HA]^b = \frac{K_{DC} \beta_{tot} K_A^{z+b} [HA]^{z+b}}{[H^+]^z K_{D,HA}^{z+b}}$$ (71)

The dimeric form is predominant for the organophosphorus extractants, such as bis-2,4,4-trimethyl pentyl phosphinic acid (Cyanex 272) (Ricey, 2006b). Thus, the overall extraction reaction of a metal with an organophosphorus acid extractant can be represented by Eq. (72). The corresponding expression for the extraction equilibrium constant is given by Eq. (73).

$$M^{z+} + \frac{z + b}{2} (HA)_2 \rightleftharpoons MA_z(HA)_b + zH^+$$ (72)

$$K_{tot} = \frac{[MA_z(HA)_b] [H^+]^z}{[M^{z+}] [HA]_2}$$ (73)

The extraction equilibrium constant, Eq. (73), is valid in the special case under the assumptions that the aqueous solubility of the metal complex is negligibly small and that all of the extractant molecules are present in the organic phase in the dimeric form. These assumptions were used to enable the mechanistic modeling of the extraction separation of Co, Ni, and Li in Publication III as shown in Section 3.2.3.

### 3.2.2 Aqueous phase speciation

The aqueous phase in the liquid-liquid extraction of cobalt, nickel, and lithium contains ions that are products of the dissolution of the compounds present in the electrolyte solution (CoSO₄, NiSO₄, NH₃, H₂SO₄ and Li₂SO₄) and their speciation in the electrolyte. The hydrolysis of cobalt and nickel was included in the speciation model because the
operation of some steps in the proposed process is intended to be at a pH of around 7, where precipitation of the metal hydroxides is possible, but undesirable. For instance, hydroxides of nickel and cobalt will precipitate from a 20 mM (~1 g/L) solution of each metal at pH 9.3 and 8.4, respectively, as calculated from solubility products logKsp(Ni(OH)₂) = -10.5 and logKsp(Co(OH)₂) = -12.2 (Puigdomenech, 2016). The precipitation pH of the metals lowers when the concentration of the individual metals increases, but increases as the ionic strength of the multi-metal solution increases. The detailed description of the aqueous phase reactions considered in the present study was presented in Publication III.

3.2.3 Interfacial and organic phase chemistry

Depending on extraction conditions, organophosphorus acid–based extractants form with metal ion complexes of variable stoichiometry. These complexes are partitioned into the organic phase. The extractant-to-metal molar ratio for divalent metal ions changes from four (tetrahedral complex) to two (polymer formation) as the loading of extractant increases and less extractant molecules are available for metal complexation (Thomas, 2010). At the excess of extractant complexes, (HA)₂, M₂₂(HA)₂ are first formed in the case of a divalent metal ion (Figure 16). When the organic phase is deficient in extractant molecules, in comparison to the available amount of divalent metal cations, the complexes M₂₂ are formed.

![Diagram](image_url)

Figure 16. Complex formation equilibrium involving divalent metal and phosphinic acids. Retrieved from (Wilson et al., 2014).

The liquid–liquid extraction of a given cation by an organophosphorus acid–based extractant can be described by assuming two stepwise reactions (Mantuano et al., 2006; Mansur et al., 2002), the first one of which is an ion transfer at the interface of the aqueous and organic phases:
\[ Mn^{n+} + m(\text{HA})_2 \rightleftharpoons MA_n(\text{HA})_{2m-n} + nH^+ \]  
(74)

and the second reaction occurring in the bulk organic phase at a deficiency of extractant molecules:

\[ MA_n(\text{HA})_{2m-n} \rightleftharpoons MA_n + \frac{2m-n}{2}(\text{HA})_2 \]  
(75)

In the cases of cobalt and nickel, the metals are extracted first according to the interfacial reaction Eq. (76) and Eq. (78). The extraction reactions have the concentration-based extraction equilibrium constants, Eq. (77) and Eq. (79).

\[ Co^{2+} + 2(\text{HA})_2 \rightleftharpoons CoA_2(\text{HA})_2 + 2H^+, \]  
(76)

\[ K_{\text{LLX.1}}^{Co} = \frac{[CoA_2(\text{HA})_2][H^+]^2}{[Co^{2+}][\text{HA})_2]^2}. \]  
(77)

\[ Ni^{2+} + 2(\text{HA})_2 \rightleftharpoons NiA_2(\text{HA})_2 + 2H^+, \]  
(78)

\[ K_{\text{LLX.1}}^{Ni} = \frac{[NiA_2(\text{HA})_2][H^+]^2}{[Ni^{2+}][\text{HA})_2]^2}. \]  
(79)

Then, the formed metals-extractant complexes break down in the bulk organic phase when high organic loading is achieved, Eq. (80) and Eq. (82). The respective concentration-based extraction equilibrium constants are represented by Eq. (81) and Eq. (83).

\[ CoA_2(\text{HA})_2 \rightleftharpoons CoA_2 + (\text{HA})_2, \]  
(80)

\[ K_{\text{LLX.2}}^{Co} = \frac{[CoA_2][\text{HA})_2]}{[CoA_2(\text{HA})_2]}, \]  
(81)

\[ NiA_2(\text{HA})_2 \rightleftharpoons NiA_2 + (\text{HA})_2, \]  
(82)
At an excess of the extractant, lithium is extracted by organophosphorus extractants in reaction with two dimeric extractant molecules (Hano et al., 1992; Zushi et al., 2000)

\[
Li^+ + 2\overline{(HA)_2} \rightleftharpoons LiA \cdot 3HA + H^+,
\]

Lithium is extracted at lower acidity in comparison to cobalt and nickel. Under the studied conditions, the organic phase is loaded to a high extent by cobalt and nickel, and the extraction of lithium is assumed to proceed with only one dimeric extractant molecule according to the reaction Eq. (85). The reaction in Eq. (85) leads to the expression of the concentration-based extraction equilibrium constant shown in Eq. (86).

\[
K_{Llx,2}^{Ni} = \frac{[NiA_2][\overline{(HA)_2}]}{[NiA_2(HA)_2]}.
\]

3.2.4 Synergistic effect of solvating reagents on extraction

As discussed in Section 2.5.2, organophosphorus acid extractants may form polymeric metal complexes with ligand:metal stoichiometries 2:1 at high loadings of the organic phase. This causes problems in industrial application, as third phase formation may occur. A solution to the problem can be found in the addition to the solvent of a solvating extractant, such as tri-n-butyl phosphate (TBP) or tri-n-octylamine (TOA), that can increase the solubility of the metal complexes. In addition, these extractants can improve the selectivity of metals extraction (Suzuki et al., 2012; Atanassova, Kurteva & Dukov, 2016).

The extraction of the metal complex adduct of a divalent metal can be written in this case, Eq. (87), as discussed in Section 2.4.3.1. The formation of the polymeric complexes is prevented by the stabilization of the 2:1 ligand:metal complexes by the solvating extractant molecules.
\[ M^{2+} + 2HA + 2B \rightleftharpoons MA_2B_2 + 2H^+ \]  

(87)

### 3.2.5 Extraction distribution of ammonia

Acidic organophosphorus extractants are used frequently in the form of their ammonium salts in order to facilitate pH control. The salts are prepared by partial pre-neutralization to a specific degree of conversion. In addition, ammonium is known to be extracted by the organophosphorus extractants (Inoue, Nakayama & Watanabe, 1986). It is important, therefore, to study the extraction behaviour of ammonia with the extractant, in addition to that of metal ions. According to Eq. (88), ammonium is extracted with organophosphorus extractants as an ion-pair \( \text{NH}_4^+ (\text{HA})_4 \) in the low pH region (pH<6). The concentration-based extraction equilibrium constant for the extraction reaction can be expressed in the form of Eq. (89).

\[
\text{NH}_4^+ + 2.5(\text{HA})_2 \rightleftharpoons \text{NH}_4\text{A}(\text{HA})_4 + H^+. \\
K_{\text{LLX},1}^{\text{NH}_4^+} = \frac{[\text{NH}_4\text{A}(\text{HA})_4][H^+]}{[\text{NH}_4^+][\text{(HA)}_2]^{2.5}}
\]  

(89)

At higher pH (pH>6), ammonia exists in the organic phase as complex \( \text{NH}_4\text{A} \) (Inoue et al., 1986; Lindell et al., 2000), which is formed according to the reaction in Eq. (90), which has the concentration-based extraction equilibrium constant in the form of Eq. (91).

\[
2\text{NH}_4^+ + (\text{HA})_2 \rightleftharpoons 2\text{NH}_4\text{A} + 2H^+. \\
K_{\text{LLX},2}^{\text{NH}_4^+} = \frac{[\text{NH}_4\text{A}]^2[H^+]^2}{[\text{NH}_4^+]^2[\text{(HA)}_2]^2}
\]  

(91)

A single-phase microemulsion is formed at an ammonia/organic acid molar ratio equal to 1 at a high aqueous ammonia concentration (Lindell et al., 2000). The microemulsion contains reversed micelles enclosing water. It is the breakdown of the microemulsion upon contact with an acidic aqueous phase in the loading stage of the liquid–liquid extraction that is assumed here to follow the reaction in Eq. (90). The presence of water in the microemulsion is neglected here.
3.3 Activity coefficient models for aqueous electrolytes

The speciation of electrolytes in the aqueous solutions play an important role in the liquid–liquid extraction of metals because only certain ionic species are extracted by extractants, and the availability of these species at certain conditions determines extraction efficiency. The electrolyte speciation in aqueous solutions can be calculated using appropriate reaction equilibrium constants and an ionic activity coefficient model applicable to electrolyte solutions (Casas, Papangelakis & Liu, 2005; Casas, Crisóstomo & Cifuentes, 2005; Cifuentes, Casas & Simpson, 2006; Yue et al., 2014).

(Casas et al., 2005) compared three activity coefficient models: the extended Debye-Hückel equation; the Pitzer model with binary ion interaction parameters; and the Bromley-Zemaitis model, in application to the aqueous solutions of high ionic strength encountered in hydrometallurgical processes.

The extended Debye-Hückel model is characterised by its simplicity. There is only one species-specific parameter, the distance of the closest approach of ions \( \hat{a} \). As this parameter is not a directly measurable quantity, reasonable results may be obtained by choosing values close to the hydration radius, often in the range of 3.5 to 6.2 Å (Zemaitis et al., 1986). The activity coefficients can be calculated using the equation

\[
\ln \gamma_i = - \frac{A_{DH} z_i^2 \sqrt{I}}{1 + \hat{a} B_{DH} \sqrt{I}} + \hat{B} I \quad (92)
\]

where \( \hat{a} \) is the distance of the closest approach of the \( i \)-th ionic species, \( z_i \) is the charge of the \( i \)-th species, \( A_{DH} \) and \( B_{DH} \) are the Debye–Hückel parameters, which are defined functions of the kind of solvent and the temperature, \( \hat{B} \) is the parameter to account for interactions other than electrostatic and \( I \) is the ionic strength of the electrolyte solution.

The definitions of the Debye–Hückel parameters \( A_{DH} \) and \( B_{DH} \) appearing in Eq. (92) are

\[
A_{DH} = \left( \frac{e}{\varepsilon_0 \varepsilon_r k_B T} \right)^3 \frac{2 d_o N_A}{8 \pi} \quad (93)
\]

\[
B_{DH} = \frac{2 e d_o N_A}{\varepsilon_0 \varepsilon_r k_B T} \quad (94)
\]
where \( e \) is the elementary charge, \( \varepsilon_r \) is the relative permittivity of the solvent, \( \varepsilon_0 \) is the permittivity of free space, \( k_B \) is Boltzmann constant, \( d_0 \) is the solvent density, and \( N_A \) is the Avogadro constant.

The extended Debye–Hückel model is a modification of the classical Debye–Hückel model that is valid for binary interactions. In order to correct the activity coefficient for those cases where interactions other than electrostatic come into play, the same value of the \( B \) parameter is included for all participating species. The model is valid for aqueous electrolyte solutions with moderate (up to \( I = 1 \) M) ionic strength (Casas, Alvarez & Cifuentes, 2000; Casas et al., 2005).

The Pitzer model can be theoretically applied to simulate highly concentrated systems (up to \( 10 \) \( m \) in ionic strength) (Pitzer, 1991; Casas et al., 2005). However, it requires a large number of parameters to quantify the physicochemical interactions among all of the species present in the solution. Therefore, considerable simplification, by omission of several interaction parameters, is often necessary, which results in a loss of predictive ability. The activity coefficient for an ion \( i \) can be calculated using the simplified form of the Pitzer model in which only second-order interaction coefficients together with the long-range electrostatic interactions are considered (Pitzer, 1991; Casas et al., 2005):

\[
\log \gamma_i = \left( \frac{z_i^2}{2} \right) f'(I) + 2 \sum_i \lambda_{ij}(I) m_i + \sum_j \sum_k \left[ \left( \frac{z_j^2}{2} \right) \lambda'_{jk}(I) \right] m_j m_k \tag{95}
\]

where \( m \) is the molal concentration, \( z \) is the charge, \( i, j, \) and \( k \) are ions,

\[
f'(I) = - \frac{2 \ln 10}{3} A_{DH} \left( \frac{2}{b} \ln (1 + b \sqrt{I}) + \frac{\sqrt{I}}{1 + b \sqrt{I}} \right)
\]

where \( A_{DH} \) is the Debye–Hückel parameter, \( b \) is assigned a constant value of 1.2, \( \lambda' \) is the derivative of \( \lambda \) with respect to \( I \), and \( \lambda \) is the second-order interaction coefficient between ions \( i \) and \( j \). \( \lambda \) is a function of the ionic strength and can be expressed as
\[ \lambda_{ij}(I) = \beta_{ij}^{(0)} + \frac{2\beta_{ij}^{(1)}}{\alpha_1^2 I} [1 - (1 + \alpha_1 \sqrt{I}) \exp(-\alpha_1 I)] + \frac{2\beta_{ij}^{(2)}}{\alpha_2^2 I} [1 - (1 + \alpha_2 \sqrt{I}) \exp(-\alpha_2 I)] \]

As discussed by (Casas et al., 2005), for 1:1, 2:1, 3:1, and 4:1 electrolytes, the \( \beta^{(2)} \) term is omitted, \( \alpha_1 \) has a value of 2.0, and the adjustable parameters become \( \beta^{(0)} \) and \( \beta^{(1)} \). For 2:2 electrolytes, \( \alpha_1 = 1.2, \alpha_2 = 12.0 \), and there are three adjustable parameters \( \beta^{(0)}, \beta^{(1)} \) and \( \beta^{(2)} \). For higher charge types of electrolytes, such as 3:2, \( \alpha_1 \) and \( \alpha_2 \) may have different values.

The Bromley-Zemaitis model is an example of Specific ion Interaction Theory (SIT theory) and presents a convenient way to simulate multiphase and multicomponent inorganic systems (Casas et al., 2005; Zemaitis et al., 1986). This model can describe the solution speciation over a wide range of concentration (0.1 to 30 molal). However, the model requires three temperature-dependent parameters per cation-anion pair to make the prediction accurate. The activity coefficients can be calculated using the equation

\[
\log \gamma_{\pm} = -\frac{A_{DH}|z_+z_-|\sqrt{I}}{1 + \sqrt{I}} + \frac{(0.06 + 0.6B)|z_+z_-|I}{\left(1 + \frac{1.5}{|z_+z_-|I}\right)^2} + BI + CI^2 + DI^3
\]  

(96)

where \( A_{DH} \) is the Debye–Hückel parameter, and \( B, C, \) and \( D \) are temperature-dependent Bromley parameters for one pair of cation–anion.

The main advantage of the extended Debye–Hückel model is its simplicity, as there is only one species-specific parameter, which can be assigned a reasonable value. The advantage of the Pitzer model is that it can be theoretically applied to predict speciation in highly concentrated solutions. The accuracy can be achieved at the cost of a large number of parameters to quantify the physicochemical interactions among all the components present in the solution. Significant effort is required to estimate the unknown parameters for more uncommon systems. Considerable simplifications, by omission of several interaction parameters, on the other hand, may result in a loss of predictive ability. The Bromley-Zemaitis model is able to produce consistent predictions in multiphase and multicomponent systems, yet requires a significant number of model parameters. Therefore, the extended Debye–Hückel model is the most convenient aqueous activity
coefficient model which is able to produce reasonable predictions with minimum number of required parameters. The extended Debye–Hückel model is employed in Publications II and III.

In Publication I, another correlation, Eq. (97), derived from the Debye-Hückel Equation, was used to consider the effect of the ionic strength on the sulfate-bisulfate equilibrium and sulfate-copper sulfate equilibrium by using correlations $\log K_{S-BS} = 1.99 - \Delta \log K_{S-BS}$ for the former and $\log K_{CuSO_4} = 2.35 - \Delta \log K_{CuSO_4}$ for the latter. $\Delta \log K$ describes the effect of the ionic strength on the equilibrium. Please refer to Publication I for more details.

$$\Delta \log K = 0.51 \left( \frac{\sqrt{I}}{1 + 1.50\sqrt{I}} - CI \right) \chi + CI \quad (97)$$

The value of $\chi = 4$ for bisulfate ($K_{S-BS}$), and $\chi = 8$ for copper sulfate ($K_{CuSO_4}$). At a relatively low ionic strength range ($I<0.5$), the value of $C = 0.09$ was used for both electrolytes, whereas the value of $C = 0.01$ was used up to $I = 3$ (Tamminen et al., 2013).

### 3.4 Numerical methods

#### 3.4.1 Modelling a single extraction stage

According to the modelling approach conventionally applied in the mechanistic modelling of extraction equilibrium, a model of the liquid–liquid extraction equilibrium consists of nonlinear algebraic equations for the equilibrium constants of all the reactions of the assumed mechanism and linear algebraic equations of mass and electrical charge balances for the species in the system. In addition, an equation to calculate ionic activity coefficients is used to account for aqueous phase non-ideality. The equilibrium composition of the process phases can be calculated from their initial composition by simultaneous solution of the equations. The equations constitute the model for the liquid–liquid extraction equilibrium. The model can be solved since it is possible to formulate the same number of independent equations as there are variables (species).

The model can be solved using, for example, the Newton-Raphson method (Salmi, Mikkola & Wärnä, 2010). The method is used for solving nonlinear systems of algebraic equations through searching for successively better approximations to the solutions of these systems of equations (Ypma, 1995)
where \( F \) is the system of continuously differentiable functions, \( J \) is the Jacobian matrix for the system \( F \), \( x \) is the approximation to the solution of the system \( F \), \( n \) is the number of the iteration number.

The Newton-Raphson method requires a good initial approximation to the solution of the system; otherwise, erroneous or inaccurate results can be obtained (Salmi et al., 2010; Ypma, 1995).

Alternatively, a rate-based approach can be used for solution of the model (Kuitunen, 2014; Salmi et al., 2010). Since reversible chemical reactions proceed until an equilibrium is reached, the solution of a system of ordinary differential equations at plateau gives the same result as the solution of the system of nonlinear algebraic equations. Therefore, for a heterogeneous two-phase reaction in a batch reactor, the element balance equation, Eq. (99), can be used to calculate the concentrations of either the aqueous or organic phase species, together with the total mass balance equation, Eq. (100), used to solve the concentrations of the species in the other phase.

\[
\frac{d(V_{Aq})}{dt} = -\varphi \eta V_{tot}
\]

\[
V_{Aq} \frac{dc_{Aq}^i}{dt} + V_{Org} \frac{dc_{Org}^i}{dt} = 0
\]

where \( V_{tot} \) is the total volume of the batch reactor, \( V \) is the volume of aqueous or organic phase, \( c \) is the concentration of a species in the aqueous or organic phases, \( i \) is the index of the species in the system, \( t \) is the reaction time, \( r \) is the generation rate of an individual species, and \( \varphi = \frac{V}{V_{tot}} \) is the holdup of the aqueous or organic phase.

For an elementary reversible reaction, Eq. (101), a reaction rate equation, Eq. (102), is formed directly from the reaction stoichiometry in agreement with the mass action law. The expression of the reaction equilibrium constant, Eq. (103), sets the relationship between the forward and backward parts of the reversible reactions. The forward reaction rate constant can be assigned to be \( k_f = 1000 \), the same for all the reactions, since its value does not influence equilibrium but rather affects the time required to reach it.
\[
\alpha A + \beta B + \ldots \rightleftharpoons \gamma C + \delta D + \ldots \\
(101)
\]

\[
R_j = k_{f,j} \left( \frac{a_A^\alpha a_B^\beta \ldots - a_C^\gamma a_D^\delta}{K_j} \right) \\
(102)
\]

\[
K_j = \frac{k_{f,j}}{k_{r,j}} \\
(103)
\]

where \( k_f \) and \( k_r \) are the reaction rate constants of the forward and backward reactions, respectively. \( K \) is the equilibrium constant, \( i \) is the index of species and \( j \) is the index of equilibrium reactions.

The rate of a reaction step, \( R_i \), is related to the generation rate of an individual species, \( r_i \), by Eq. (104).

\[
r_i = \sum_{j=1}^{S} \theta_{ij} R_j \\
(104)
\]

where \( \theta \) is the stoichiometric coefficient of the species.

With this mathematical manipulation, the nonlinear algebraic equations for the equilibrium constants and linear algebraic equations for element balance are converted into ordinary differential equations (ODEs). In the case of a reversible heterogeneous reaction encountered in liquid–liquid extraction, the following equations for aqueous and organic phase species need to be solved simultaneously:

\[
\frac{dc^{Aq}_i}{dt} = -\sum_{j=1}^{S} \theta_{ij} R_j \\
(105)
\]

\[
\theta_{kj} \frac{dc^{Org}_k}{dt} = -\theta_{ij} \frac{V_{Aq}}{V_{Org}} \frac{dc^{Aq}_i}{dt} \\
(106)
\]

The ordinary differential equations can be solved simultaneously as an initial value problem by integration. In such a way, the solution of the model can be significantly
simplified. A model solution can be obtained faster, and, at the same time, the accuracy of the solution can be easily controlled by solver settings.

**Example: extraction of copper(II) by a cation exchanger**

As discussed in Section 3.1.1, copper(II) is extracted by a chelating cation extractant according to the reaction

\[
Cu^{2+} + 2\overline{HA} \rightleftharpoons \overline{CuA_2} + 2H^+ \tag{E1}
\]

which has the concentration based extraction equilibrium constant

\[
K_{ex,Cu} = \frac{c_{CuA_2}c_H^2}{c_{Cu}c_{HA}^2} \tag{E2}
\]

**Nonlinear system of equations**

The mass balance for the cation exchange reaction Eq. (E1) is

\[
c_{Cu}^*V_{Aq} + c_{CuA_2}^*V_{Org} - c_{Cu}^0V_{Aq} - c_{CuA_2}^0V_{Org} = 0 \tag{E3}
\]

\[
c_{HA}^* + c_{CuA_2}^* - c_{HA}^0 - c_{CuA_2}^0 = 0 \tag{E4}
\]

The electrical charge balance for the cation exchange reaction Eq. (E1) is

\[
c_H^* + 2c_{Cu}^* - c_H^0 - 2c_{Cu}^0 = 0 \tag{E5}
\]
The equilibrium composition of the aqueous and organic phases can be calculated by the simultaneous solution of Equations E2 – E5, given their initial compositions, phase ratio \( \frac{V_{\text{Aq}}}{V_{\text{Org}}} \), and the value for the extraction equilibrium constant, Eq. (E2).

**Rate-based approach**

The concentration-based extraction rate for the reaction in Eq. (E1) is

\[
\mathcal{R}_{\text{ex,Cu}} = k \left( c_{\text{Cu}} c_{\text{HA}}^2 - c_{\text{CuA}_2} c_{\text{H}}^2 / K_{\text{ex,Cu}} \right)
\]

(E6)

The generation rates for the individual species

\[
\begin{align*}
    r_{\text{Cu}} &= -\mathcal{R}_{\text{ex,Cu}} \\
    r_{\text{HA}} &= -2\mathcal{R}_{\text{ex,Cu}} \\
    r_{\text{CuA}_2} &= \mathcal{R}_{\text{ex,Cu}} \\
    r_{\text{H}} &= 2\mathcal{R}_{\text{ex,Cu}}
\end{align*}
\]

(E7)

The element balance equations for the individual species

\[
\begin{align*}
    \frac{dc_{\text{Cu}}^{\text{Aq}}}{dt} &= -\mathcal{R}_{\text{ex,Cu}} \\
    \frac{dc_{\text{H}}^{\text{Aq}}}{dt} &= 2\mathcal{R}_{\text{ex,Cu}} \\
    \frac{dc_{\text{HR}}^{\text{Org}}}{dt} &= -2 \frac{V_{\text{Aq}}}{V_{\text{Org}}} \frac{dc_{\text{Cu}}^{\text{Aq}}}{dt}
\end{align*}
\]

(E8)
The equilibrium composition of the aqueous and organic phases can be calculated using the rate-based approach by simultaneous solution of Equations E8 given the initial composition of the phases, phase ratio \( \frac{V_{Aq}}{V_{Org}} \), and the value for the extraction equilibrium constant, Eq. (E2). The reaction rate constant can be assigned a value, for example \( k_t = 1000 \), as discussed above.

Solving the equations presented above with the initial concentrations of copper and protons in the aqueous phase 0.016 mol/L and 0.001 mol/L, respectively, while that of extractant and copper-extractant complexes in the organic phase 0.01 mol/L and 0 mol/L, respectively, and taking the extraction equilibrium constant equal to 30, one can calculate the composition of the process phases at equilibrium (Figure 17). The phase ratio \( \frac{V_{Aq}}{V_{Org}} \) is taken to be 0.5.

Figure 17. Solution of the phase equilibrium of copper(II) extraction with a chelating cation exchange extractant, using the rate-based approach.
3.4.2 **Estimation of model parameters**

Mechanistic mathematical models are used in chemical engineering to aid in different engineering tasks such as process design, analysis, and process control system development. The models used often contain parameters that need to be estimated from experimental data. The reliability of the models depends on the depth and precision of the theoretical background used in the model development and on the accuracy of the parameter estimates. Consequently, the progress in fruitful utilisation of the models depends on the reliability of the parameters estimated. After the model parameters are estimated and their reliability is proved, the model can be used for various tasks with confidence.

Traditionally, the values of model parameters are obtained using, *e.g.* Gaussian approximations, and the reliability of the point estimates is analysed using a linearised model. However, the emergence of efficient Markov chain Monte Carlo (MCMC) methods has made the Bayesian approach a standard tool in quantifying the uncertainty in parameters (Solonen, 2011). MCMC methods are used to approximate the posterior distribution of a parameter of interest by random sampling in a probabilistic space (Geyer, 2011). MCMC methods aim at generating a sequence of random samples, whose distribution asymptotically approaches the posterior distribution as the number of samples increases (Figure 18). As the name of the methods states the method consists of two parts. The term *Monte Carlo* refers to the methods that are based on random number generation, *e.g.*, random sampling. *Markov Chain* refers to the sequence of samples generated so that each new point depends only on the previous point.

![Figure 18. The path of the metropolis sampler (blue line), when sampling a non-Gaussian target (contours given by black lines).](image-url)

---

71
The general procedure of the MCMC methods in parameter estimation (Figure 18) is as follows. To begin with, parameters $\theta$ are estimated based on measurements $y$ using, e.g., a least squares approach. The estimated parameters are used for the initialisation of the chain. New candidate $\theta_{\text{new}}$ is randomly generated from a suitable proposal distribution that may depend on the previous data point of the chain (this is the Monte Carlo part). For a pair of parameter values, it is possible to compute which is a better parameter value, by computing how likely each value is to explain the data, $y$, given a proposal distribution of parameters. If the new randomly generated parameter, $\theta_{\text{new}}$, value is better than the previous one, it is added to the chain of parameter values with a certain probability, determined by how much better it is (this is the Markov chain part). If the new candidate, $\theta_{\text{new}}$, is worse than the last one, it is rejected, and a new candidate is randomly generated again. When a candidate is accepted, a new candidate is generated. The procedure is repeated until a desired chain length is achieved. Gradually the approximated posterior distribution of the parameters (within the contours in Figure 18) is explored.

MCMC helps to solve the parameter estimation problem in a statistical manner, and the entire distribution of the parameters can be explored. It is especially useful and convenient when a model contains many parameters. In that case, the exploration of the distributions of parameters using contour plots is inconvenient.

In this study, an open source MCMC code package (Laine, 2017) was used. This toolbox provides tools to generate and analyse a Metropolis-Hastings MCMC chain using multivariate Gaussian proposal distribution (Haario et al., 2006; Laine, 2017). In Publications I–III, the nonlinear regression modelling approach was used for the estimation of the model parameters, and the MCMC algorithm was used for estimating the reliability of the modelling results. Also, the MCMC algorithm was used for model discrimination in Publication I and in search of an optimal experimental design in Publication II.

### 3.4.3 Simulation of counter-current extraction cascades

Modelling and simulating process flowsheets of chemical plants is a basic task in chemical engineering and is intended for quantitative description of the plants for their optimal design and control (Boyadjiev, 2010). Process flowsheets show a combination of mutually influenced process steps and the equipment selected to carry out the process steps, the stream connections, stream flow-rates and compositions, and the operating conditions. It is the steady-state mass and energy balances that are behind the flow–sheet calculations. The model of a plant comprises a combination of the models for the separation processes, which are supplemented with the equations for the interactions between them. Therefore, when the models of the process steps are available, the problem
of chemical plant modelling becomes the introduction of the equations linking the sub-models of the process steps. The plant simulation task is accomplished by the efficient and accurate solution of the plant model using a simulation method.

**Process simulation**

Process flowsheets represent a combination of process steps which are connected in a definite way by process streams. The streams are examined as informational because they transfer information (without change) from one process step to another, containing quantitative data on quantity and composition of the material stream (energy balance is often neglected in the process flow-sheets where temperature effects are not of interest).

The model of a chemical plant is built from mathematical structures, providing a connection between inlet regime variables \((irv)\), outlet regime variables \((orv)\), constructive variables \((a)\), and variables \((b)\) characterising the state of the equipment. The inlet and outlet regime variables represent the parameters of the inlet and outlet streams of a process step. The constructive variables are the constructive parameters of the equipment. The parameters characterising the state of the equipment account for some effects of quasi-stationary processes, such as extractant degradation or diluent evaporation. The model of each process step is represented by a system of equations that describe the dependencies between all the variables:

\[
f(irv^i, orv^i, a^i, b^i) = 0 \quad (107)
\]

The combination of the models of all the process steps \((i = 1, ..., i_{tot})\), where \(i_{tot}\) is the total number of the process steps in the process), Eq. \((107)\), supplemented with the equations describing the connections between the process steps, Eq. \((108)\), gives the complete model of the whole process.

\[
irv^i = orv^{i-1} \quad (108)
\]

The streams that do not realize connections between the process steps are the inlet and outlet streams of the whole process. The outlet streams of the whole process can be calculated only if all the inlet streams are specified.
Simulation methods

The simulation of a chemical process represents the utilisation of methods and algorithms for the determination of the outlet regime variables, \( \text{ORV} \), by solution of the process model, \( G \), in Eq. (109), when the process inlet regime variables (\( \text{IRV} \)), constructive variables, (\( \text{CV} \)) and equipment state variables (\( \text{ESV} \)) are known:

\[
\text{ORV} = G(\text{IRV}, \text{CV}, \text{ESV})
\]  

There are three basic approaches available to solve this problem: simultaneous equations, simultaneous-modular, and sequential-modular. The simultaneous approaches require a global solution of the system comprising Eqs. (107) and (108). There are computing problems usually encountered in the simultaneous approaches coming from the large number of variables and equations, the nonlinearity of the equations, and the small number of variables in the individual equations. In the simultaneous equations approach, the problems are solved entirely by mathematical means, which obstructs the close scrutiny of the physical relevance of the results obtained in the progression to the solution. The simultaneous modular approach requires the identification of the groups of equations that can be solved simultaneously with respect to one of the output variables (Chen and Stadtherr, 1985). The sequential modular approach is used in a wide range of applications due to its simplicity (Kisala et al., 1987). However, the sequential-modular approach may require a longer computational duration when many iterations are needed for model solution. In the sequential modular approach, the process step models are solved in the sequence in which the process steps appear in the process under the condition that all inlet regime variables are regulated.

The hierarchical organisation of the process modules within the process plays a central role in the sequential-modular approach. There are two types of hierarchical organisations of process steps in a chemical plant system (Figure 19): acyclic, when there are no recirculating streams (Process Steps I and II), and cyclic, when there are recirculating streams (Process Steps III, IV, V, VI), or sequences of the process steps. The composition of Stream 3 can be easily calculated as a result of the simulation of Blocks I and II, if the composition and flow rate of Stream 1 are known. However, calculating the composition of Stream 4 requires the characteristics of Stream 8 to be known, along with the composition of Stream 3.
Figure 19. Chemical plant system that contains acyclic and cyclic parts.

The Process Steps III, IV, V and VI are organised in a cycle that makes the calculation of Stream 4 more complicated. In practice, the problem is solved iteratively. First, an assumption on the values of input regime variable for Stream 8 is made. Then, Modules III, IV, V and VI are simulated, and new values for Stream 8 are estimated. After that, the simulation of Modules III, IV, V and VI are repeated again until the values for Stream 8 do not change any more. At that point, Modules III, IV, V and VI are considered as an independent contour. Since chemical plants often have many recycling streams, the simulation of the chemical plant system requires decomposition of the system into acyclic parts and independent contours. The blocks in the acyclic parts are simulated only once, whereas the blocks in the separate independent contours are simulated repeatedly.

**Counter-current process simulation**

The simulation of an idealised counter-current liquid–liquid extraction process, as depicted in Figure 20, can be done by applying the sequential modular approach to the process model solution. The composition of pregnant leach solution is usually fixed, since it depends on leaching process performance. The composition of the lean electrolyte can be assumed to be fixed as well, since it depends on product metal recovery process (Figure 3). The organic phase is recycled between the process steps in the loading and stripping stages counter-currently to the aqueous solution. The counter-current motion of the process phase makes the process consist of only cyclic parts. Therefore, the process can only be simulated by an iterative solution of the process model. Each of the process stages represents an equilibrium extraction stage that can be modelled employing the approach discussed in Section 3.4.1 above. According to this approach, the outlet streams’ compositions can be calculated when the compositions of all the inlet streams and their flowrates are defined. However, only pregnant leach solution and lean electrolyte compositions and total extractant concentration in organic phase are known. The exact organic phase composition is not defined at any of the inlet streams; only the total extractant concentration is specified.
Figure 20. A schematic representation of a counter-current liquid–liquid extraction process in which the loading and stripping steps are organised in a series. The blue arrows represent the aqueous electrolyte solution in the loading stage, the brown arrows represent organic streams and the green arrows represent the strip liquor.

The difficulty can be bridged if the compositions of all the organic streams in the loading step are assigned reasonable values. For example, the streams can be assumed to be a pure organic phase containing no metal ions extracted. In the same manner, the compositions of all the aqueous outlet streams in the stripping step can be assigned to be the same as the composition of the lean electrolyte. Now, having the inlet organic phase composition known in the loading stages, the outlet aqueous phase composition in the loading stages can be calculated in a series starting from the first one (L 1). Finally, the raffinate composition is calculated. Then, having the composition of the organic stream coming from the first loading stage estimated, the compositions of the rich electrolyte, and all the organic streams, in the stripping stages can be calculated in series in the same manner starting from the first stripping stage (S 1). The composition estimated in the first iteration is used in the subsequent one, until the stopping criteria are met.

When the compositions of all of the streams are calculated after each iteration, the mass balance in the entire extraction circuit is required to be checked. At the steady state, the amount of substance transferred from pregnant leach solution to loaded organic in the loading step is equal to the amount of the substance transferred from the loaded organic to the rich electrolyte in the stripping step. Thereafter, the target function can be formulated by Eq. (110). The iterations can be stopped when $MB$ becomes smaller than a small fixed $\varepsilon > 0$. 

---

**Diagram Description**

- **Sequence of simulation in loading stages**
- **Sequence of simulation in stripping stages**
- **PLS**
- **Lean electrolyte**
- **Rich electrolyte**
- **Raffinate**

---

**Equation Reference**

Eq. (110)
\[ MB = \sum_{i=1}^{N} (\Delta C_{L,i} \cdot F_{PLS} - \Delta C_{S,i} \cdot F_{RE})^2 \]  

(110)

where \( i \) is the index of an element extracted in the process, \( N \) is the total number of the elements extracted in the process, \( \Delta C_{L,i} = C_{PLS,i} - C_{Raffinate,i} \) is the difference in the concentration of an element in pregnant leach solution and raffinate, \( \Delta C_{S,i} = C_{RE,i} - C_{LE,i} \) is the difference in the concentration of an element in the rich electrolyte and the lean electrolyte, \( F_{PLS} \) is the flowrate of the aqueous solution in the loading step and \( F_{RE} \) is the flowrate of the aqueous electrolyte solution in the stripping step.

The simulation approach described above was used for the analysis of the chemical iron transfer in the copper liquid–liquid extraction process and in optimisation of liquid–liquid extraction fractionation of cobalt, nickel and lithium in Publications II and III, respectively.
4 Hydrometallurgical Process Development

Hydrometallurgical process development usually originates in the need to produce a valuable product; then the available raw materials are analysed and processing routes considered (Forsén and Aromaa, 2013). Chemical composition, mineralogy, particle size, volume, etc. are analysed with the aim of estimating their potential for recovery of the valuable product and establishing the most promising process routes. Actual process development starts with process synthesis and continues with process design. The objective of process synthesis is to determine the optimal processing route, subject to predefined process constraints and performance criteria, from numerous alternatives, to convert given raw materials into desired products (Babi et al., 2015; Tula et al., 2017). The objective of process design is to determine the values of the design variables of the unit operations in the selected flowsheet (Tula et al., 2017).

When a new hydrometallurgical process is being developed, a comparison of process alternatives and process optimisation is usually made, based on the experience of scientists and engineers, as well as on extensive experimentation (Rintala et al., 2011). However, the application of mathematical modelling and optimisation can aid significantly in hydrometallurgical process development: clarification of the interactions between process steps, utilisation of validated models for process optimisation and the ability to identify the optimal process (Nfor et al., 2009). Raw experimental data can serve as a superstructure of process options and guide the process synthesis. Furthermore, process design can be based on validated mathematical models of process steps in model-based process design.

The availability of meaningful objective functions to measure process performance is critical for successful process synthesis and process design. Purity in the product stream and recovery of the target metals from the raw materials are widely applied measures of process performance, although they often determine technical feasibility only. They do not measure the economical potential of the alternative processes. However, it is desirable to base process synthesis decisions upon costs over the complete process. The information needed to precisely estimate the profitability of the process and its internal rate of return is not available at the very beginning of process development, which makes the task of hydrometallurgical process development very challenging.

In addition to technical feasibility, health, safety, and environmental aspects play an important role in process development and implementation. Early implementation of health, safety, and environmental principles is essential to the success of development of hydrometallurgical processes, and can prevent negative consequences in the later stages of process development (Edwards et al., 2013). Any economic advantage of liquid–liquid extraction over other separation processes for metals can be lost if the required operating conditions are too harsh (Rydberg et al., 2004). For example, too high a loss of solvent from the system, too corrosive process solutions, or their high toxicity may make a process option economically infeasible or unacceptable from the point of view of health, safety, and environment.
4.1 Algorithm-based process synthesis

The task of hydrometallurgical process synthesis was defined in Publication IV. It is to identify the most suitable sequence of unit operations and the most effective combination of operating parameters to obtain the desired purification and yield with the least economic effort. Process synthesis, therefore, involves the analysis of the problem to be solved, and, generation, evaluation and screening of process alternatives so that the best process option can be identified. A hydrometallurgical process typically consists of leaching, concentration and purification, and product recovery steps (Figure 3). Several alternative unit operations are available for each process step. For instance, one of a number of leaching agents can be employed for leaching valuable metals. Liquid–liquid extraction, ion exchange and/or selective precipitation can be employed for purification and concentration. Crystallisation, chemical precipitation or electrowinning can be used for product metal recovery.

As it has been discussed above, meaningful objective functions to ground the comparison of different process alternatives in hydrometallurgical process synthesis are required. It was demonstrated in Publication IV that key performance indicators (KPIs) introduced by Winkelnkemper and Schembecker (2010) could be used to evaluate the suitability of different process alternatives in the early stages of process development. The indicators assess the selectivity and estimate the relative costs of purification.

**Purification rating**

For assessment of the purification of one step as a percentage of the purification of the total process to be designed, the purity of the initial mixture $P_0$ and the target purity $P_f$ must be considered as given boundaries of the purification process. Winkelnkemper and Schembecker (2010) defined a purification performance index ($PPI$) as:

$$PPI_l = \frac{\tanh^{-1}(2P_l - 1) - \tanh^{-1}(2P_{l-1} - 1)}{\tanh^{-1}(2P_f - 1) - \tanh^{-1}(2P_0 - 1)}$$

(111)

where $P_l$ is the purity after the current purification step, and $P_{l-1}$ is the purity after the previous purification step.

Due to the high nonlinearity of the arctangent function, $PPI$ is a balanced measure of purity over the whole purity range of a purification process. It evenly rates purification process steps, when high purity improvement requires moderate effort and conversion and recovery steps and when small purity improvement requires great effort. Thus, $PPI$ can be used to connect the purification performance with the projected effort.
4.1 Algorithm-based process synthesis

Estimation of recovery cost

The influence of single purification steps on total process costs is readily quantifiable using a separation cost indicator (SCI) defined by Winkelnkemper and Schembecker (2010), as shown in Eq. (112). The separation cost indicator depends on the normalized purification rating (PPI), yield (Y) and the specific costs. In the present case, the specific costs are leaching cost, $k_L$, and the specific cost of purification steps, $k_{pur,t}$.

$$SCI_1 = Y_1 \cdot \frac{1}{PPI} \cdot \left( k_L + k_{pur,t} \cdot \frac{1}{1-Y_1} \right)$$  \hspace{1cm} (112)

The task of process synthesis is the minimisation of the total specific production costs for the process. Therefore, the sum of specific costs of the process steps can be taken as the target function in an algorithm-based process design:

$$SCI_{tot} = \sum_{l=1}^{n} SCI_1$$  \hspace{1cm} (113)

In this way, the KPIs are suitable for an initial synthesis of a purification process when not enough data for rigorous optimisation is available.

Ant colony optimisation for process synthesis

The solution of an optimisation problem in the process synthesis of a hydrometallurgical process requires a suitable and efficient algorithm; one that is capable of identifying the minimum value of the target function and the corresponding sequence of extraction and purification steps, with their optimal operating parameters where several alternative options are available (Figure 21). Algorithms based on extensive searches for the optimal solution are not preferred due to the high computational efforts required (Raeesi, Pishvaie & Rashtchian, 2008). Moreover, gradient-based algorithms are not suitable due to the complexity of the task and the potential availability of multiple optimum points. However, the problem can be addressed in an efficient manner through the use of metaheuristics to find approximate solutions (Raeesi et al., 2008; Biswas, Chakraborti & Sen, 2009). Such algorithms as simulated annealing, genetic algorithms, differential evolution, etc., are often applied in the solution of this category of optimisation task.
The stochastic metaheuristic ant colony optimisation (ACO) algorithm, among others, has been found to be promising for the efficient synthesis of chemical separation processes (Raeesi et al., 2008; Rintala et al., 2011; Chunfeng and Xin, 2002). The algorithm imitates the foraging behaviour of ants in search of short paths between their nest and food sources (Blum, 2005). In the same way, ACO is typically used to find the shortest path from the first cell to the last in the structure to be optimised. This naturally resembles hydrometallurgical process synthesis, in which the most feasible and economic processing route has to be identified to produce a valuable product from a raw material, as depicted in Figure 21.

A hydrometallurgical process chain is built of individual process steps: leaching, solvent extraction, stripping, chemical precipitation, etc. However, in general the process steps are considered in the developed ACO-based algorithm as black boxes with inputs and outputs and could just as well be continuous (e.g. liquid–liquid extraction) and even consist of multiple stages. An output from a unit operation is an input for the next one in the constructed process route. A model for each unit operation comprises mass balance equations.

An algorithm-based method for the synthesis of hydrometallurgical processes using limited amounts of experimental data was presented in Publication IV. In this method, an ACO-based algorithm is used to identify the most economic process alternative in an iterative manner. The purification performance index measures purity improvement, and the separation cost indicator is used as an objective function for the comparison of process alternatives. The detailed description of the method was presented in Publication IV.
4.2 Model-based process design

Model-based process design can be implemented by employing mechanistic models for process steps and a simulation method, as discussed in Section 3.4.3. This approach is common in chemical engineering, and is implemented in many commercial software packages used for process simulation and optimisation, for example, HSC Sim for metallurgical applications and Aspen HYSYS for the energy industry. However, mechanistic models are not available for all possible separation processes and systems in hydrometallurgy. Therefore, a continuous investigation of the chemistry involved in separation processes and the development of corresponding models are ongoing in research institutions and in industry. Model-based process design is extremely useful in testing different process configurations and their performance. It helps to carry out detailed preliminary investigations before expensive tests on a pilot scale. In this study, the sequential modular simulation approach (Section 3.4.3) was applied to perform a simulation of the liquid–liquid extraction separation of copper and iron in Publication II and the extraction fractionation of cobalt, nickel and lithium in Publication III.
5 Results and Discussion

5.1 Extraction equilibrium of Cu and Fe with a hydroxyoxime extractant

5.1.1 Experimental methods

Experimental studies were carried out on the liquid–liquid extraction equilibria of copper and iron with a hydroxyoxime extractant in order to collect data for Publications I and II. Only a brief explanation of the experimental procedures used are presented here. More details on the experimental design are presented in Publications I and II.

Extraction and stripping experiments were carried out on an orbital shaker in 50 mL separation funnels with a 30 min equilibration time at 20 °C. The organic to aqueous (O/A) phase ratios, the amount of metals in both aqueous and organic phase and the initial acidity of the aqueous phase were varied in different experiment sets.

Only one parameter was variable in each experiment set. In copper extraction experiments, the initial acidity was varied in the first loading experiment set, whereas the organic to aqueous phase ratio was varied in all the other loading and stripping experiment sets. In the iron loading experiments, the organic to aqueous phase ratio was varied in all the experiment sets. Since the equilibrium acidity was not adjusted in all the experiments, this approach facilitated fast and simple data acquisition in the shaking experiments. Yet, the data collected in such a way were sufficient for model discrimination and validation.

In the loading experiments, aqueous phases, with known iron and copper contents and acidity, were contacted with the metal-free organic phases of known extractant concentrations. In the stripping experiments, metal-free aqueous phases of known acidity were contacted with the loaded organic phases with known metals and extractant concentrations.

The iron and copper content in the aqueous phase was analysed using inductively coupled plasma mass spectrometry, or ICP-MS (Agilent technologies, Agilent 7900). The H₂ cell gas line was used for improved interference removal on $^{56}$Fe with intense plasma-based polyatomic overlaps. Therefore, no ArO⁺ interference problem was experienced during the analysis of iron in the calibration range 1-500 ppb. Alternatively, isotopes with lower abundances could be used, resulting in lower sensitivity and thus higher detection limits. The internal standard contained $^{72}$Ge, $^{115}$In, and $^{118}$In in the ICP-MS analysis. A Mettler Toledo T50 titrator with a DG 111-SC electrode was used to measure the total acidity in the aqueous phase in the experiments on copper extraction. The end point in titration of acidic solutions containing copper was set at pH 4.3 as copper hydroxides are formed at higher pH. Measurements of the pH were carried out with a Consort C3010 pH meter using a SenTix Mic glass electrode.
The oxime concentration in the metal-free organic phases was measured by the ultimate loading method using a standard 0.1 M NaOH solution (Sigma-Aldrich, AR grade) and a Mettler Toledo T50 titrator with a DG 111-SC electrode. The method is based on the stoichiometric reaction of 2 moles of oxime in an aliphatic diluent per mole of copper at pH 4.3, liberating acid which is determined by potentiometric titration with standard sodium hydroxide solution. The initial copper sulfate solution was prepared to have copper in excess in comparison with the estimated oxime concentration to be measured. The initial pH was adjusted to pH 4.3. The organic phase and the copper sulfate solution were placed in a beaker. The pH electrode and glass paddle stirrer were placed in the beaker as well. Vigorous mixing was ensured. As the pH of the mixture reached 3.5, the titration was stopped for 2 minutes to allow for complete mixing, then the titration was continued slowly until pH 4.3 was reached.

5.1.2 Extraction equilibrium

In the present study, liquid–liquid extraction of copper and iron(III) from sulfuric acid solutions with hydroxyoxime extractant Acorga M5640 in the aliphatic diluent Exxsol D80 was studied in a wide concentration range of copper, iron and extractant concentrations. Figure 22 shows that a simple linear regression model, Eq. (57), which is usually used to analyse the equilibrium in ideal solutions, is unable to fully explain all the variation in the collected data. The experimental design of the extraction and stripping experiments on copper extraction is shown in Table 3, while that for iron extraction is presented in Table 4. As discussed in Publications I and II, the nonideality of both the aqueous and organic phases explains the deviation from the straight line of slope 2 in copper extraction and slope 3 in the extraction of iron(III), since the concentrations vary significantly and are rather high in many of the data points.
Figure 22. The classical log–log representation of extraction equilibrium: a) loading and stripping equilibria of copper liquid–liquid extraction, b) the equilibrium distribution of iron(III) at different equilibrium pH levels and under different experimental conditions. The experimental conditions are presented in Table 3 and Table 4.

Table 3. Experimental design of the extraction and stripping experiments. (Publication I)

<table>
<thead>
<tr>
<th>Extraction set ID</th>
<th>Data points</th>
<th>C(Cu)₀, g/L</th>
<th>pH₀</th>
<th>HA, vol-%</th>
<th>Loading₀, %</th>
<th>O/A range</th>
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<tr>
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<td>28</td>
<td>5</td>
<td>0.11…3.91</td>
<td>10</td>
<td>0</td>
<td>1/1</td>
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<tr>
<td>E2</td>
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<td>1</td>
<td>1.4</td>
<td>10</td>
<td>0</td>
<td>1/10 … 10/1</td>
</tr>
<tr>
<td>E3</td>
<td>25</td>
<td>5</td>
<td>1.4</td>
<td>10</td>
<td>0</td>
<td>1/10 … 10/1</td>
</tr>
<tr>
<td>E4</td>
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<td>25</td>
<td>1.4</td>
<td>10</td>
<td>0</td>
<td>1/10 … 10/1</td>
</tr>
<tr>
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<td>30</td>
<td>25</td>
<td>1.4</td>
<td>25</td>
<td>0</td>
<td>1/10 … 10/1</td>
</tr>
<tr>
<td>E6</td>
<td>29</td>
<td>32</td>
<td>1.4</td>
<td>25</td>
<td>0</td>
<td>1/10 … 10/1</td>
</tr>
<tr>
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<td>45</td>
<td>1.4</td>
<td>25</td>
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<table>
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<th>C(Cu)₀, g/L</th>
<th>C(H₂SO₄)₀, g/L</th>
<th>HA, vol-%</th>
<th>Loading₀, %</th>
<th>O/A range</th>
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<td>10</td>
<td>90</td>
<td>2/1 … 10/1</td>
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<td>10</td>
<td>90</td>
<td>2/1 … 10/1</td>
</tr>
<tr>
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<td>15</td>
<td>0</td>
<td>190</td>
<td>10</td>
<td>90</td>
<td>2/1 … 10/1</td>
</tr>
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<td>S4</td>
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<td>0</td>
<td>190</td>
<td>25</td>
<td>80</td>
<td>2/1 … 10/1</td>
</tr>
</tbody>
</table>
Mechanistic mathematical modelling was employed to develop models capable of predicting the equilibrium compositions of the process phases from their known initial compositions and volumetric phase ratios in the liquid–liquid extraction of copper and iron. The models were developed as described in Section 3.1, and the models’ solutions were realized, as explained in Sections 3.4.1 and 3.4.3. The models’ parameters were estimated using the MCMC method, as described in Section 3.4.2.

It was observed that the value of the apparent equilibrium constant of the extraction reaction, Eq. (58), for copper extraction Eq. (61), changes systematically when fitted individually against data for each extractant concentration (Figure 23a). The same trend of a decreasing equilibrium constant with an increase of extractant concentration was reported by Hu and Wiencek (2000), Lin, Huang & Juang (2002), and Bazin, Hodouin & Zouadi (2005) in the extraction systems with hydroxyxime extractants LIX64N, LIX84 and LIX 984 (see Table 1 for the molecular structure of the extractants), respectively, in aliphatic diluents. This behaviour was explained through the nonideality of the organic phase. It is evident that a different value of apparent equilibrium constant is needed for each total extractant concentration.
5.1 Extraction equilibrium of Cu and Fe with a hydroxyoxime extractant

Figure 23. Dependency of the apparent extraction equilibrium constant on the total extractant concentration: a) Copper extraction. Blue squares – the apparent extraction equilibrium constant in the loading stage was estimated individually for each total extractant concentration; Red circles – the apparent extraction equilibrium constant in the stripping stage was estimated individually for each total extractant concentration; Blue line – the function $K_{L,LX} = K_{L,LX,0} \cdot (1 - \tanh(\alpha \cdot [HA]_{tot}))$ was used for data fitting with all the data in the loading stage; Red line – the linear function $K_{L,LX} = K_{L,LX,0} - \alpha \cdot [HA]_{tot}$ was used for data fitting with all the data in the stripping stage; b) Iron extraction. Blue squares – the apparent extraction equilibrium constant in the loading stage was estimated individually for each total extractant concentration; Blue line – the function $K_{L,LX} = K_{L,LX,0} \cdot (1 - \tanh(\alpha \cdot [HA]_{tot}))$ was used for data fitting with all the data in the loading stage.

Agarwal et al. (2012) argued that the organic phase nonideality can be modelled by the extractant dimerization equilibrium, Eq. (114)\(^2\), since inclusion of the equation in their model significantly improved the explanation of their experimental data. However, the introduction of Eq. (114) into the equation for the concentration-based copper extraction equilibrium constant, Eq. (115)\(^2\), using a mass balance of extractant, Eq. (116), gives Eq. (117) in which the term $\frac{1}{(1+2K_{D})^2}$ does not depend on extractant concentration. Therefore, in the author’s opinion, dimerisation of the extractant molecules in organic phase cannot explain the observed organic phase nonideality. At least the dimerisation constant and the extraction equilibrium constants cannot be estimated simultaneously from the same data set. Whewell and Hughes, (1979) reported that the ratios of the parameters could be determined quite precisely; however, the absolute values remained uncertain. In order to overcome this difficulty, the extractant dimerisation has to be studied independently from the extraction equilibrium. For example, a vapour–liquid equilibrium measurement technique could be used for that purpose. Otherwise, an

\(^2\) The Eqs. (52) and (53) in this section repeat the Eqs. (12) and (16) to increase the clarity of the thesis.
empirical function can be used to correlate the apparent extraction equilibrium constant and the total extractant concentration.

\[ K_D = \frac{[HA]_2}{[HA]^2} \]  \hspace{1cm} (114)

\[ K_{LLX}^{Cu} = \frac{[CuA_2] \cdot [H^+]^2}{[Cu^{2+}] \cdot [HA]^2} \]  \hspace{1cm} (115)

\[ [HA]_{tot} = [HA] + 2([HA]_2) = [HA] \cdot (1 + 2K_D) \]  \hspace{1cm} (116)

\[ K_{LLX}^{Cu} = \frac{[CuA_2] \cdot [H^+]^2}{[Cu^{2+}] \cdot ([HA] \cdot (1 + 2K_D))^2} = K_{LLX}^{Cu} \cdot \frac{1}{(1 + 2K_D)^2} \]  \hspace{1cm} (117)

In Publications I and II, a hyperbolic tangent function, Eq. (118), was applied to account for the dependence between the total extractant concentration and the apparent extraction equilibrium constants of copper and iron in the extraction step. The data for iron extraction are not described as well as they are for copper extraction. Large uncertainty was observed in the experimental data with low extractant concentration, due to the low extraction percentage of iron in these experiments. Therefore, a large error is associated with the outlying data point in Figure 23b.

The hyperbolic tangent function is just an empirical function, although it appears to represent the dependence well. When selecting an empirical function, the primary concern is limiting the number of parameters (the parameters must be well discriminated) and, secondly, physically meaningful extrapolation of the function beyond the experimental range. The general hyperbolic tangent function shown in Figure 24a gives an ordinate scaled between (-1, 1). The form \((1-\tanh(x))\) gives a decreasing function for positive \(x\) values. The form \((1-\tanh(ax))\) introduces a scaling factor for \(x\). The form of the function used in the current study shown in Figure 24b gives us a monotonically decreasing function with two adjustable parameters only. Thus, the function used in the current study, Eq. (118), gradually decreases when the total extractant concentration decreases, and has a maximum value (for \([HA]_0 < 0\)), when the total extractant concentration approaches zero. The same trends are observed in the experimental data (Figure 23a and b).

\[ K_{LLX} = K_{LLX,0} \cdot (1 - \tanh(\alpha \cdot [HA]_0)) \]  \hspace{1cm} (118)
A linear function, \( K_{\text{LLX}} = K_{\text{LLX},0} + \alpha \cdot [HA]_{\text{tot}} \), was applied for the same purpose in modelling copper stripping, due to the fact that only two levels of extractant concentration were studied in copper stripping. The estimated values of the parameters are shown in Table 5.

### Table 5. Comparison of the correction functions for the model predicting equilibrium in the liquid–liquid extraction of copper.

<table>
<thead>
<tr>
<th>Loading</th>
<th>Parameter</th>
<th>Value</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{\text{LLX}} = K_{\text{LLX},0} (1 - \tanh(\alpha \cdot [HA]_{\text{tot}})) )</td>
<td>( K_{\text{LLX},0}^{Cu} )</td>
<td>50.23</td>
<td>3.24</td>
</tr>
<tr>
<td></td>
<td>( \alpha^{Cu} )</td>
<td>3.16</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>( K_{\text{LLX},0}^{Fe} )</td>
<td>0.0215</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>( \alpha^{Fe} )</td>
<td>3.342</td>
<td>0.893</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stripping</th>
<th>Parameter</th>
<th>Value</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{\text{LLX}} = K_{\text{LLX},0} + \alpha \cdot [HA]_{\text{tot}} )</td>
<td>( K_{\text{LLX},0}^{Cu} )</td>
<td>13.77</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>( \alpha^{Cu} )</td>
<td>(-23.16)</td>
<td>0.00</td>
</tr>
</tbody>
</table>
The linear function predicts a negative $K_{LLX}$ value very shortly after the range of the experimental data. This is acceptable, since an extractant concentration higher than 0.55 M is not practically used due to high viscosity. The stripping of iron from the loaded organic phase was also studied. However, it was found that the same modelling approach could not be used in that case due to the very low stripping efficiency, independent of experimental conditions (Publication II).

Figure 25 shows how the model for copper extraction, supplemented with the hyperbolic tangent function is able to predict the extraction isotherms well at different conditions with uncontrolled equilibrium acidity. Goodness of fit for the iron liquid–liquid extraction equilibrium model, supplemented with the hyperbolic tangent function, is demonstrated in Figure 26.

Figure 25. Extraction isotherms of copper extraction at various initial aqueous copper concentrations and at uncontrolled equilibrium acidity. The apparent equilibrium constant of copper extraction is corrected using function $K_{Cu}^{LLX} = 50.23 \cdot (1 - \tanh(3.16 \cdot |HA|_{tot}))$. a–c) HA 10%; d–f) HA 25%; g) HA 5%; h) HA 17%. Please refer to Publication I for more details.
Figure 26. Goodness of fit of the iron(III) liquid–liquid extraction model. The experiments were performed with uncontrolled equilibrium acidity. Please refer to Publication II for more details.

After the models for the extraction equilibrium of copper and iron were developed separately, a combined model capable of predicting competitive extraction of the metals was devised and validated using the data collected in optimal experiments (Publication II). The good prediction of the experimental data by the combined model demonstrated in Publication II proved the validity of the modelling approach used in this study and enables reliable utilisation of the developed models in process design and optimisation.

5.1.3 Significance of organic phase nonideality

The dependence of the apparent extraction equilibrium constant on the extractant concentration can affect the design of the copper liquid–liquid extraction process. It was shown, in Publication II, that there is an optimum extractant concentration at which the extractant is used most efficiently. The existence of the optimum originates from organic phase nonideality. The dependence of copper extraction performance is demonstrated in Figure 27. The curves are calculated using the developed model with corrected apparent extraction equilibrium constant. Initial aqueous and organic copper concentrations are correspondingly 45 g/L and 0 g/L, O/A equals 1, and the equilibrium acidity is 0.77 M. The organic phase nonideality has to be considered in the process design along with the physical limitations (high viscosity of concentrated extractant leading to high operational costs) of utilising high extractant concentrations in copper liquid–liquid extraction with hydroxyoxime extractants.
5 Results and Discussion

Figure 27. Extraction of copper and loading of extractant in copper liquid–liquid extraction depending on extractant concentration. A single phase contact was simulated. Red lines – $K_{LLX} = 19.78$; Blue lines – $K_{LLX} = 50.23 \cdot (1 \cdot \tanh(3.16 \cdot [HA]_{tot}))$; Dashed lines – loading; Solid lines – extraction. (Publication I)

5.1.4 Model-based analysis of Fe transfer in Cu extraction process

The application of the extraction equilibrium model developed for the analysis of the chemical iron(III) transfer in the copper extraction process was demonstrated in Publication II. The extraction circuit configuration was kept simple (two extraction stages in series, with counter-current flow of the aqueous and organic phases and a single stripping stage, as depicted in Figure 28). In a copper extraction process, the efficiency of copper transfer from pregnant leach solution to rich electrolyte via consecutive extraction and stripping steps can be increased by increasing the extractant concentration or changing the relative flowrates of the organic and aqueous phases (the O/A ratio). However, those operational parameters influence iron transfer to the organic phase and, consequently, to the rich electrolyte, too. However, the presence of iron in rich electrolyte requires bleed for iron control that causes losses of electrolyte additives, copper and acid (Schlesinger et al., 2011b; Thomas, 2010). Therefore, it is important to study such operation conditions that maximise copper transfer and simultaneously minimise the transfer of iron.

As demonstrated in Publication II, it was found that the higher the copper loading of the organic in the extraction stages, the less iron is transferred from the pregnant leach solution to rich electrolyte, and, consequently, the less bleed is required, leading to a more efficient process operation. The reason is that copper has higher affinity towards hydroxyoxime extractants than iron, and, therefore, copper is preferentially loaded onto the organic phase preventing iron loading. Iron transfer and the required bleed increases
with an increase in the organic to aqueous phase ratios in both the extraction and stripping stages. In loading, the higher the organic to aqueous phase ratio the more extractant is available to extract both copper and iron. In stripping, the phase ratio does not affect the stripping efficiency of iron much, and, therefore, the more iron is loaded the more is transferred to rich electrolyte. Therefore, the phase ratios have to be carefully adjusted to keep the bleed for iron control in the strip electrolyte at acceptable levels.

Also, it was confirmed that due to excellent selectivity of the hydroxyoxime extractant, the co-extraction of iron and its transfer from pregnant leach electrolyte to rich electrolyte was very small in comparison to that of copper. However, the industrial copper extraction cascades operate on large-scale 5 to 400 kt copper per year (Schlesinger et al., 2011a). The small iron transfer becomes significant when the copper extraction process is run dynamically over a long time. Therefore, those operations that bleed for iron control should put significant focus not only on the selectivity of extractants, but also on the minimisation of iron transfer by determining the optimal process parameters using equilibrium-based models. The developed process simulation tool can help study the process operation limits, decreasing the costs for expensive experimentation on the pilot or industrial scale.

Figure 28. Process configuration used for analysis of the copper liquid–liquid extraction process. Thick and thin lines show organic and aqueous streams, respectively.
5.2 Extraction of Co, Ni and Li with organophosphorus extractants

5.2.1 Extraction equilibrium

The model for calculating the composition of the aqueous and organic phases at equilibrium in the liquid−liquid extraction of cobalt, nickel and lithium from sulfate solution using Cyanex 272 extractant was developed as described in Section 3.2 and fitted against the pH-extraction isotherms published by Virolainen et al. (2017). The values of the model parameters (extraction equilibrium constants in Eqs. (77, 79, 81, 83 and 86)) were estimated and are presented in Table 6. The values of the model parameters were estimated for Cyanex 272 extractant, unmodified and modified with 5% v/v trioctylamine (TOA), to check how the modification affects the values of the model parameters. The modifier was used to decrease the organic phase viscosity at high loading as discussed in Section 3.2.4. As shown in Table 6, the values of all the corresponding parameters are of the same order of magnitude for both organic phases. The difference in the values is small and can be explained by the fact that the modification of the extractant only slightly changes the chemistry of the extraction due to the ability of TOA to solvate the metal-extractant complexes in the organic phase. The goodness of fit presented in Figure 29a and b for both the organic phases suggests a good description of the experimental data by the developed model.

<table>
<thead>
<tr>
<th></th>
<th>1 M Cyanex 272</th>
<th>1 M Cyanex 272 + 5% v/v TOA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{LLX,1}^{Co}$</td>
<td>$\log K_{LLX} = -5.94$</td>
<td>$\log K_{LLX} = -6.43$</td>
</tr>
<tr>
<td>$K_{LLX,1}^{Ni}$</td>
<td>$\log K_{LLX} = -9.69$</td>
<td>$\log K_{LLX} = -9.97$</td>
</tr>
<tr>
<td>$K_{LLX}^{Li}$</td>
<td>$\log K_{LLX} = -6.54$</td>
<td>$\log K_{LLX} = -6.71$</td>
</tr>
<tr>
<td>$K_{LLX,2}^{Co}$</td>
<td>$\log K_{LLX} = -1.64$</td>
<td>$\log K_{LLX} = -2.28$</td>
</tr>
<tr>
<td>$K_{LLX,2}^{Ni}$</td>
<td>$\log K_{LLX} = -1.06$</td>
<td>$\log K_{LLX} = -0.72$</td>
</tr>
</tbody>
</table>

The dependence of the distribution ratio, calculated using Eq. (4), on equilibrium pH is shown in Figure 29c and d. The figures demonstrate that the model fitted against fraction

3) The standard deviation of the parameter estimates is estimated using the Markov chain Monte Carlo method.
5.2 Extraction of Co, Ni and Li with organophosphorus extractants

Extracted is able to predict the equilibrium distribution of the metals in the liquid–liquid extraction. Since the range of distribution ratio is accurately measured from about 0.1 to 10 (Rydberg et al., 2004), the model predicts best the distribution ratio of the metals between 0.01 and 100. Large experimental error is associated with the data points outside this range and explains the presence of the outliers in the figure.

The behaviour of the experimental data for cobalt extraction in Figure 29c suggests that it is important to be confident in the accuracy of the distribution coefficient measurements. A wrong conclusion about the change of the extraction mechanism could be made based on the behaviour of distribution coefficient in pH range 6 to 8 alone. The data are explained simply by the fact that cobalt was completely recovered (within the measurement accuracy) from the aqueous solution in the experiment at pH > 6.

Figure 29. Dependence of the metals’ extraction from the simulated sulfate leachate of Li-ion battery waste on the equilibrium pH. The composition of the sulfate leachate was 14 g/L Co, 0.5 g/L Ni and 2.8 g/L Li. Symbols: circles Co, triangles Ni, squares Li, and lines model. Organic phases: (a) unmodified 1 M Cyanex 272 pre-neutralised with NH₃ to extents of 48%, (b) 1 M Cyanex 272 modified with 5% v/v TOA and pre-neutralised with NH₃ to extents of 48%, c) the dependence of the distribution ratio on the equilibrium pH calculated from figure a, d) the dependence of the distribution ratio on the equilibrium pH calculated from figure b. The experimental data were retrieved from Virolainen et al. (2017).
The extraction of metals with organophosphorus extractants is usually carried out with partially pre-neutralised extractant to facilitate pH control. This is necessary because the selective and efficient extraction of one of the metals from a mixture is possible in a narrow pH range. For example, the separation of cobalt and nickel with Cyanex 272 is possible at pH levels from 5 to 6.5 (Figure 29). However, since the extraction reaction proceeds with the release of protons (Eq. (74)), the difference in the acidity of the leach solution and raffinate can be significant. The utilisation of the extractant in partially neutralised form allows keeping the pH in the desired limits, in agreement with the overall ion exchange reaction, Eq. (119).

\[ M^{n+} + m(\text{HA})_2 + n\text{NH}_4\text{A} \rightleftharpoons \overline{\text{MA}}_n(\text{HA})_{2m} + n\text{NH}_4^+ \]  

The values of the model parameters (the extraction equilibrium constants in Eqs. (89) and (91)) for the equilibrium distribution of ammonia were estimated separately using the data presented by Inoue et al. (1986). The capacity of the fitted model of predicting the equilibrium in loading and stripping stages with partially pre-neutralised extractant was validated with the experimental data retrieved from Virolainen et al. (2017). As can be seen in Figure 30 and Figure 31, the fitted model predicts the loading and stripping equilibria well.

Figure 30. Extraction isotherms of a) Co and b) Ni for the organic phases: unmodified 1 M Cyanex 272 (blue), 1 M Cyanex 272 modified with 5% TOA (red) used in the equilibrium experiments for the simulated sulfate leachate of Li-ion battery waste. Full circles – experimental results; empty circles – modelling results. Equilibrium pH was not controlled. The experimental data were retrieved from Virolainen et al. (2017).
5.2 Extraction of Co, Ni and Li with organophosphorus extractants

Figure 31. Stripping isotherms of (a) Ni and (b) Co, with 0.025 M H$_2$SO$_4$ solutions from the unmodified 1 M Cyanex 272 (blue), and 1 M Cyanex 272 modified with 5% TOA (red). Full circles – experimental results; empty circles – modelling results. Equilibrium pH was not controlled. The experimental data were retrieved from Virolainen et al. (2017).

The model presented in Publication III accounts for the extraction equilibrium of metal ions and ammonia and thus widens the applicability of the model for process design.

5.2.2 Model-based process design

The model presented in Publication III and described in Section 3.2 can be employed to design and analyse a continuous counter-current process for the separation of the metals from Li-ion battery leachates by process simulation. Recently, Virolainen et al. (2017) suggested a simplified flowsheet (Figure 32), in which cobalt and nickel were selectively extracted from the leachate with Cyanex 272, yielding pure lithium raffinate. Cobalt and nickel were consequently separated in the stripping stage and obtained as pure products. The purpose of the process simulations was to study how the varying leachate composition affects the process performance. The process performance can be regulated by the adjustment of process operation parameters, such as O/A phase ratio, number of stages and composition of the scrubbing and stripping solutions. The developed model provides an opportunity to test the whole process in continuous mode rather than each of the process steps separately. In this way, extensive experimentation on an expensive pilot scale can be limited.
Figure 32. Flowsheet for the continuous counter-current solvent extraction fractionation of metals in Li-ion battery waste leachate. LO – loaded organic; BO – barren organic; PNO – pre-neutralised organic. Thick and thin lines show organic and aqueous streams, respectively.

The composition of the fresh organic phase used in the extraction circuit was set to contain 1 M of Cyanex 272 with 5% v/v TOA and was 48% pre-neutralised with ammonia. The pre-neutralisation of the organic phase is not explicitly considered here. The main difficulty in the process design for the flowsheet in Figure 32 is the selection of appropriate operation parameters for the loading and scrubbing stages (O/A phase ratios and number of stages), since there is a recycling stream that feeds scrubbed nickel and lithium back to the first loading stage. This interconnection makes the performances of both of the stages interdependent. It was shown in Publication III that the two-loading-stage configuration was optimal, since it provided high recovery of lithium and loaded organic with high purity of cobalt and nickel. Also, it was demonstrated that there is an operation window, when a high purity (>99%) of cobalt and nickel in the loaded organic phase and lithium in the raffinate can be recovered with high yields (>98%).

The performance of the interconnected loading and scrubbing stages of the processes with varying leachate compositions is presented in Table 7. The O/A ratio in the scrubbing was set to 1 in all simulations, while the O/A in the two-stage loading step was adjusted so that the equilibrium pH of 7.5 was maintained in the second loading stage. The same scrubbing solution (0.3 g/L Ni and pH 1.4) was used in all the processes. The simulations showed very good performance of the processes with different leachate compositions under the condition that the equilibrium pH of 7.5 was maintained in the last loading stage by adjustment of the O/A phase ratios in the loading and scrubbing stages. Cobalt was recovered completely from the leachates into the LO, and most of the lithium (>99%) was left in the raffinate. At the same time, complete recovery of nickel was not achieved due to low pH (between pH 5 and 6 depending on the leachate) in the first loading stage with the highest recovery corresponding to the leachates II and III with the highest nickel concentration. Notably, the higher recovery of nickel was accompanied by the lower purity of lithium in the raffinate; however, the underlying reason was the higher nickel
5.2 Extraction of Co, Ni and Li with organophosphorus extractants

concentration in the leachates. Therefore, a higher Ni/Co ratio in leachate impedes pure lithium recovery in the process.

Table 7. Performance of the interconnected loading and scrubbing stages of the processes with varying leachate composition. Two-stage loading step with the equilibrium pH of 7.5 maintained in the second loading stage and leachate pH 3.5. The O/A in the scrubbing stage was 1 in all simulations. The fresh organic phase contained 1 M of Cyanex 272 that was 48% neutralised and 5% v/v TOA. Scrubbing solution: 0.3 g/L Ni and pH 1.4.

<table>
<thead>
<tr>
<th>Leachate</th>
<th>Co, Ni, Li, g/L</th>
<th>Source</th>
<th>O/A</th>
<th>( R_{\text{Li}}^{\text{LO}} )</th>
<th>( R_{\text{Ni}}^{\text{LO}} )</th>
<th>( R_{\text{Co} + \text{Ni}}^{\text{LO}} )</th>
<th>( c_{\text{Ni}}^{\text{LO}} )</th>
<th>( c_{\text{Ni}}^{\text{LO}} )</th>
<th>( c_{\text{Ni}}^{\text{LO}} )</th>
<th>( c_{\text{Ni}}^{\text{LO}} )</th>
<th>( c_{\text{Ni}}^{\text{LO}} )</th>
<th>( c_{\text{Ni}}^{\text{LO}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>14.0 0.5 2.8</td>
<td>Virolainen et al. (2017)</td>
<td>0.57</td>
<td>99.57 99.99 99.98</td>
<td>100 88.59 0.62</td>
<td>0.57 99.57 99.99</td>
<td>99.98 100 88.59 0.62</td>
<td>99.57 99.99 99.98</td>
<td>100 88.59 0.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>16.7 11.0 1.4</td>
<td>Nan et al. (2006)</td>
<td>0.72</td>
<td>98.48 99.95 99.98</td>
<td>100 98.45 4.59</td>
<td>0.72 98.48 99.95</td>
<td>99.98 100 98.45 4.59</td>
<td>98.48 99.95 99.98</td>
<td>100 98.45 4.59</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>11.3 11.5 1.8</td>
<td>Y. Yang, Xu &amp; He (2017)</td>
<td>0.67</td>
<td>98.98 99.94 99.96</td>
<td>100 98.73 5.76</td>
<td>0.67 98.98 99.94</td>
<td>99.96 100 98.73 5.76</td>
<td>98.98 99.94 99.96</td>
<td>100 98.73 5.76</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>25.1 2.5 6.2</td>
<td>Nguyen et al. (2014)</td>
<td>0.72</td>
<td>99.65 99.98 99.96</td>
<td>100 94.37 1.25</td>
<td>0.72 99.65 99.98</td>
<td>99.96 100 94.37 1.25</td>
<td>99.65 99.98 99.96</td>
<td>100 94.37 1.25</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The rather low amount of nickel, in comparison to that of cobalt, in leachates I and IV leads to the low concentration of nickel in the loaded organic (Table 7). Subsequently, it does not allow pure nickel to be obtained in the aqueous phase after nickel stripping stages, due to the co-stripping of some cobalt (Figure 33). The problem could be solved by either the utilisation of leachates with higher nickel concentration, or by increasing the concentration of nickel in the scrub solution. The nickel from the scrub solution can be extracted in the latter case, increasing the content of nickel in the loaded organic. However, mass balance has to be taken into account to keep the amount of stripped nickel higher than the amount used in scrubbing. In the former case, the leachate of the desired composition can be prepared by combining spent batteries of different types or mixing different leachates.
Figure 33. Performance of the two-stage stripping of Ni from loaded organic with variable Ni concentration. The loaded organic phase contains 11 g/L Co; O/A equals 1. Red: the purity of Ni in loaded strip liquor; blue: the stripping efficiency of Ni; black dashed line: 99% stripping efficiency. Ni concentration in loaded organic: solid line = leachate I; dashed line = leachate II; dotted line = leachate III; dash-dot line = leachate IV.

It was shown in Publication III that the process is applicable to separating cobalt, nickel, and lithium from leachates of different compositions. The process can be tuned for treatment of different leachates by adjustment of the O/A phase ratios in the loading and scrubbing stages. The proposed process flowsheet constitutes a simple and effective alternative for the recovery of valuable metals from the spent Li-ion batteries. In comparison to the processes presented by (Nguyen et al., 2014; Nguyen et al., 2015), the process presented here process consists of only one extraction circuit using Cyanex 272 extractant, providing pure fractions of all three metals.

5.3 Algorithm-based process synthesis

A method to aid the synthesis of hydrometallurgical processes was developed, as explained in Section 4.1. The method employs the Key Performance Indicators (KPI) introduced by Winkelnkemper and Schembecker (2010) to assess and compare different process options, as well as the Ant Colony Optimisation (ACO) technique as an optimisation algorithm. The results of the method application to hydrometallurgical process synthesis were presented in Publication IV.

Identification of the best process scheme was realised in an iterative manner. A superstructure of a search domain that contains the collected experimental data is needed for the method to work. All the processes that can be constructed are present in the
superstructure. Alternative process routes are created by a combination of the process step options with the operating parameters as shown in Figure 21. All the process routes created constitute the superstructure of the solutions. All the process routes from the superstructure are evaluated, and the best one is identified. Instead of enumeration of all the possible alternative processing routes, the ACO allows efficient identification of the most promising process steps and combines them to create the most promising processing routes.

The ACO algorithm was shown to be very efficient in its application to process synthesis. The practical applicability of the method to hydrometallurgy was demonstrated by investigating zinc recovery from argon oxygen decarburisation (AOD) dust with two alternative leaching methods, as well as the recovery of lanthanides from nickel metal hydride (NiMH) batteries. In the first zinc recovery process, 150-minute normal batch leaching with 0.5 M H₂SO₄ was used, and in the other 270-minute batch leaching with H₂SO₄ was done by controlling the pH (>3.0). In both cases, the leachate was extracted with D2EHPA at pH 4.27 and stripped with circulating solution from zinc electrolysis. Although the set target purity of zinc in the stripped electrolyte (final product) was not reached, this case study revealed the power of the method in hydrometallurgical process design.

For lanthanides recovery, the ACO-based method suggested a process in which the raw material is leached with 1.3 M HCl, the leachate is extracted with D2EHPA at pH 2.2, organic phase is stripped with 2.0 M HCl and 99% pure Ln-oxalates are precipitated with oxalic acid at pH 0.6. The set target product purity was exceeded in this case. The successful application of the method in the case studies corroborates the potential of the suggested method for the automated synthesis of hydrometallurgical processes.

A critical assumption in the procedure described here is that the calculation of the yields and purities in a given stage from experimental data remains reasonably accurate under all conditions included in the optimisation. For higher accuracy, one may perform a second iteration with refined experimental data once the most promising process schemes have been identified. It is also straightforward to include any kind of numerical simulations to calculate the purity and yield in a given stage.
6 Conclusions

Hydrometallurgy enables the production of metals that are essential to modern society in an environmentally and economically sustainable way. Among other hydrometallurgical methods, liquid–liquid extraction is widely included in processing routes of various base, precious and other technologically valuable metals. The availability of highly selective extractants and advances in the engineering of the technology make it possible.

The need to recover the valuable metals from such challenging raw materials as low-grade ores and End-of-Life goods requires the development of new hydrometallurgical processes. Modelling and simulation are able to decrease costs and improve efficiency of hydrometallurgical process development. In addition, they can help improve the performance of those processes already in operation. Moreover, the initial stages of process development can be partially automated.

In the current thesis, a general approach to the modelling and simulation of liquid–liquid extraction processes has been formulated. A mechanistic mathematical model of a liquid–liquid extraction equilibrium has to describe aqueous phase speciation, interfacial extraction reactions and organic phase speciation. The rate-based approach to a model solution allows fast calculations with a controlled level of accuracy. The nonlinear regression modelling approach allows the estimation of model parameters, and the Markov chain Monte Carlo (MCMC) algorithm can be used for estimating the reliability of the modelling results. The counter-currently operated processes can be simulated using the mechanistic model and the sequential-modular approach. The process simulation tools developed in such a way can help in researching the process operation under various conditions, decreasing the costs of experimentation on the pilot or industrial scale.

A mechanistic mathematical model capable of predicting the liquid–liquid extraction equilibrium of copper and iron(III) from a sulfate solution with a hydroxyoxime extractant in wide range of copper, iron and extractant concentrations was developed. The modelling of both the loading and stripping steps was implemented. The organic phase nonideality was found to significantly affect the extraction performance of both metals and was described by empirical functions. The developed model enabled the simulation of a multistage copper extraction process and prediction of the iron transfer from pregnant leach solution to rich electrolyte in the process. The factors influencing the transfer of iron as the main contaminant in the process were studied. It was found that the higher the copper loading of the organic in the extraction stages, the less iron was transferred. The iron transfer also increased with an increase in the organic to aqueous phase ratios in both the loading and stripping stages. The developed process simulation tool enables the quantification of the iron transfer and is, therefore, useful in its minimisation.

A mechanistic mathematical model for the equilibrium of the liquid–liquid extraction of cobalt, nickel and lithium from a sulfuric acid solution with an organophosphorus extractant was developed and validated. The model was employed for the analysis of an extraction process for the fractionation of Li-ion battery leachates of different
compositions. The process flowsheet, where cobalt and nickel were recovered together from the leachate in the loading step, leaving lithium in the raffinate and where, subsequently, cobalt and nickel were separated and purified in the selective stripping step, was found to be very flexible. The process was shown to be applicable to the separation of cobalt, nickel and lithium from leachates of different compositions. The process can be tuned for the treatment of different leachates by adjusting the O/A phase ratios in the loading and scrubbing stages. It was found that a high Ni/Co ratio in a leachate impedes pure lithium recovery in the process. However, the higher the nickel concentration in the leachate, the higher purity of nickel is obtained in the stripped fraction. The process scheme allows the adjustment of the process performance to the changing market value of the metals.

In the current research, a simple and efficient automated process synthesis method, applicable to the early stages of hydrometallurgical process development, was developed. The method makes use of experimental data for the construction of a superstructure of process alternatives. Key performance indicators were used to assess and compare different process alternatives. The algorithm, based on the ant colony optimisation technique, was employed to efficiently identify the most promising process alternative in an iterative manner. The method is considered applicable for the development of any chemical purification processes that involve the simultaneous selection of unit processes and their sequence in a processing route, the selection of mass separating agents and the definition of operating parameters.

Two case studies demonstrated the practical applicability of the method. The recovery of zinc from argon oxygen decarburisation dust and the recovery of lanthanides from nickel metal hydride batteries were studied. For zinc recovery, the synthesised process consists of leaching with controlled pH 3, extraction with D2EHPA at pH 4.27 and striping with circulating solution from zinc electrolysis and meets the requirements for the level of impurities in the final product. For lanthanides recovery, the synthesised process consists of leaching with 1.3 M HCl, extraction with D2EHPA at pH 2.2, stripping with 2.0 M HCl and precipitation of 99% pure Ln-oxalates with oxalic acid at pH 0.6. The achieved product purity exceeded the initial specifications.

The studies presented in the current thesis broaden the horizons for future research work. The modelling and simulation tools, as well as the method for automated process synthesis, were developed to use the experimental data in the most effective way in hydrometallurgical process development. Mechanistic models enable exploring the operation of liquid–liquid extraction processes in wide range of conditions. The application of automated process synthesis facilitates testing different process routes and configurations during the hydrometallurgical process development. It is also possible to combine the two methods. It is straightforward to utilise the simulation tools in the algorithm-based process synthesis to increase accuracy. In addition, the same simulation approach can be used for the design of a process where copper, iron, cobalt and nickel are separated in two successive liquid–liquid extraction circuits and an iron precipitation stage. The results of the process simulations can be validated with the data collected in
the continuous counter-current operation of a pilot plant. Furthermore, the same mechanistic modelling approach could be used to describe the liquid–liquid extraction equilibrium in the extraction of valuable compounds in biotechnology. The difference would be that, along with reactive extraction, the extraction of the compounds by physical extraction would also be significant.
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Publication I

Vasilyev, F., Virolainen, S., Sainio, T.

Modeling the phase equilibrium in liquid–liquid extraction of copper over a wide range of copper and hydroxyoxime extractant concentrations

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Chemical Engineering Science
Vol 171, pp. 88–99, 2017
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Modeling the phase equilibrium in liquid–liquid extraction of copper over a wide range of copper and hydroxyoxime extractant concentrations

Fedor Vasilyev, Sami Virolainen, Tuomo Sainio

School of Engineering Science, Lappeenranta University of Technology, Skinnarilankatu 34, FI-51800 Lappeenranta, Finland

HIGHLIGHTS

• A mechanistic model for copper liquid-liquid extraction equilibrium.
• A useful empirical correlation for organic phase non-ideality is introduced.
• MCMC is used for identification of the best models with significant parameters.
• The model is shown to be applicable over a wide range of operating conditions.

ABSTRACT

The phase equilibrium in the loading and stripping stages of liquid–liquid extraction of copper with hydroxyoxime extractant in kerosene was studied over a wide range of Acoura M5640 extractant (5–25 vol%) and copper (1–45 g/L) concentrations. A mechanistic mathematical model explaining the phase equilibrium was developed and validated. The model accounts for the non-ideality of both the aqueous and the organic phases. The composition of the aqueous sulfate solution was calculated through speciation of the electrolytes with an ion association model. The concentration of the extractant in the organic phase has a strong effect on the equilibrium constant of the extraction reaction. The organic phase non-ideality in the loading stage was described with an empirical correlation. The model parameters were fitted against the experimental data using nonlinear regression analysis. A Markov chain Monte Carlo algorithm was used to assess the reliability of the modeling results. The model has a significantly wide range of application than previous models and thus facilitates the optimization of extractant concentration.

ARTICLE INFO

Article history:
Received 2 January 2017
Received in revised form 30 March 2017
Accepted 2 May 2017
Available online 4 May 2017

Keywords:
Liquid-liquid extraction
Equilibrium modeling
MCMC
Copper
Acorga M5640

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1. Introduction

Liquid–liquid extraction of copper is the most widely used application of liquid–liquid extraction in the metallurgical industry (Schlesinger et al., 2011; Tamminen et al., 2013). Within the hydrometallurgical method of pure copper production, liquid–liquid extraction is responsible for the purification and concentration of copper from a pregnant leach solution (PLS) to generate an electrolyte for the electrowinning of high quality copper cathodes. This process scheme accounts for about 20% of primary copper production in the world (Schlesinger et al., 2011).

The copper liquid–liquid extraction process with hydroxyoxime extractants can be represented as interfacial, reversible, competitive reactions of copper(II) cation, protons, and cationic impurities on the aqueous side with chelating hydroxyoxime extractant molecules on the organic side. Hydroxyoxime extractants exhibit high selectivity for copper over other metallic cations, especially iron, which is the main impurity in the process. This allows the concentration and purification of copper in the organic phase and the rejection of impurity species in the PLS to the raffinate.

Extraction of copper in the range of low aqueous copper concentrations with hydroxyoxime-type extractants has been extensively studied and reported in the literature (Agarwal et al., 2012; Arminian et al., 2000; Hett et al., 1973; Komasa et al., 1980; Piotrowicz et al., 1989; Tanaka, 1990a,b,c). It has been considered sufficient, since according to Kordosky et al. (2006), copper liquid–liquid extraction was applied in order to concentrate and purify copper from solutions generated in heap and dump leaching. In these cases, the PLS typically contained 0.5–8 g/L of copper.
However, significant progress in the leaching of high-grade copper sulfide ores and copper concentrates and the application of pressure oxidation leaching has enabled the feeding of liquid–liquid extraction with PLS containing up to 43 g/L of copper. This also requires the use of high extractant concentrations (Kordosky et al., 2006; Schlesinger et al., 2011).

Even though there are many studies on the extraction equilibria of copper with hydroxyoximes (Aminian et al., 2000; Doungdeethaveeratana and Sohn, 1998; Gouvea and Morais, 2010; Molnar and Verbaan, 2003; Ochronowicz and Chmielewski, 2013; Sridhar and Verma, 2011), data on extraction in a wide range of conditions, especially in the range of high aqueous copper concentrations, are still insufficient. The equilibrium of liquid–liquid extraction is usually represented in terms of loading extraction isotherms (Agarwal et al., 2010; Deep et al., 2010; Ferreira et al., 2010). However, this representation cannot show the influence of all the variations in the extraction conditions on the phase equilibrium in a compact form. On the other hand, mechanistic mathematical models are reliably able to predict phase equilibrium and create the isotherms under any operating conditions within the calibration range. Information concerning the mechanistic mathematical modeling of the extraction equilibrium of copper(II) with the hydroxyoxime extractants from a sulfate medium is scarce in the literature.

The equilibrium of copper liquid–liquid extraction has usually been described using a simple concentration-based mass action law, when the concentrations of copper and sulfuric acid in the aqueous phase were low or their variation was small. Otherwise, the non-ideality of the aqueous phase was taken into account by introducing the activity formulation of an extraction equilibrium constant (instead of a concentration-based mass action law) using activity coefficient models for aqueous species (Agarwal et al., 2012; Piotrowicz et al., 1989; Tanaka, 1990a). The non-ideality of the organic phase has been observed when a model with a single parameter for the extraction equilibrium constant was applied to solutions with widely varying total extractant concentrations (Agarwal et al., 2012; Hu and Wiencek, 2000; Lin et al., 2002; Piotrowicz et al., 1989). Non-ideality has also been observed with different values of the apparent extraction equilibrium constant for different total extractant concentrations. Agarwal et al. (2012) and Piotrowicz et al. (1989) tried to explain this phenomenon by the dimerization of the hydroxyoxime molecules in the organic phase; an additional parameter, the dimerization equilibrium constant, was introduced into the models. Agarwal et al. (2012) found that this improved the model fit, whereas Piotrowicz et al. (1989) found that the dimerization of oxime could be neglected for hydroxyoxime concentrations up to 20 vol%.

Although Agarwal et al. (2012) and Alguacil et al. (2004) reported data and models for the equilibrium of the copper extraction from the aqueous system CuSO₄–H₂SO₄ with Acorga M5640 extractant in an aliphatic diluent, the studies cover only low aqueous copper concentrations. Yet for processes with concentrated PLS solution conditions, it is relevant that these models have not covered 5–35 vol% of extractant in the organic phase and up to 43 g/L of copper in the aqueous phase (Schlesinger et al., 2011). Nor, to our knowledge, has mechanistic mathematical modeling been used to predict the equilibria of the stripping stage of liquid–liquid extraction of copper. To sum up, there is no mechanistic model available in the literature that allows the prediction of the composition of the process phases of copper liquid–liquid extraction equilibrium with a hydroxyoxime extractant in the wide PLS and extractant concentration ranges.

In this work, a mechanistic mathematical model able to explain the equilibrium of copper liquid–liquid extraction in wide concentration ranges of copper and hydroxyoxime extractant was correlated. The developed model was verified with extensive experimentally collected data on the equilibrium of the loading and stripping stages in wide concentration ranges. A new formulation for the copper extraction reaction equilibrium constant was suggested to improve the model prediction. A Markov chain Monte Carlo (MCMC) algorithm (Haario et al., 2006) was used to estimate the reliability of the modeling results.

### 2. Materials and methods

#### 2.1. Materials

The extractant used was Acorga M5640 (Cytec), whose active substance is 2-hydroxy-5-nonylsalicylaldoxime. The extractant was used after washing twice with 3 M H₂SO₄. The washed organic and samples taken from the batch equilibrium experiments were centrifuged for 10 min at 4000 rpm prior to analyses to ensure complete phase disengagement. As a diluent, aliphatic diluent kerocane Exxelor D80 (Exxon Mobil) was used. An organic solution of the required hydroxyoxime concentration was prepared by dissolving the washed organic in the solvent. Aqueous stock solutions of copper were prepared by dissolving copper(II) sulfate pentahydrate (Fluka, AR grade), or copper(II) sulfate (VWR Chemicals, AR grade) in purified water (ELGA VEDIUA CENTRA R120), and the pH value was adjusted using H₂SO₄ (Merck, AR grade).

### Nomenclature

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Description</th>
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<tbody>
<tr>
<td>MCMC</td>
<td>Markov chain Monte Carlo</td>
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<tr>
<td>MSE</td>
<td>mean squared error</td>
</tr>
<tr>
<td>PLS</td>
<td>pregnant leach solution</td>
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<tr>
<td>SE</td>
<td>standard error</td>
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<table>
<thead>
<tr>
<th>Letters</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>parameter in regression model</td>
</tr>
<tr>
<td>I</td>
<td>ionic strength</td>
</tr>
<tr>
<td>G</td>
<td>number of experimental groups</td>
</tr>
<tr>
<td>HR</td>
<td>protonated hydroxyoxime</td>
</tr>
<tr>
<td>K</td>
<td>equilibrium constant</td>
</tr>
<tr>
<td>k</td>
<td>reaction rate constant</td>
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<tr>
<td>M</td>
<td>number of measured responses</td>
</tr>
<tr>
<td>N</td>
<td>number of experimental points in an experimental group</td>
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<thead>
<tr>
<th>Subscripts and superscripts</th>
<th>Description</th>
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<tbody>
<tr>
<td>R</td>
<td>deprotonated hydroxyoxime</td>
</tr>
<tr>
<td>r</td>
<td>reaction rate</td>
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<tr>
<th>Equations</th>
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<tr>
<td>D</td>
<td>dimerization</td>
</tr>
<tr>
<td>eq</td>
<td>equilibrium</td>
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<tr>
<td>Exp</td>
<td>measured experimental data</td>
</tr>
<tr>
<td>f</td>
<td>forward</td>
</tr>
<tr>
<td>i</td>
<td>index of chemical reactions</td>
</tr>
<tr>
<td>Mod</td>
<td>data calculated with model</td>
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<tr>
<td>LLX</td>
<td>liquid–liquid extraction</td>
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<tr>
<td>r</td>
<td>reverse</td>
</tr>
<tr>
<td>S</td>
<td>solution</td>
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<tr>
<td>tot</td>
<td>total</td>
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<thead>
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<th>Description</th>
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<tbody>
<tr>
<td>pH</td>
<td>reaction rate</td>
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<table>
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<th>Nomenclature</th>
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<td>N</td>
<td>number of experimental points in an experimental group</td>
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</table>

**Information concerning the mechanistic mathematical modeling**

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Even though there are many studies on the extraction equilibria of copper with hydroxyoximes (Aminian et al., 2000; Doungdeethaveeratana and Sohn, 1998; Gouvea and Morais, 2010; Molnar and Verbaan, 2003; Ochronowicz and Chmielewski, 2013; Sridhar and Verma, 2011), data on extraction in a wide range of conditions, especially in the range of high aqueous copper concentrations, are still insufficient. The equilibrium of liquid–liquid extraction is usually represented in terms of loading extraction isotherms (Agarwal et al., 2010; Deep et al., 2010; Ferreira et al., 2010). However, this representation cannot show the influence of all the variations in the extraction conditions on the phase equilibrium in a compact form. On the other hand, mechanistic mathematical models are reliably able to predict phase equilibrium and create the isotherms under any operating conditions within the calibration range. Information concerning the mechanistic mathematical modeling of the extraction equilibrium of copper(II) with the hydroxyoxime extractants from a sulfate medium is scarce in the literature.

The equilibrium of copper liquid–liquid extraction has usually been described using a simple concentration-based mass action law, when the concentrations of copper and sulfuric acid in the aqueous phase were low or their variation was small. Otherwise, the non-ideality of the aqueous phase was taken into account by introducing the activity formulation of an extraction equilibrium constant (instead of a concentration-based mass action law) using activity coefficient models for aqueous species (Agarwal et al., 2012; Piotrowicz et al., 1989; Tanaka, 1990a). The non-ideality of the organic phase has been observed when a model with a single parameter for the extraction equilibrium constant was applied to solutions with widely varying total extractant concentrations (Agarwal et al., 2012; Hu and Wiencek, 2000; Lin et al., 2002; Piotrowicz et al., 1989). Non-ideality has also been observed with different values of the apparent extraction equilibrium constant for different total extractant concentrations. Agarwal et al. (2012) and Piotrowicz et al. (1989) tried to explain this phenomenon by the dimerization of the hydroxyoxime molecules in the organic phase; an additional parameter, the dimerization equilibrium constant, was introduced into the models. Agarwal et al. (2012) found that this improved the model fit, whereas Piotrowicz et al. (1989) found that the dimerization of oxime could be neglected for hydroxyoxime concentrations up to 20 vol%.

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2.2. Experimental procedure

Extraction and stripping experiments were carried out on an orbital shaker in 50 mL separation funnels, with 30 min equilibration time and at 20 °C. Organic to aqueous (O/A) phase ratios were varied. In the loading experiments, aqueous phases with known copper content and acidity were brought into contact with copper-free organic phases of known extractant concentration. In the stripping experiments, copper-free aqueous phases of known acidity were brought into contact with loaded organic phases with known copper and extractant concentrations. The experimental design of the extraction and stripping experiments is shown in Table 1 and in the supplementary materials. In extraction experiment E1, the initial acidity was varied, and the organic to aqueous phase ratio (O/A) was kept constant. In all the other extraction experiments, E2–E9, only O/A was varied. The equilibrium acidity was not controlled in all the experiments. The loaded organic phases for the stripping experiments (S1–S4) were prepared by bringing fresh organic phases of known extractant concentrations into contact with the aqueous phase containing 45 g/L of copper at pH 4.3. Each experiment was replicated three times. The equilibrium copper concentration in the organic phase, the equilibrium acidity of the aqueous phase, and the free oxime-extractant concentration in the organic phase were measured. The copper concentration in the organic phase was calculated from the mass balance. The volume change due to mixing was neglected.

Copper content in the aqueous phase was analyzed by ICP-MS (Agilent technologies, Agilent 7800), and acidity was measured by titration with a standard 0.1 M NaOH (Sigma-Aldrich, AR grade) solution using a Mettler Toledo T50 titrator with a DG 111-SC electrode. The same instrument was used to measure the total free oxime concentration in the organic phases by the ultimate loading method. Measurements of the pH were carried out with a Consort C3010 pH meter using a SenTix Mic glass electrode.

3. Extraction and stripping equilibrium model

The distribution equilibrium of copper between the aqueous and organic phases in liquid–liquid extraction with a hydroxyoxime extractant depends on the chemistry and physics of the process.

3.1. Interfacial and organic phase chemistry

The core of liquid–liquid extraction of copper is the ion transfer between the aqueous and organic phases according to a reversible two-step mechanism (Flett et al., 1973):

\[
Cu^{2+} + H_2O + Cu(ROH)_n + H^+ \rightarrow Cu_2(ROH)_n + 2H^+ + nH_2O
\]

where the overbar denotes the species in the organic phase, \( R \) denotes deprotonated hydroxyoxime, and \( HR \) denotes a protonated hydroxyoxime molecule.

The overall extraction reaction, Eq. (3), leads to the expression of the concentration-based extraction equilibrium constant, Eq. (4), which is the same for the two-step mechanism.

\[
Cu_2(ROH)_n + 2HR \rightleftharpoons Cu_2(ROH)_{n+2} + 2H_2O
\]

\[
K_{ex} = \frac{[Cu_2(ROH)_{n+2}]}{[Cu_2(ROH)_n][HR]^2}
\]

When concentrations of species in both phases are small (ideal solutions), the equilibrium of copper extraction is traditionally described and analyzed by slope analyses using a simple linear regression model derived from Eq. (4) (Ritcey and Ashbrook, 1984):

\[
\log D = \log K_{ex} + 2 \log[HR] + 2 \cdot \log pH
\]

where \( D = \frac{[Cu_2(ROH)_{n+2}]}{[Cu_2(ROH)_n][HR]^2} \). A linear relationship of \( \log D \) vs. equilibrium pH and \( \log[HR] \) is usually observed with a slope of around 2, which shows the stoichiometry of the extraction reaction, whereas the intersection term gives an estimate for the extraction equilibrium constant, \( K_{ex} \) (Ritcey and Ashbrook, 1984; Szymanski and Borowk-Resterna, 1991). However, due to the non-ideality of the aqueous and organic phases, there are considerable deviations from Eq. (5) in systems with high copper and extractant concentrations (Agarewal et al., 2012; Komatsua et al., 1980).

When the concentration of hydroxyoximes in the organic phase is high, phenomena such as the association of unreacted hydroxyoximes, the polymerization of the copper-hydroxyoxime complexes, and the solvation of complexes with unreacted hydroxyoxime molecules may occur (Szymanski and Borowk-Resterna, 2004). Hydroxyoxime molecules may occur (Szymanski and Borowk-Resterna, 1991). The characteristic feature of hydroxyoxime extractants is to undergo self-association due to the presence of the oximino group (=NOH), which is a weak proton acceptor (Szymanski, 1993). Most likely only two oxime molecules participate in the association, meaning dimerization (Szymanski, 1993). In this work, other numbers of molecules involved in self-association were also tested, but this did not show an improvement in model fit. The dimerization of extractant molecules can be described using the equilibrium constant determined for a given system:

Table 1

<table>
<thead>
<tr>
<th>Extraction Experiment set ID</th>
<th>Data points</th>
<th>C(Cu), g/L</th>
<th>pH, vol%</th>
<th>HR, vol%</th>
<th>Loading, %</th>
<th>O/A range</th>
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<tbody>
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<td>E1</td>
<td>28</td>
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<td>0.11–0.19</td>
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<th>HR, vol%</th>
<th>Loading, %</th>
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<td>25</td>
<td>80</td>
<td>2/1–1/10</td>
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<tr>
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<td>10</td>
<td>50</td>
<td>2/1–1/10</td>
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<tr>
<td>S4</td>
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<td>80</td>
<td>2/1–1/10</td>
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</table>
The dimerization depends mainly on the diluent. Dimerization constants are in the order of a few units (L/mol) in aromatic hydrocarbon diluents (Saitte and Szymanowski, 2004; Szymanowski and Borowiak-Resterna, 1991; Szymanowski, 1993). Therefore, the higher the extractant concentration in the organic phase, the more deviation from the straight line, according to Eq. (5), will be observed (Agarwal et al., 2012; Komazawa et al., 1980; Piotrowicz et al., 1989).

According to Szymanowski and Borowiak-Resterna (1991), polymerization of the copper-oxime complex is not usually observed in systems with commercial copper extractants, and there is little probability of solution of the copper complex by hydroxoxime molecules. However, the reaction of the copper(II) cation with the dimeric extractant has been considered by Russell and Ricke (1980), while Amores et al. (1997) have also considered the formation of another copper complex present in the organic phase (1997) according to reaction Eq. (8), and the extraction mechanism enabled a better explanation of their experimental data on copper extraction equilibrium.

$$\text{Cu}^2+ + 2\text{HR} \rightarrow \text{CuHR}_2^+ + 2\text{H}^+ \quad \text{(8)}$$

However, this is deemed unlikely here that copper-extractant complexes are formed to a significant extent according to Eq. (8). This is because the structure of the dimer significantly reduces its adsorption on the phase interface and thus limits the probability of its reaction with the copper cations in the aqueous phase. It is more likely that the complex is formed in the bulk organic phase in a solution reaction with the unreacted hydroxyoxime, as in Eq. (9), or with the dimer, as in Eq. (11).

$$\text{Cu}^2+ + 2\text{HR} \rightarrow \text{HR} + \text{CuHR}_2 \quad \text{(9)}$$

$$K_D = \frac{[\text{HR}][\text{CuHR}_2]}{[\text{Cu}^2+][\text{HR}]} \quad \text{(10)}$$

$$K_D = \frac{[\text{HR}][\text{CuHR}_2]}{[\text{Cu}^2+][\text{HR}]} \quad \text{(11)}$$

$$K_D = \frac{[\text{HR}][\text{CuHR}_2]}{[\text{Cu}^2+][\text{HR}]} \quad \text{(12)}$$

To conclude, equilibrium liquid-liquid extraction of copper is governed by the interfacial chelating reaction, Eq. (3). However, when the extractant concentration is high, the reaction equilibrium may be influenced by organic phase non-ideality, which can be caused by extractant dimerization Eq. (6) and/or by the solvation of the extracted complex Eq. (9) or Eq. (11). All these phenomena, Eqs. (3), (6), (9), and (11), are considered in this work in order to find the best way to explain the measured experimental data using mechanistic mathematical modeling.

### 3.2. Aqueous-side chemistry

In liquid–liquid extraction of copper from concentrated sulfate solutions, the aqueous phase contains the dissociation products of electrolytes CuSO₄ and H₂SO₄ so that the principal species present in the solution are cupric ion (Cu²⁺), bisulfate (HSO₄⁻), cupric sulfate (CuSO₄(H₂O)), and sulfate ion (SO₄²⁻). The concentration of undissociated H₂SO₄ is negligibly small (Casas et al., 2000). Therefore, not all the copper in the aqueous solution is available for the reaction with the hydroxoxime extractant in the form of Cu₂⁺. In the same way, the degree of sulfuric acid dissociation affects the liquid–liquid phase equilibrium. The higher the concentrations of copper sulfate and sulfuric acid, the more non-ideal is the aqueous phase, and the more there is deviation from the straight-line relationship of Eq. (5) (Agarwal et al., 2012; Komazawa et al., 1980; Piotrowicz et al., 1989; Tanaka, 1990a). Thus, speculation in the aqueous phase has to be taken into account when modeling liquid–liquid extraction of copper from concentrated aqueous solutions. The aqueous phase model used in this study contains the reactions presented in Table 2.

### 3.2.1. Numerical methods in solution

The model of the copper liquid–liquid extraction phase equilibrium consists of non-linear algebraic equations for the equilibrium constants of all the reactions of the assumed mechanism and of mass balance equations for the species in the system. In addition, a semi-empirical equation is used to account for aqueous phase non-ideality by correcting the equilibrium constants of the aqueous phase reactions.

The model equations can be solved for the equilibrium composition of the process phases using, for example, the Newton-Raphson algorithm. However, a good initial guess is needed, since otherwise, erroneous or inaccurate results can be obtained. An alternative is a rate-based approach (Raittinen, 2014; Salmi et al., 2010), where both the forward and reverse parts of the reactions are represented as irreversible, and a reaction rate equation is formed for each of them according to the mass action law Eq. (17). The forward reaction rate constant was chosen to be $k_f = 1000$, the same for all the reactions, since it does not influence equilibrium but influences the time required to reach it. The expression of the reaction equilibrium constant Eq. (18) sets the relationship between the forward and backward parts of the reversible reactions. With this mathematical manipulation, all the nonlinear algebraic equations are converted into differential equations that can be solved simultaneously.
where $k_i$ and $k_r$ are the reaction rate constants of the forward and reverse reactions, respectively. $K$ is the equilibrium constant, $r_i$ is the reaction rate, $i$ is the index of equilibrium reactions, $[A]$ and $[B]$ are molar concentrations of components, and $s$ and $p$ are stoichiometric coefficients of the forward or reverse reactions.

In theory, the same model described above can be used to predict the equilibrium of both the extraction and stripping stages of the copper solvent extraction process. However, in practice, different equilibrium constants may be needed, due to the large difference in the acidity of the extraction and stripping stages of the copper liquid–liquid extraction.

### 3.4 Parameter estimation and model selection

The unknown model parameters were estimated by nonlinear regression fitting of the experimentally measured total copper concentration in the aqueous phase, the total acidity in the aqueous phase, and the total free oxime concentration in the organic phase; in other words, the expression in Eq. (19) was minimized. A similar approach was used when Russell and Rickel (1990) fitted the model parameters by minimizing the sum of squares of the difference between the calculated and experimentally measured copper concentration in the organic phase. The estimation of model parameters has traditionally been done by fitting logD only (Agarwal et al., 2012; Alguacil et al., 2004; Dusgdeethaveeratana and Sohn, 1998; Tanaka, 1990b), but the approach used in this work is more accurate, since it directly utilizes experimentally measured data. The logarithmic function has a different behavior of errors in comparison with the function responses (concentration in the aqueous phase, the total acidity in the aqueous phase or is the total extractant concentration in the organic phase).

The selection of the most appropriate model for the copper liquid–liquid extraction of copper was done by the following principle: the preferable model was the one with the minimum mean squared error (MSE). Eq. (20), explaining the experimental data well enough according to visual observations of the loading isotherms and with the minimum number of parameters (Beck and Arnold, 1977).

\[
\text{MSE} = \frac{\text{Res}}{N - m - p} \quad (20)
\]

where $p$ is the number of fitted parameters in the model.

4. Results

#### 4.1 Modeling of loading stage

In the present study, liquid–liquid extraction of copper from sulfuric acid solutions with hydroxoyxime extractant Acorga M5640 in the aliphatic diluent Exxon D80 was studied with 218 phase equilibrium experiments according to the design of experiments in Table 1. The measured experimental data are presented as supplementary material. Fig. 1 shows that a simple linear regression model, Eq. (5), which is usually used to analyze the equilibrium in ideal solutions, is unable to explain well all the variation in the collected experimental data. An underlying reason may be the non-ideality of both the aqueous and organic phases, since the concentrations are rather high in many of the data points.

### Table 2

<table>
<thead>
<tr>
<th>Model ID</th>
<th>Model</th>
<th>Equations</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Overall equilibrium complexation reaction</td>
<td>Eq. (3)</td>
</tr>
<tr>
<td>2</td>
<td>Overall equilibrium complexation reaction</td>
<td>Eq. (3) and (6)</td>
</tr>
<tr>
<td>3</td>
<td>Overall equilibrium complexation reaction</td>
<td>Eq. (3), (6), and (7)</td>
</tr>
<tr>
<td>4</td>
<td>Overall equilibrium complexation reaction</td>
<td>Eq. (3) and (9)</td>
</tr>
</tbody>
</table>

Fig. 1. Overview of the experimental data using the classical log-log representation.

All the modeling in the current study was done in Matlab. An open source MCMC code package developed by Laine (2015) was used to estimate the reliability of the modeling results.
The parameters of the models in Table 3 were estimated from the experimental data and are shown in Table 4 together with indicators of their significance and their goodness of fit. According to the MSE values, the best fit is obtained with Models 2 and 3; however, the superiority of these models over Model 1 is small and is owed to a higher number of parameters. Although Model 4 provides a fit that is better than Model 1 according to MSE value, the difference is small, and parameter $K_{S1}$ is not significant ($t$-stat $< 1.2$) according to the $t$-test. There is 23% probability that $K_{S1} = 0$ according to the $p$-value. Therefore, the differences in predictive power between Models 1–3 are rather small, and in these circumstances, the preference should be given to the simplest model with the minimum number of parameters, i.e., Model 1. Moreover, the parameters $K_{LLX}$ and $K_{D}$ are heavily correlated (correlation coefficient 0.96) according to the posterior distribution of parameters obtained with the MCMC method (Fig. 2), which reveals that the parameters are linearly dependent on each other. Therefore, the parameters cannot be determined simultaneously. The same applies to the parameters $K_{LLX}$ and $K_{S1}$ in Model 3 (Fig. 3). It is worth noting that the estimated values of the dimerization constant are lower than expected for the system with aliphatic diluents. This indicates the relatively low importance of the dimerization phenomenon in the extraction mechanism.

Although Model 1 seems to provide a compromise between the simplicity of the model and the goodness of fit, the explanation of the experimental data by the model cannot be admitted to be sufficiently good, as can be seen from Figs. 4 and 5. An overprediction of organic copper concentration and a corresponding underprediction of aqueous copper concentration is observed for experiments with 10 vol% reagent concentration, whereas an underprediction...
is observed for experiments with 17 vol% and 25 vol% concentrations (Fig. 4). The same is observed with the predictions of Models 2–4. This fact suggests that there is a dependency in the phase equilibrium that is not accounted for by Models 1–4. The same was observed by Hu and Wiencek (2000), and the suggested explanation was the non-ideality of the organic phase.

4.1.2. Empirical correction for organic phase non-ideality

It was observed that the value of the equilibrium constant of the extraction reaction, Eq. (3), changes systematically when fitted individually against data for each extractant concentration (Table 5). There were 15 experimental points in each data set for a fixed extractant concentration, which makes identification of the equilibrium constant comparable and reliable. The correlation of the equilibrium constant and the total extractant concentration is characterized by the correlation coefficient $-0.95$ with a 4.5% probability that there is no correlation ($p$-value = 0.045). The same trend of a decreasing equilibrium constant with an increase of extractant concentration (Table 5) was reported by Hu and Wiencek (2000) and Lin et al. (2002) in the extraction systems with hydroxynoxime extractants LIX64N and LIX84 in aliphatic diluents. This behavior was explained through the non-ideality of the organic phase. In this work, no other correlations with other varying experimental conditions were found to be significant using correlation analysis.

An excellent fit is observed when Model 1 is individually fitted for each extractant concentration data set (Fig. 6). The calculated copper loading (filled symbols) is very close to the experimental values (open symbols) in all cases. The lines are added to demonstrate the shape of the loading isotherm at a hypothetical constant

![Fig. 4](image)

Measured equilibrium concentrations of copper in aqueous and organic phases at uncontrolled equilibrium acidity. (a) Cu0.1 g/L, HR 10%; (b) Cu0.5 g/L, HR 10%; (c) Cu0.25 g/L, HR 5%; (d) Cu0.25 g/L, HR 17%; Modeled values are calculated with the one-parameter Model 1 that includes aqueous speciation and interfacial extraction reaction. Simultaneous fitting for experimental sets E1–E9.

![Fig. 5](image)

Goodness of fit of the one-parameter Model 1 in the experiments with uncontrolled equilibrium acidity. Simultaneous fitting for experimental sets E1–E9.

<table>
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<tr>
<th>$HR_{tot}$, vol%</th>
<th>$HR_{tot}$, M</th>
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<th>t-stat</th>
<th>$p$-value</th>
<th>MSE</th>
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<td>1.07</td>
<td>6.06</td>
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<td>7.259e-4</td>
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</table>

![Table 5](image)

Table 5 Dependency of the copper liquid–liquid extraction equilibrium constant in the loading stage on the total extractant concentration. O/A ratio was varied while keeping all other initial conditions the same.
These results suggest that equilibrium Model 1 successfully accounts for aqueous phase non-ideality. However, it is unable to explain the non-ideality of the organic phase, because a different value of $K_{LLX}$ is needed for each [HR]$_{tot}$.

Two functions were considered in order to account for the dependence between the total extractant concentration and the extraction equilibrium constant (Table 6): a linear function ($K_{LLX} = K_{LLX,0} + A/\mathrm{[HR]}_{\text{tot}}$) and a hyperbolic tangent function ($K_{LLX} = K_{LLX,0}/\left(1 + \tanh\left(A/\mathrm{[HR]}_{\text{tot}}\right)\right)$). Both functions were used to calculate the apparent extraction equilibrium constant for Model 1 described earlier in Table 4. The nonlinear hyperbolic tangent function is clearly able to predict the nonlinear variations in the experimental data better in comparison to the linear function, according to the MSE value. The hyperbolic tangent function is also characterized by a gradual approaching of the $x$-coordinate with increasing extractant concentrations that is more natural in comparison with the linear function. MSE values with both functions are also lower than those of all the considered mechanistic Models 1–4 (Table 4), which confirms the significance of the correlation of the extraction equilibrium constant and the total extractant concentration.

Fig. 7 demonstrates a very good fit of the experimental data by Model 1, supplemented with a correction of the apparent extraction equilibrium constant by the two-parameter hyperbolic tangent function. Fig. 8 shows how well the corrected model is able to predict the loading isotherms with uncontrolled equilibrium acidity. Comparing Figs. 7 and 8 with Figs. 4 and 5, it can be seen that the correction of the equilibrium constant using the hyperbolic tangent function enables a more accurate explanation of the equilibrium phase composition. Hence, organic phase non-ideality is obviously present in the liquid–liquid extraction with hydroxoyxime extractants in aliphatic diluents.

The utilization of the hyperbolic tangent function allows not only a correction for the organic phase non-ideality and thus for the improvement of the model fit, but it also enhances the identifiability of the model parameters (Fig. 9). Parameters $K_{LLX}$ and $A$ of the hyperbolic tangent function in Fig. 9 are less correlated (correlation coefficient 0.81) than the parameters $K_{LLX}$ and $K_{\text{dim}}$ (dimerization constant) in Fig. 2, which once again proves the superiority of Model 1 with the corrected apparent equilibrium constant over Models 2–4.

Since the apparent extraction equilibrium constant depends on the extractant concentration, it affects the copper liquid–liquid extraction process design. Calculated using the developed model,
Fig. 10 demonstrates how the extraction of copper from the aqueous phase increases nonlinearly with the increase in the extractant concentration in the organic phase. The effect is insignificant until the extractant concentration reaches 0.25 M ($C_{24}^{14}$ vol%). A further increase in the extractant concentration leads to a less pronounced increase in copper extraction. If there was no effect of organic phase non-ideality on the copper extraction, loading of the extractant in the organic phase could be expected to increase slowly starting from the extractant concentration of about 0.14 M (~8 vol%). However, according to the developed model, loading gradually decreases due to organic phase non-ideality. Thus, in addition to the physical limitations (high viscosity of concentrated extractant leading to high operational costs), there are also chemical limitations to the application of high extractant concentrations in copper liquid–liquid extraction with hydroxyoxime extractants.

4.2. Stripping stage modeling

Since modeling the loading stage of the copper liquid–liquid extraction with aqueous speciation and a corrected extraction reaction equilibrium constant gives an excellent result, the same approach was applied to modeling the equilibrium of the stripping stage of the process. The extraction equilibrium constant for Model 1 (Table 3) was fitted against the collected experimental data individually for each set of data points with a given total extractant concentration and acidity of the aqueous phase. There were 15 experimental points in each data set. Table 7 shows that the equilibrium constant of the extraction reaction in the stripping stage depends on the concentration of the extractant in the organic phase, just as in the loading stage. The variation in the extractant equilibrium constant due to the variation in the aqueous phase acidity is negligible. This is seen in Table 7, where the 95% confidence intervals ($K_{LLX} \pm 2SE$) of the equilibrium constants, with the same extractant concentrations but different acidities, overlap.

A linear correction function for the apparent equilibrium constant of the extraction reaction in the stripping stage was fitted against the experimental data. The estimated model parameters in Table 6 are significantly different from the parameters estimated for the loading stage. The difference may be explained by the large differences in the acidity in the stripping and loading stages. In other words, the speciation model for the aqueous phase is not accurate at very high acid concentrations, and this inaccuracy is included in the values of the parameters of the linear correction function. However, the determined stripping stage parameters are significant, since the estimated standard error (SE) is small compared to the values of the parameters. Figs. 11 and 12 demonstrate a satisfactory fit of the experimental data. This verifies the good applicability of the fitted model to explain the phase equilibrium in the stripping stage of the liquid–liquid extraction of copper from the extractant diluted in the organic phase.
5. Conclusions

A mechanistic mathematical model was developed to explain the equilibrium of the loading and stripping stages of liquid–liquid extraction of copper from concentrated aqueous sulfate solutions with a hydroxyoxime extractant in an aliphatic diluent in a wide range of copper and extractant concentrations. The model was validated against an extensive amount of new experimental data. Several mechanistic mathematical models that included the speciation of aqueous phase species, reversible interfacial extraction reactions, the dimerization of extractant molecules in the organic phase, and the solvation of the extracted complex in the organic phase were considered. Nonlinear regression analysis was used to fit the model parameters against the collected experimental data. In addition, a Markov chain Monte Carlo (MCMC) algorithm was used to identify correlations in the estimated parameters.

Table 7

<table>
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<tr>
<th>Experiment ID</th>
<th>HR$_{tot}$, vol%</th>
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<th>[H$_2$SO$<em>4$]$</em>{tot}$</th>
<th>K$_{1,2}$</th>
<th>SE</th>
<th>MSE</th>
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</thead>
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<tr>
<td>S2</td>
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<td>3.91</td>
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<td>3.959e-4</td>
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<tr>
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<td>3.42</td>
<td>2.32</td>
<td>0.018</td>
<td>3.951e-4</td>
</tr>
</tbody>
</table>

Fig. 10. Extent of extraction of copper and utilization of extractant in copper liquid–liquid extraction depending on extractant concentration. The curves are calculated using the developed model with corrected apparent extraction equilibrium constant and Model 1. Initial aqueous and organic copper concentrations are correspondingly 45 g/L and 0 g/L, O/A = 1, and equilibrium acidity is 0.77 M.

Fig. 11. Goodness of fit for the one-parameter model for the stripping stage (experiments S1–S4) with uncontrolled equilibrium acidity. The model contains the two-parameter linear function for the correction of organic phase non-ideality.
parameters of the considered models and to prove the reliability of the models. It was found that the extraction is best modeled by an ion association model to describe the titration of aqueous phase species and the overall reversible interfacial extraction reaction. However, it was observed that the value of the equilibrium constant of the extraction reaction was heavily correlated with the total concentration of the extractant in the organic phase. This is evidence of organic phase non-ideality. Neither the dimerization of the unretracted extractant molecules nor the solvation of the copper-extractant complexes was sufficient to explain the organic phase non-ideality, and too many parameters led to poor identifiability. The organic phase non-ideality was taken into account by an empirical correction of the extraction equilibrium constant. The suggested correction function is the hyperbolic tangent function \( K_{\text{ex}} = 50.23 \left( 1 - \tanh(3.16 \cdot [H_2SO_4]) \right) \) for the loading stage and the linear function \( K_{\text{ex}} = 13.77 - 3.16 \cdot [H_2SO_4] \) for the stripping stage. The developed models were shown to serve as excellent explanations of the measured experimental data.

Acknowledgements

The work was part of Show Case 1 in DIMECC’s research program SIMP - System integrated metal processing. The participating organizations were Lappeenranta University of Technology, Aalto University, University of Oulu, Outotec (Finland) Oy, and Boliden Oy. The authors would like to thank the DIMECC for financial support.

Appendix A. Supplementary material

The online version, at http://dx.doi.org/10.1016/j.ces.2017.05.003, contains the supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.ces.2017.05.003.

Fig. 12. Experimental and calculated loading isotherms in stripping experiments S1–S4. Initial acidity of the stripping solution: (a) 160 g/L H_2SO_4; (b) 190 g/L H_2SO_4. The measured values have been calculated with the two-parameter linear function for correction of organic phase non-ideality.


Publication II

Vasilyev, F., Virolainen, S., Sainio, T.

Modeling the liquid–liquid extraction equilibrium of iron(III) with hydroxyoxime extractant and equilibrium-based simulation of counter-current copper extraction circuits

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Modeling the liquid–liquid extraction equilibrium of iron (III) with hydroxyoxime extractant and equilibrium-based simulation of counter-current copper extraction circuits

Fedor Vasilyev, Sami Virolainen, Tuomo Sainio

Lappeenranta University of Technology, Laboratory of Separation Technology, P.O. Box 20, FI-53851 Lappeenranta, Finland

HIGHLIGHTS

- A mechanistic model for iron (III) liquid–liquid extraction equilibrium is developed.
- A useful empirical correlation for organic phase non-ideality is used.
- The model is shown to be applicable over a wide range of operating conditions.
- D-optimal design of experiments was used for model validation.
- Influence of iron (III) on the copper liquid–liquid extraction process was analyzed.

ABSTRACT

The phase equilibrium in the loading and stripping stages of the liquid–liquid extraction of iron (III) with hydroxyoxime extractant in kerosene was studied over a wide range of hydroxyoxime extractant (Acorga M5640, 3–25 vol–%) and iron (1.5–45 g/L) concentrations. A mechanistic mathematical model explaining the phase equilibrium in the loading stage was developed and validated with new experimental data. The model accounts for the non-ideality of both the aqueous and the organic phases. The composition of the aqueous sulfate solution was calculated through speciation of the electrolytes with an extended Debye–Hückel model. The organic phase non-ideality in the loading stage was described with an empirical correlation that accounts for the effect of extractant concentration on the extraction equilibrium constant. The model parameters were fitted against measured experimental data using nonlinear regression analysis. A mechanistic mathematical model explaining the co-extraction of iron in copper liquid–liquid extraction was developed and validated using D-optimal experiment design and the Markov chain Monte Carlo algorithm. The model facilitates the optimization of copper liquid–liquid extraction circuits, as iron is the most common impurity in industrial systems, making process operations challenging.

1. Introduction

About 20% of primary copper is produced by the hydrometallurgical method, which involves the leaching of copper-bearing ores or concentrates with sulfuric acid solutions followed by liquid–liquid extraction with hydroxyoxime extractants and electrodissolution of high-purity cathode copper (Schlesinger et al., 2011b). Since such leaching is not selective, impurities including iron, zinc, magnesium, nickel, cobalt, and arsenic are also leached (Gotfryd and Pietek, 2013). However, the liquid–liquid extraction process produces relatively pure copper (II) sulfate solutions for electrowinning due to the high copper selectivity of the hydroxyoxime extractants used for purification and concentration. The purity requirements with respect to the content of most contaminants in copper electrolytes are not particularly high because of the position of the copper in the electrochemical series. Therefore, no special attention is paid to their levels when they occur within relatively broad but acceptable limits (Gotfryd and Pietek, 2013). This applies especially to nickel, cobalt, arsenic, and antimony. Cobalt might even be desirable in the electrolytes to prevent corrosion of insoluble lead anodes. However, the amount of iron (III) that is present in electrolytes is more strictly restricted and controlled, as its reduction at the cathode competes with the copper electrodeposition reaction. This lowers the current efficiency of copper plating (Schlesinger et al., 2011c).
Even though hydroxyoxime extractants have been proven to be very selective towards copper (Szymanski, 1991; Kabugo et al., 2017), the transfer of iron (III) and other impurities from the pregnant leach solution (PLS) to rich electrolyte (RE) is inevitable (Gutfryd and Pietek, 2013; Mohnar and Verbaan, 2003). Most of the iron (III) transfer is due to chemical extraction, while entrainment contributes to a minor extent (Thomas, 2010). The buildup of impurities in the electrolyte is controlled by bleeding a small portion of the electrolyte from the tank house, which increases operational costs. Therefore, the transfer of impurities and especially of iron (III) must be minimized. This can be done through the accurate selection of an extractant formulation that can provide high enough selectivity with regard to iron (III) and other impurities as well as careful design of the liquid–liquid extraction process. Mechanistic mathematical modeling of iron (III) co-extraction may serve for the latter purpose.

The liquid–liquid extraction of metals with hydroxyoxime extractants is generally presented as interfacial, reversible, and competitive reactions of metal cations and protons on the aqueous side, with chelating cation exchange extractant molecules on the organic side. Depending on the extracting selectivity, one of the metal cations is extracted selectively over others. The extraction of iron (III) in the range of low aqueous iron concentrations with hydroxyoxime extractants has been studied and reported in the literature (Aminian and Bazin, 2000; Ocaña and Alguacil, 1998; Parus et al., 2011; Simpson et al., 1996; Zhang et al., 2016). However, the data on extraction in a wide range of conditions, especially in the range of high aqueous iron (III) concentrations, remain insufficient. Agarwal et al. (2012), Aminian and Bazin (2000), Ocaña and Alguacil (1998), and Simpson et al. (1996) studied the effect of the presence of iron (III) in the aqueous solution on the extraction of copper, when copper was extracted preferably. Iron (III) was found to have a minor effect on copper extraction. However, there were no attempts to quantify how much iron (III) is actually co-extracted with copper under different extraction conditions. Even so, the information is critical for copper liquid–liquid extraction process design, as it is important to predict under which process operation conditions the iron (III) transfer from the PLS to RE is minimized. In sum, there is no model available in the literature that allows the prediction of the equilibrium composition of the process phases of the liquid–liquid extraction of copper in the presence of iron (III) with a hydroxyoxime extractant in wide PLS and extractant concentration ranges.

In this work, a mechanistic mathematical model explaining the equilibrium of iron (III) liquid–liquid extraction in wide ranges of iron (III) and hydroxyoxime extractant concentrations was correlated. The developed mechanistic model was verified with new experimental data on the equilibrium of the loading stage. This model was then combined with a previously developed model for copper liquid–liquid extraction equilibrium (Vasilyev et al., 2017). The combined model was verified with experimental data collected using D-optimal experiments. The verified combined model was then used to optimize a copper liquid–liquid extraction circuit, with the aim to minimize iron (III) transfer from PLS to RE.

2. Materials and methods

2.1. Materials

The extractant employed in this study was Acorga M5640 (Cytec), with an active substance of 2-hydroxy-5-nonylsalicylaldoxime. It was used after washing two times with 3 M H2SO4. The washed organic as well as samples taken from the batch equilibrium experiments were centrifuged for 10 min at 4000 rpm prior to analyses to ensure complete phase disengagement. Aliphatic kerosene Exxonol D80 (ExxonMobil) was used as a diluent. Aqueous stock solutions of iron (III) and copper (II) were prepared by dissolving exsiccated iron (III) sulfate (Sigma–Aldrich, AR grade) and copper (II) sulfate (VWR Chemicals, AR grade) in purified water (Elga Veolia Centria R120). The acidity was adjusted with H2SO4 (Merck, AR grade).

2.2. Experimental procedure

Extraction and stripping experiments were carried out on an orbital shaker in 50 mL separation funnels, with a 30 min equilibration time at 20 °C. The contact time was chosen based on data presented elsewhere (Ocaña and Alguacil, 1998; Simpson et al., 1996). The organic to aqueous (O/A) phase ratios were varied. In the loading experiments, aqueous phases with known iron and copper contents and acidity were contacted with the metal-free organic phases of known extractant concentrations. In the stripping experiments, metal-free aqueous phases of known acidity were contacted with the loaded organic phases with known metals and extractant concentrations.

The design of the experiments to study the extraction and stripping equilibrium of iron (III) is shown in Table 1. One-factor-at-a-time strategy was used in the experimental designs aiming at collecting sufficient data to visually assess the influences of the variable experimental conditions on iron extraction equilibrium and to fit a model predicting the equilibrium. In all the extraction (E1–E9)
and stripping (S1–S5) experiments, only the O/A was varied, keeping the initial phases composition constant. The equilibrium acidity was not controlled in all the experiments. The loaded organic phases for the stripping experiments (S1–S5) were prepared by contacting fresh organic phases of known extractant concentrations with an aqueous phase containing 39 g/L of iron (III) at a pH of 1.06. The loaded organic phases were typically stored overnight before the stripping experiments. Each experiment was replicated twice. The equilibrium iron concentration and equilibrium pH in the aqueous phase were measured. The iron concentration in the organic phase was calculated from mass balance. Volume changes due to mixing were neglected.

Iron and copper content in the aqueous phase was analyzed via ICP–MS (Agilent Technologies, Agilent 7900). A Mettler Toledo T50 pH meter equipped with a Consort C3010 pH meter using a SenTix Mic glass electrode (Sigma–Aldrich, AR grade). Measurements of the pH were carried out with a Consort C3010 pH meter using a SenTix Mic glass electrode.

2.3. Numerical methods, parameter estimation, and model selection

The model of the liquid–liquid extraction phase equilibrium consists of non-linear algebraic equations for the equilibrium constants of all the reactions in the assumed mechanism and of mass balance equations for the elements in the system. In addition, a semi-empirical equation is used to account for aqueous phase non-ideality by correcting the equilibrium constants of the aqueous phase reactions. A rate-based approach (Kuitunen et al., 2008) was used to solve the model equations in the same manner as reported elsewhere (Vasilyev et al., 2017).

Unknown model parameters are estimated by non-linear regression fitting of experimentally measured total iron concentrations in the aqueous phase, minimizing the weighted sum of squared residuals (Eq. 1).

\[
\text{Res} = \sum_{i=1}^{n} \sum_{j=1}^{N} \left( \frac{y_{\text{meas}} - y_{\text{calc}}}{\text{max}(y_{\text{meas}}, y_{\text{calc}})} \right)^2.
\]  

where Res is the weighted sum of squared residuals, Y is the total equilibrium molar concentration of iron, j is the number of experiments, N is the total number of experiments in the experimental group, p is the number of parameters, and G is the total number of experimental groups.

Since the range of the measured values of the total concentration was very wide, giving high weights to some experimental results while disregarding others, the experimental data were weighted inside the data groups (E1–E13 or S1–S5). Hence, the data from different groups had equal importance in the estimation of the model parameters.

Selection of the most appropriate model for the iron liquid–liquid extraction equilibrium in our study was done according to the following principle: the model with the minimum mean squared error (MSE, Eq. (2)), explaining the experimental data well enough according to visual observations of the loading isotherms, and with the minimum number of parameters is preferable (Beck and Arnold, 1977).

\[
\text{MSE} = \frac{\text{Res}}{N - p}.
\]  

where p is the number of fitted parameters in the model.

All modeling in the current study has been done in Matlab. An open source MCMC code package developed by Laine (2015) was used for estimating the reliability of the modeling results.

2.4. Model-based D-optimal design of experiments

Since the capability of a model to represent a physical system must ultimately be assessed by comparing the model’s predictions with actual measured behavior, the combined model for predicting the extraction of copper and iron from mixed aqueous solutions has to be validated against experimental data. The technique of design of experiments (DoE), which is an important link between the experimental and modeling worlds, was used for that purpose. The use of DoE here is intended to obtain the maximum information from an experimental apparatus being modeled by devising experiments that will yield the most informative data, in a statistical sense, for use in the model validation (Frischauer and Marchetti, 2008). Since parameter estimates for the equilibrium constants of the extraction reactions of copper and iron are the
most critical for the model validity. D-optimalDoE, which mini-
mizes the volume of confidence region for all the parameters, was selected for choosing the conditions for the test experiments. The number of experiments was arbitrarily chosen to be 15 to min-
imize the laboratory workload while collecting a sufficiently large amount of data.

D-optimality minimizes the determinant of the variance–co-
variance matrix (Eq. (3)) that contains partial derivatives of the model response with respect to the model parameters under cer-
tain experimental conditions (Franceschini and Marchietto, 2000). The sensitivities are calculated at each experimental point, and the process is iterative. One has to sort out many experimental designs, X, to find the one that minimizes the function (Eq. (4)) at a fixed parameters estimate, θ. This is a hard combinatorial problem that can be solved, for example, using the Markov chain Monte Carlo (MCMC) algorithm (Haario et al., 2006).

\[
\text{var} \theta 
\propto \left| J^{-1} \right| 
\min M(X, \theta) - \min h \log |\det J|.
\]

where \( J = \partial^2 f(X, \theta) / \partial \theta \partial \theta \) – the sensitivity of the responses to the parameters, \( h \) – the model, which consists of equations describing the equilibrium concentrations depend on the experimental conditions, \( X \) (initial phase compositions and O/A phase ratios), and parameters estimate, \( \theta \).

3. Results and discussion

3.1. Speciation in the system Fe2(SO4)3–H2SO4–H2O

The electrolyte speciation in concentrated aqueous solutions can be determined using appropriate equilibrium constants and ionic activity coefficient models derived from the Debye–Hückel theory (Casas et al., 2000; Casas et al., 2005). The model is valid for aqueous electrolyte solutions with moderate (up to 1 M) ionic strength (Casas et al., 2000; Casas et al., 2005). The model has three temperature-dependent parameters, \( A \), \( B \), and \( g \), whose values at room temperature are 0.5114 kg/mol, 0.3288 kg/mol/A, and 0.0410 kg/mole, respectively, and one parameter for each of the species, the “hard-core diameter,” \( a_i \). Fig. 1 shows the calculated distribution of species using the extended Debye–Hückel model and the speciation reactions (Table 2) for the system Fe2(SO4)3–H2SO4–H2O at 20 ºC and various concentrations of sulfuric acid and ferric ion. The calculations indicate that the FeSO4+ and Fe(SO4)2+ are predominant iron species in the system. The relative concentration of ferric ion decreases with an increase of total iron concentration; the maximum relative concentration of ferric ion in the considered conditions is at the lowest total iron concentration (0.1 g/L) and amounts to 65% of all the iron in the system (Fig 1A). When the concentration of sulfuric acid is variable, the relative concentration of ferric ions increases with an

<table>
<thead>
<tr>
<th>Chemical reaction</th>
<th>Equation for equilibrium constant</th>
<th>log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}^+ + \text{HSO}_4^- = \text{H}_2\text{SO}_4^- )</td>
<td>( K_1 = \frac{[\text{H}_2\text{SO}_4^-]}{[\text{H}^+][\text{HSO}_4^-]} )</td>
<td>1 (5)</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{SO}_4^{2-} = \text{H}_2\text{SO}_4^- )</td>
<td>( K_2 = \frac{[\text{H}_2\text{SO}_4^-]}{[\text{H}^+][\text{SO}_4^{2-}]} )</td>
<td>2.08 (6)</td>
</tr>
<tr>
<td>( \text{Fe}^{2+} + \text{SO}_4^{2-} = \text{FeSO}_4^{+} )</td>
<td>( K_3 = \frac{[\text{FeSO}_4^+]}{[\text{Fe}^{2+}][\text{SO}_4^{2-}]} )</td>
<td>0.04 (7)</td>
</tr>
<tr>
<td>( 2\text{Fe}^{3+} + 3\text{HSO}_4^- = \text{Fe}_2\text{SO}_4^3^- + 3\text{H}^+ )</td>
<td>|</td>
<td></td>
</tr>
<tr>
<td>( 2\text{Fe}^{3+} + 3\text{SO}_4^{2-} = \text{Fe}_2\text{SO}_4^3^- )</td>
<td>|</td>
<td></td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 3\text{HSO}_4^- = \text{CuSO}_4^3^- + 3\text{H}^+ )</td>
<td>|</td>
<td></td>
</tr>
</tbody>
</table>

The pH of solutions in copper liquid–liquid extraction is usually

\[
\log K_i = -a_i \sqrt{\frac{a_i}{1 + a_i B_i}} + B_i. 
\]

where \( a_i \) is the hard-core diameter of the \( i \)-th ionic species, \( z_i \) is the charge of the \( i \)-th species, \( M \) and \( A \) are the Debye–Hückel param-}

eters, and \( f \) is the ionic strength of the electrolyte solution.

This is a modification of the classical Debye–Hückel model, and it is valid for binary interactions. In order to correct the activity coefficient for those cases where molecular interactions—other than electrostatic ones—come into play, the same value in the \( B \) parameter is included for all participating species. The model is valid for aqueous electrolyte solutions with moderate (up to \( 1 \) M) ionic strength (Casas et al., 2000; Casas et al., 2005). The model has three temperature-dependent parameters, \( A \), \( B \), and \( g \), whose values at room temperature are 0.5114 kg/mol, 0.3288 kg/mol/A, and 0.0410 kg/mole, respectively, and one parameter for each of the species, the “hard-core diameter,” \( a_i \).
increase of acidity (Fig. 1B). However, the relative concentration of ferric ion is still very small: 3.4% at 20 g/L of sulfuric acid.

3.2. Modeling of the loading stage

Liquid–liquid extraction of a given metal by an acidic extractant is the ion transfer between the aqueous and organic phases according to an overall equilibrium reaction (Hett et al., 1973; Ritcey and Ashbrook, 1984):

\[ \text{Me}^{n+} + n\text{HR} \rightarrow \text{MeR} + n\text{H}^+ \]  
(12)

In the case of iron (III), the overall extraction reaction takes the form shown in Eq. (13), which leads to the expression of the concentration-based extraction equilibrium constant, Eq. (14).

\[ \text{Fe}^{3+} + 3\text{HR} \rightarrow \text{FeR} + 3\text{H}^+ \]  
(13)

\[ K_{\text{Fe}^{3+}} = \frac{[\text{FeR}]}{[\text{Fe}^{3+}]^3[\text{HR}]^3} \]  
(14)

When concentrations of species in both phases are small (ideal solutions), the equilibrium of extraction is traditionally described and analyzed by slope analyses using a simple linear regression model derived from Eq. (14) (Ritcey and Ashbrook, 1984):

\[ \log D = \log K_{\text{Fe}^{3+}} + 3 \log [\text{HR}] - 3 \log \text{pH} \]  
(15)

where \( D = \frac{[\text{FeR}]}{[\text{Fe}^{3+}]} \). A linear relationship of \( \log D \) vs. equilibrium \( \text{pH} \) and log \( [\text{HR}] \) should be observed with a slope of 3, which shows the stoichiometry of the extraction reaction, whereas the intersection term gives an estimate for the extraction equilibrium constant, \( K_{\text{Fe}^{3+}} \) (Ocaña and Alguacil, 1998; Simpson et al., 1996; Siyanowska, 1993). However, due to the non-ideality of the aqueous and organic phases, there are considerable deviations from Eq. (15) in systems with high and variable salinity and extractant concentrations (Ryberg et al., 2004; Siyanowska, 1993).

In the present study, the liquid–liquid extraction of iron (III) from sulfuric acid solutions with hydroxamine extractant Arcoa M5640 in the aliphatic diluent Exxsol D80 was studied through 126 phase equilibrium experiments (experimental design in Table 1). Fig. 2 shows that a simple linear regression model with hydroxyoxime extractants. The behavior was explained through the non-ideality of the organic phase in all these cases. Vasilyev et al. (2017) suggested the use of a hyperbolic tangent function, \( K_{\text{Fe}^{3+}} = K_{\text{Fe}^{3+}}^0 (1 - \tanh [HR]) \), to take into account the correlation between the extraction equilibrium constant and the total extractant concentration in the organic phase. The two parameters, \( K_{\text{Fe}^{3+}}^0 \) and \( A \), were estimated using the whole data set (E1–E13), and significant values were obtained using the MCMC algorithm (see Table 4). The goodness of fit for the model, corrected for the organic phase non-ideality extraction equilibrium...
constant, is presented in Fig. 4, which indicates acceptable modeling results.

3.3. Stripping stage modeling

Since modeling the loading stage of the iron liquid–liquid extraction with aqueous speciation and a corrected extraction reaction equilibrium constant gives an excellent result, the same approach was attempted to model the equilibrium of the stripping stage of the process. The data on the stripping stage were collected according to the experimental plan presented in Table 1. There were ten equilibration experiments in each of the five data sets. Fig. 5A presents the equilibrium stripping isotherms of iron, where only the O/A phase ratio was variable in each data set. The higher the phase ratio, the higher the aqueous iron concentration that can be achieved; however, only a small portion of the iron loaded onto the organic phase can actually be stripped in a single stripping stage, as indicated in Fig. 5B. Even the acid concentration had little effect on the stripping efficiency. The results confirm that the stripping of iron (III) with concentrated sulfuric acid is difficult (Yu et al., 1989). The reason for this is that iron (III) forms polynuclear complexes with the extractant molecules in the bulk organic phase (Smith et al., 2003), and the polynuclear complex iron cannot enter the interface between the aqueous and organic phases. Special measures such as the addition of reducing agents to the stripping acid (Liu et al., 2014) or utilization of oxalic acid as a stripping agent (Zhang et al., 2016) may be needed to improve the stripping efficiency. However, development of a method for the complete stripping of iron (III) from a loaded hydroxyoxime extractant is beyond the scope of the current study.

Attempts were made to fit the extraction equilibrium constant for the same model as for the loading stage against the collected experimental data individually for each set of data points, with a given total extractant concentration and acidity of the aqueous phase and for the whole data set. These attempts to fit the model were not successful. Typically, some 10% of the iron (III) loaded onto the organic phase can be expected to be stripped in back-extraction under the studied conditions (Fig. 5B).

3.4. Modeling of simultaneous copper and iron liquid–liquid extraction

In the case of the extraction of copper from single-metal aqueous solution by a hydroxyoxime extractant, the overall extraction reaction, Eq. (16) (Flett et al., 1973), leads to the expression of the concentration-based extraction equilibrium constant, Eq. (17) (Vasilyev et al., 2017). The extraction equilibrium constant takes the form $K_{Fe^{3+}} = 50.23 \left(1 - \tanh \left(3.16 \frac{C_1}{C_0} \left[H_2R_{tot}^{\text{HR}} \right] \right) \right)$, taking into account organic phase non-ideality. However, scant data are available on the modeling of liquid–liquid extraction equilibrium of copper in the case of extraction from aqueous solutions containing impurities such as iron (III) (Agarwal et al., 2012; Ocaña and Alguacil, 1998; Simpson et al., 1996). Once proven models for copper and iron are available, it would be interesting to check whether they are capable of predicting the extraction equilibrium from mixed copper–iron aqueous solutions. The models for the liquid–liquid extraction equilibrium of copper and iron were combined to check their validity in the case of multi-metal extraction systems. A model-based D-optimal design of experiments (DoE) approach

<table>
<thead>
<tr>
<th>Experiment set ID</th>
<th>$K_{Fe^{3+}}$</th>
<th>t-stat</th>
<th>p-value</th>
<th>Number of observations</th>
<th>MSE</th>
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<tbody>
<tr>
<td>E1-E13</td>
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<td>1.32</td>
<td>0.19</td>
<td>126</td>
<td>0.0028</td>
</tr>
<tr>
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<td>0.0002</td>
</tr>
<tr>
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</tr>
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</tr>
<tr>
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<td>0.79</td>
<td>10</td>
<td>0.0013</td>
</tr>
<tr>
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<td>0.78</td>
<td>9</td>
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</tr>
<tr>
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<td>1.34</td>
<td>0.21</td>
<td>10</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

Fig. 3. Goodness of fit of the iron (III) liquid–liquid extraction model in the experiments with uncontrolled equilibrium acidity. Simultaneous fitting for experimental sets E1–E13.

Table 3

| Dependency of the iron (III) liquid–liquid extraction equilibrium constant in the loading stage on total extractant concentration.
<table>
<thead>
<tr>
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</tr>
<tr>
<td>E13</td>
<td>0.0004</td>
<td>1.34</td>
<td>0.21</td>
<td>10</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

Fig. 5. Goodness of fit of the iron (III) liquid–liquid extraction model in the experiments with uncontrolled equilibrium acidity. Simultaneous fitting for experimental sets E1–E13.

Table 4

The parameters of the correction function for the model predicting equilibrium in the liquid–liquid extraction of iron (III).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimate</th>
<th>Estimated 95% CI</th>
<th>Estimated SE</th>
<th>t-stat</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{Fe^{3+}}$</td>
<td>0.0215</td>
<td>(0.015–0.028)</td>
<td>0.003</td>
<td>6.24</td>
<td>6.35e-9</td>
</tr>
<tr>
<td>A</td>
<td>3.542</td>
<td>(1.575–5.110)</td>
<td>0.895</td>
<td>3.74</td>
<td>2.77e-4</td>
</tr>
</tbody>
</table>
was used to select the experimental conditions for the experiments on liquid–liquid extraction with a hydroxyoxime extractant from mixed aqueous solutions containing high amounts of copper and iron.

\[
\begin{align*}
\text{Cu}^{2+} + 2\text{HR} & \rightarrow \text{CuR}_2^{2+} + 2\text{H}^+
\end{align*}
\]

(16)

\[
K_{\text{CuL}} = \frac{[\text{CuR}_2^{2+}][\text{H}^+]}{[\text{Cu}^{2+}][\text{HR}^2]}
\]

(17)

Table 5 presents the developed D-optimal DoE using the MCMC algorithm. Initial aqueous phase acidity and total extractant concentration were chosen manually with the idea of using the chemicals that were readily available in the laboratory. The volumetric phase ratio, O/A, was set to be the same in all the experiments. Only initial concentrations of copper and iron in the range of 0–50 g/L of each metal in the aqueous phase were the subjects of alternation during the iterative development of the DoE using the MCMC algorithm.

Fig. 6A demonstrates how the D-optimal DoE, developed using the MCMC algorithm, distributed the experimental conditions in the set design space. The initial copper and iron concentrations are distributed along the diagonal line, with the highest deviation in the center of the design space. This indicates that the extraction equilibrium is the most sensitive to the value of the model parameters when the aqueous phase contains twice as many moles of copper than iron. The approach to convergence with the MCMC algorithm is shown in Fig. 6B.

Good prediction of the experimental data with the combined model (Fig. 7) validates the ability of the model to predict the extraction equilibrium in the liquid–liquid extraction of copper with hydroxyoxime extractant in the presence of iron in the aqueous phase. It is also likely that this modeling approach would be valid with other impurities in a copper liquid-liquid extraction system.

3.5. Equilibrium model-based study of copper liquid–liquid extraction in the presence of iron

Information on how much iron is transferred under different operational conditions, e.g., relative flowrates in the process stages and extractant concentrations, is needed to optimize the performance of the copper liquid–liquid extraction process. In this section, application of the developed extraction equilibrium models for analysis of the chemical iron (III) transfer in the process is demonstrated.

While keeping the extraction circuit configuration simple (two extraction stages in series, with counter-current flow of the aqueous and organic phases and a single stripping stage, as depicted in Fig. 8), the efficiency of copper transfer can be increased by increasing the extractant concentration or changing the relative flowrates of the organic and aqueous phases (the O/A ratio). However, those operational parameters influence iron transfer to the organic phase, and consequently to the RE, too. The model for simultaneous copper and iron liquid–liquid extraction that was verified in the previous section was used to simulate the extraction stages of the circuit, whereas a model for copper stripping (Vasilyev et al., 2017) was used to simulate the stripping stage. Based on the iron stripping experiments (Section 3.3), it was assumed that 10% of the loaded iron is stripped.

In the simulations, the PLS contained 15–45 g/L copper, 40 g/L iron, and 20 g/L H$_2$SO$_4$ which corresponds to the leach solution after pressure oxidation leaching (Schlesinger et al., 2011a). The lean electrolyte (LE) coming from electrowinning back to stripping contained 35 g/L copper, 3 g/L iron, and 175 g/L H$_2$SO$_4$ (Thomas, 2010). The phase ratio (O/A) was 3.5 and 1.3 in the extraction...
and stripping stages, respectively. Fig. 9 shows the performance of the extraction circuit depending on the copper concentration in the PLS and the extractant concentration in the organic phase. The concentration of iron in the LO increases with an increase in the extractant concentration, but it decreases with an increase of the copper content in the PLS. This is because the more free extractant (not loaded with copper) is available in organic phase, the more pronounced the extraction of iron, and consequently the larger the iron transfer to RE, as around 10% of the loaded iron is stripped in the stripping stage. Thus, the organic phase must be loaded with copper as much as possible in the extraction stage to prevent chemical iron transfer.

The small iron transfer becomes significant when the copper extraction process is run dynamically over a long time. For example, a transfer of 1 mg/L of iron per 1 m³/h of electrolyte in the process with a 250 m³/h flow rate of electrolyte per train results in a need to bleed about 720 m³ per year per train according to Eq. (18). This causes losses of electrolyte additives, copper, and acid (Schlesinger et al., 2011b; Thomas, 2010). Therefore, those operations that bleed for iron control should put significant focus not only on the selectivity of extractants but also on the minimization of iron transfer by determination of the optimal process parameters using equilibrium-based models.

\[
F_{\text{Bleed}} = F_{\text{Electrolyte}} \frac{C_{\text{Fe}}^{\text{LO}}}{K_{\text{Fe}}}.
\]  

Fig. 6. A. Visualization of the D-optimal DoE developed using the MCMC algorithm. B. Convergence plot.

Fig. 7. Comparison of experimental and modeling results for the extraction in the systems containing copper (I) and iron (II).

Table 5

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>[Cu] M</th>
<th>[Fe] M</th>
<th>C(H₂SO₄), g/L</th>
<th>[HR] M</th>
<th>O/A, mL/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.30</td>
<td>0.47</td>
<td>5</td>
<td>0.31</td>
<td>1</td>
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<tr>
<td>2</td>
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<td>0.24</td>
<td>5</td>
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<td>1</td>
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<tr>
<td>3</td>
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<td>0.46</td>
<td>5</td>
<td>0.18</td>
<td>1</td>
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<tr>
<td>4</td>
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<td>0.42</td>
<td>5</td>
<td>0.18</td>
<td>1</td>
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<tr>
<td>5</td>
<td>0.23</td>
<td>0.45</td>
<td>5</td>
<td>0.18</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
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<td>0.5</td>
<td>0.18</td>
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</tr>
<tr>
<td>7</td>
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<td>0.5</td>
<td>0.31</td>
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<tr>
<td>8</td>
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<td>0.16</td>
<td>0.5</td>
<td>0.31</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>0.29</td>
<td>0.47</td>
<td>0.5</td>
<td>0.18</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>0.39</td>
<td>0.40</td>
<td>0.5</td>
<td>0.18</td>
<td>1</td>
</tr>
<tr>
<td>11</td>
<td>0.60</td>
<td>0.74</td>
<td>0.05</td>
<td>0.18</td>
<td>1</td>
</tr>
<tr>
<td>12</td>
<td>0.26</td>
<td>0.10</td>
<td>0.05</td>
<td>0.31</td>
<td>1</td>
</tr>
<tr>
<td>13</td>
<td>0.44</td>
<td>0.22</td>
<td>0.05</td>
<td>0.31</td>
<td>1</td>
</tr>
<tr>
<td>14</td>
<td>0.41</td>
<td>0.63</td>
<td>0.05</td>
<td>0.31</td>
<td>1</td>
</tr>
<tr>
<td>15</td>
<td>0.27</td>
<td>0.13</td>
<td>0.05</td>
<td>0.31</td>
<td>1</td>
</tr>
</tbody>
</table>
where $F$ is the volumetric flow rate and $C_{\text{RE Fe target}}$ is the iron concentration required in rich electrolyte.

The operation of the circuit can be adjusted to favor maximum loading of the organic phase with copper to minimize the co-extraction of iron, while maintaining copper recovery at an acceptable level. This can be done by manipulating the relative flowrates of the organic and aqueous phases in both the extraction and stripping stages (Fig. 10). Copper recovery and organic loading are opposing process performance parameters, and thus achieving maximum levels for both at the same time is not possible. Both the recovery of copper and the copper loading of the organic are more sensitive to changes of the phase ratio in stripping when the phase ratio in the extraction is high. Again, the higher the copper loading of the organic in the extraction stages, the less iron is transferred from the PLS to RE and the less bleed is required. Iron transfer and the required bleed increases with an increase in the phase ratios in both the extraction and stripping stages. High copper concentrations in the PLS along with high selectivity of the extractant result in low iron transfer and consequently low volumes of bleed for all the studied phase ratios in the extraction and stripping stages.

Performance optimization of the extraction circuit, with the aim to minimize the iron transfer from the PLS to RE and keep the copper recovery and organic loading at a desirable level, can be accomplished by solving the constrained nonlinear optimization problem, Eq. (19).

$$\min \left( \frac{F_{\text{RE}}}{O_{\text{A extr}}} \right)$$

subject to

$$R_{\text{Cu}} > R_{\text{min}}$$
$$L_{\text{Cu}} > L_{\text{min}}$$
$$10\% < C_{\text{HR}} < 30\%$$

where $f(\ldots)$ represents a mathematical model that calculates the equilibrium iron (III) concentration in RE, $R$ is recovery, $L$ is loading of the organic phase after the extraction stage, $F_{\text{RE}}$ is the iron concentration in the RE, and $C_{\text{HR}}$ is the volume percentage concentration of the extractant in the organic phase. The model, $f(\ldots)$, includes mass balance equations for copper, iron, acid and extractant, and equations for the extraction equilibrium constants for all the reactions in both extraction and stripping stages (Eqs. (5)–(10), (11), (14), (17)).

For instance, with the set target loading of more than 80% and copper recovery in the liquid–liquid extraction of more than 60%, the optimum phase ratio in the extraction stages is found to be 5 and in the stripping stage 1, as the extractant concentration is 23%. Under those optimized conditions, loading is 86% and copper recovery is 67%, whereas the iron concentration in the RE increases by 5.81 $\mu$g/L in comparison to that in the LE. This operation requires only 4.2 m$^3$/year per train in an operation with a 250 m$^3$/h electrolyte flow rate per train.

The phase ratio in each extraction stage can be adjusted by internal stage recycling, and it does not affect the capacity of the total process (Kaul and Van Wormer, 1985). However, mass trans-
fer effects can influence process operation, so the steady-state of a dynamically run process may differ from the one calculated in this article based on extraction equilibrium modeling. The performance could be enhanced by implementing an optimum series–parallel circuit configuration (Nisbett et al., 2018).

4. Conclusions

A mechanistic mathematical model was developed to explain the equilibrium of the loading stage of the liquid–liquid extraction of iron (III) from concentrated aqueous sulfate solutions with a hydroxyoxime extractant in kerosene with a wide range of iron and extractant concentrations. The model was validated against an extensive amount of new experimental data using nonlinear regression analysis. The stripping stage of the liquid–liquid extraction of iron was also studied experimentally, and it was noticed that the equilibrium constant of the extraction reaction depended on the total concentration of the extractant in the organic phase. This was explained by organic phase non-ideality and was taken into account by empirical correction of the extraction equilibrium constant with a hyperbolic tangent function.

The developed model for iron extraction was combined with a previously developed model for copper extraction. The combined model was validated against experimental data, which were collected according to iteratively determined experimental conditions using the Markov chain Monte Carlo (MCMC) algorithm with the D-optimality criterion to establish the parameters of the model. The validated model was shown to excellently predict the extraction of iron (III) in the copper liquid–liquid extraction processes.

This work helps to determine the optimal process parameters for maximization of the iron transfer in the copper liquid–liquid extraction operations that bleed for iron control. The verified combined model was used to analyze the performance of a copper liquid–liquid extraction circuit that recovers copper from the PLS obtained from pressure oxidation leaching and containing 45 g/L copper, 40 g/L iron, and 20 g/L H₂SO₄. It was shown that high copper loading of the organic phase hinders the extraction of iron, and that iron extraction increases with an increase of the O/A phase ratios in both the extraction and stripping stages. With the simulations, it was shown to be possible to optimize, in terms of minimizing the iron transfer, the phase ratios (flowrates) between the organic and aqueous phases and extractant concentrations, which are among the key design parameters in the extraction process.

Acknowledgements

The work was part of DIMECC’s research program SIMP (System integrated metals processing).

References


Fig. 10. Performance of the extraction circuit in Fig. 8 based on the phase ratios in the extraction and stripping stages. The PLS contains 40 g/L copper and the organic phase contains 25 v-% of extractant.
Publication III

Vasilyev, F., Virolainen, S., Sainio, T.

Numerical simulation of counter-current liquid–liquid extraction for recovering Co, Ni and Li from lithium-ion battery leachates of varying composition

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Separation and Purification Technology
Vol 210, pp. 530–540, 2019
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Numerical simulation of counter-current liquid–liquid extraction for recovering Co, Ni and Li from lithium-ion battery leachates of varying composition

Fedor Vasilyev, Sami Virolainen, Tuomo Sainio⁎
Lappeenranta University of Technology, School of Engineering Science, P.O. Box 20, FI-53851 Lappeenranta, Finland

ARTICLE INFO

Keywords:
Liquid–liquid extraction
Li-ion battery waste
Process design
Continuous counter-current operation
Nonlinear regression

ABSTRACT

Fractionation of Li-ion battery waste leachates into high-purity Li, Ni, and Co streams in a liquid–liquid extraction circuit was studied using numerical simulations. A new mechanistic mathematical model explaining the phase equilibrium in the loading, scrubbing, and stripping stages using bis(2,4,4-trimethylpentyl)phosphonic acid (Cyanex 272) as extractant was developed. Including the distribution equilibrium of ammonia in the model enabled simulation of metal-extraction with partially neutralized extractant. The model facilitates the design and optimization of liquid–liquid extraction circuit for fractionation of Li-ion battery leachates. Four leachates from recent research articles were selected to the study in order to cover a wide composition variation. In the separation process scheme studied, Co and Ni are first selectively extracted, yielding a pure Li raffinate, and then separated as pure products in the stripping steps. The simulation results confirm the viability of the scheme. The influence of the leachate composition on the feasible range of O/A ratios in loading and scrubbing as well as acid concentration in Ni stripping was quantified. With proper operating parameters, high recoveries of Li and Co (> 99.9%) are achieved for all leachate compositions. The leachates containing 10–25 g/L Co, > 10 g/L Ni, and > 2.5 g/L Li are particularly suitable for fractionation of the metals into high-purity (> 99%) Li, Ni, and Co streams.

1. Introduction

Li-ion batteries are widely used for powering portable electronic devices of different types due to the favorable properties of Li, which has the highest redox potential value, and the highest specific heat capacity, of any solid element [1]. Currently, Li-ion batteries account for 37% of all the rechargeable batteries produced in the world, and their share is increasing. The number of appliances powered by this type of battery is growing as well. In total, 39% of produced Li is consumed in the manufacture of batteries [1]. Moreover, a sharp increase in Li demand is expected in the near future, due to the rapid development of the electric vehicle market [2,3].

Along with Li, spent Li-ion batteries contain hazardous materials; Co and Ni, etc [1]. As the estimated operational life of Li-ion batteries is 10 years, the amount of these metals available from spent batteries, as a secondary resource, will only increase, along with an increase in the number of batteries in use [4]. Therefore, the investigation of processes for recovery and recycling of metals from spent batteries has become highly desirable, from both environmental and economic viewpoints [2,5].

In a hydrometallurgical process applied for the recovery of valuable metals from spent Li-ion batteries, the battery waste is usually leached with H3PO4 or HCl acid [6,7] after mechanical and possibly some other pretreatment [8,9]. Also, H2PO4 was reported [10] to be a suitable agent for the leaching of the cathode materials (LiCoO2) and Co recovery. In addition, some organic acids such as citric acid [11] were considered as a leaching agent. As mentioned above, along with Li, Ni, and Co, Li-ion batteries contain significant amounts of Cu (7–17%), Al (3–10%) and Fe (up to 20%) [12] that may also be leached. Cu, Al, Mn, and Fe can be removed from the leachate by precipitation [11,14], or liquid–liquid extraction with 2-hydroxy-5-nonylsalicylaldoxime (Acorga MS640) [15], leaving Li, Ni, and Co in the solution. The utilization of the hydrosalicylaldoxime reagent also allows recovery of pure Cu. Organophosphorus reagents bis(2,4,4-trimethylpentyl)phosphonic acid (Cyanex 272, Mextral 272P, PS07) and 2-ethylhexyl hydrogen(2-ethylhexyl)phosphinate (PC-88A) are solely used for separation of Co, Ni, and Li due to their good Co/Ni selectivity and low extractability of Li.
from acidic solutions [8]. The separation of Co and Ni is a well-studied application of liquid–liquid extraction in hydrometallurgy [15]. The plants that use liquid–liquid extraction for Co/Ni separation process result from ores, concentrates, precipitates, matte, various scrap materials, and waste effluents [16], operate mostly with di(2,4,4′-trimethylpentyl)phosphinic acid (Cyanex 272, Mextral 272P, P507). The active component has been shown to yield high selectivity, low aqueous phase solubility, and high chemical stability [15]. Virolainen et al. [5] showed that high Co/Ni selectivity of Cyanex 272 makes this extractant a more attractive choice than PC-88A for the fractionation of Co, Ni, and Li.

In response to the increasing necessity to recycle spent Li-ion batteries, a number of studies have suggested employing liquid-liquid extraction to recover and separate Co, Ni, and Li from battery leachates [3,5,6,11]. A challenge for utilization of the phase equilibrium and pilot data available in the literature is that the composition of the leachate may vary strongly depending on the exact Li-ion battery chemistry and leaching conditions. To the authors’ knowledge, the influence of Li battery leachate composition on the performance and operation of continuous counter-current liquid–liquid extraction processes has not been investigated.

Numerical simulation of extraction processes can aid in understanding the influence of different operation conditions on process performance. Yet, there are no detailed numerical modeling and simulation studies on the liquid–liquid extraction processes for Li-ion batteries recycling. Slope analysis is often used for determining the nature of the extracted complexes and the stoichiometry of the metal extraction reactions. Process design usually relies on McCabe-Thiele analysis, which is used for determination of the number of theoretical stages required in loading, scrubbing, and stripping steps to achieve a specified purification and recovery in a counter-current operation [18,20–22]. The method heavily relies on McCabe-Thiele analysis and does not give a good indication of the purity transfer in the process. Bourget et al. [23] introduced a simulation software that relies on the simultaneous solution of multiple equilibrium calculations based on pre-generated equilibrium data. The capabilities of the simulation tool were demonstrated in optimization of the designs parameters of a circuit for recovery of Ni and Co. Even though the modeling method allows for transfer of impurities, it requires large variations in the experimental data to predict process performance accurately over a wide range of operating conditions. Alternatively, mechanistic modeling offers higher flexibility and accuracy in process simulation and design [24,25], especially in systems with competitive extraction reactions. Calibration of the models with reasonable amount of experimental data is however still required.

An effective Li-ion battery leachate fractionation process was earlier proposed by Virolainen et al. [6] and demonstrated in continuous counter-current runs for loading, scrubbing and stripping steps individually. However, the operation of the entire process was not validated. The process focuses on the separation of Co, Ni, and Li, which is the final stage in the processing of Li-ion battery leachate when all the other impurities (e.g. Cu, Al, Mn, and Fe) are removed by either selective precipitation or liquid–liquid extraction.

The objective of this study was to examine by numerical simulations the operation of the entire process scheme proposed by Virolainen et al. [6] in application to fractionation of Li-ion battery leachates of different compositions. For this purpose, a new mechanistic mathematical model of the equilibrium liquid–liquid extraction of Li, Co, and Ni with Cyanex 272 extractant from a sulfate solution was developed. The removal of other impurities in the initial stages of the Li-ion battery leachates processing is not considered because there are several known solutions discussed above. The same process scheme was studied for fractionation of four different Li-ion battery leachates presented in the literature [6,21,26,27]. The four leachates differed significantly in the target metals concentrations (Co, Ni, and Li). For three leachates [21,26,27], different process flowsheets have been originally suggested but the designs have not been verified by continuous experimental runs or simulations. It is shown here that numerical simulations can be used for optimization of the entire process and for analysis of process operation limitations over a wide range of feed concentrations.

2. Modeling

In the current study, the liquid–liquid extraction of Co, Ni, and Li is considered to be an interphase extraction process (Fig. 1). The extraction equilibrium is modeled by taking into account the aqueous phase speciation, the competing interfacial ion exchange extraction reactions of the cations, and the formation of extracted cation-extractant complexes of different stoichiometries in the both organic phase. Acidic organophosphorus extractants are frequently used in the form of their Na or ammonium salts in order to facilitate pH control of the operations when the leaching solutions contain high concentrations (> 3 g/L) of the metals being extracted [28–30]. Hence, it is important to study, in addition to the extraction behavior of the metal ions, also the extraction of ammonia [30]. Yet, up to now, no model has been suggested that could describe the ammonia equilibrium distribution in the range of pH 2–7, corresponding to the loading and stripping steps in...
2.1. Extraction of Co, Ni, and Li

2.1.1. Aqueous phase speciation

The aqueous phase in liquid-liquid extraction contains ions that are products of the dissociation reactions listed in Table 1. The corresponding equations for the equilibrium constants (Eqs. (1–18)) are also listed in Table 1. The values of the equilibrium constants were taken from the database of Medusa software [31]. The value of the equilibrium constant for sulfuric acid in Eq. (1) was set to be small (log K < −3) to represent complete dissociation [25]. The hydroslysis reactions of Co and Ni were included in the speciation model because the operation of some steps in the process considered herein is intended to be around pH 7, where precipitation of the metal hydroxides is possible (but of course undesirable). The equilibrium constants of the hydroslysis reactions listed in Table 1 include the concentration of water, which was assumed to be constant.

In concentrated aqueous solutions, electrolyte speciation can be determined using appropriate reaction equilibrium constants and ionic activity coefficients, derived from the Debye–Hückel theory [25,32]. The extended Debye–Hückel model, Eq. (19), was used herein to calculate activity coefficients for the aqueous phase species. A discussion on the model is presented elsewhere [24,25,32]. The activity coefficient γ relates the activity a to a measured molar concentration of the species in the aqueous phase: a = γc. Activity coefficients of the species in the organic phase were assumed unity.

\[
\log y = \frac{-d_i^2 \sqrt{I}}{1 + d_i^2 \sqrt{I}} + B \tag{19}
\]

where \(d_i\) is the hard-core diameter of the i-th ionic species, \(c_i\) is the charge of the i-th species, \(A\) and \(B\) are the Debye–Hückel parameters, and \(A\) is the ionic strength of the electrolyte solution.

2.1.2. Extraction mechanism

Depending on the extraction conditions, organophosphorus acid-based extractants are known to form complexes of variable stoichiometry with metal ions. These complexes are preferentially distributed into the organic phase [18–20,28]. The extractant-to-metal molar ratio for divalent metal ions changes from four (tetrahedral complex) to two (polymer formation), as the loading of the organic phase increases and less extractant molecules are available for metal complexation [29]. The liquid–liquid extraction of a given divalent metal by an organophosphorus acid-based extractant can be described assuming two stepwise reactions [33,34], the first one of which is an ion transfer at the interface of the aqueous and organic phases, where \(M\) stands for Co or Ni:

\[M^{2+} + 2[HAX]_0 \rightleftharpoons MX(HAX)_2 + 2H^+ \] (20)

and the second of which occurs in the bulk organic phase as a breakdown of the complex \(MX(HAX)_2\):

\[MX(HAX)_2 \rightleftharpoons MX + 2[HAX] \] (21)

In the case of Co and Ni, the first extraction reaction step takes the form shown in Eqs. (22) and (24), which leads to the expression of the extraction equilibrium constants, Eqs. (23) and (25):

\[Co^{3+} + 2[HAX]_0 \rightleftharpoons CoX(HAX)_2 + 2H^+ \] (22)

\[K_{CoX}^{(2)} = \frac{[CoX(HAX)_2][H^+]^2}{[Co^{3+}][HAX]^2} \] (23)

\[Ni^{2+} + 2[HAX]_0 \rightleftharpoons NiX(HAX)_2 + 2H^+ \] (24)

\[K_{NiX}^{(2)} = \frac{[NiX(HAX)_2][H^+]^2}{[Ni^{2+}][HAX]^2} \] (25)

At high organic loading, the breakdown of the extracted complexes of Co and Ni in the bulk organic phase is described by Eqs. (26) and (28) that lead to the expression of the extraction equilibrium constants, Eqs. (27) and (29):

\[CoX(HAX)_2 \rightleftharpoons CoX + 2[HAX] \] (26)

\[NiX(HAX)_2 \rightleftharpoons NiX + 2[HAX] \] (27)

\[K_{CoX} = \frac{[CoX][HAX]^2}{[CoX(HAX)_2]} \] (28)

\[K_{NiX} = \frac{[NiX][HAX]^2}{[NiX(HAX)_2]} \] (29)

Table 1

<table>
<thead>
<tr>
<th>Chemical reaction</th>
<th>Equation for equilibrium constant</th>
<th>log K</th>
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</thead>
<tbody>
<tr>
<td>(H^+ = HSO_4^- + H_2O)</td>
<td>(K_{HSO_4} = \frac{[HSO_4^-][H^+]}{[H_2O][H^+]^2} )</td>
<td>(-9)</td>
</tr>
<tr>
<td>(H^+ = SO_4^{2-} + H_2O)</td>
<td>(K_{SO_4} = \frac{[SO_4^{2-}][H^+]}{[H_2O][H^+]^2} )</td>
<td>(-1.98)</td>
</tr>
<tr>
<td>(Co^{3+} + SO_4^{2-} \rightleftharpoons CoSO_4)</td>
<td>(K_{CoSO_4} = \frac{[CoSO_4]}{[Co^{3+}][SO_4^{2-}]} )</td>
<td>(-2.87)</td>
</tr>
<tr>
<td>(Co^{2+} + H_2O \rightleftharpoons CoOH + H^+)</td>
<td>(K_{CoOH} = \frac{[CoOH][H^+]}{[Co^{2+}][H_2O]} )</td>
<td>(-0.2)</td>
</tr>
<tr>
<td>(Co^{2+} + 2H_2O \rightleftharpoons Co(OH)_2 + 2H^+)</td>
<td>(K_{Co(OH)_2} = \frac{[Co(OH)_2][H^+]^2}{[Co^{2+}][H_2O]^2} )</td>
<td>(-1.86)</td>
</tr>
<tr>
<td>(Ni^{2+} + 2H_2O \rightleftharpoons NiOH + H_2O)</td>
<td>(K_{NiOH} = \frac{[NiOH]}{[Ni^{2+}][H_2O]} )</td>
<td>(-12.2)</td>
</tr>
<tr>
<td>(Co^{2+} + 2H_2O \rightleftharpoons Co(OH)_2 + 2H^+)</td>
<td>(K_{Co(OH)_2} = \frac{[Co(OH)_2][H^+]^2}{[Co^{2+}][H_2O]^2} )</td>
<td>(-2.34)</td>
</tr>
<tr>
<td>(Na^{+} + SO_4^{2-} \rightleftharpoons NaSO_4)</td>
<td>(K_{NaSO_4} = \frac{[NaSO_4]}{[Na^+][SO_4^{2-}]} )</td>
<td>(-2.29)</td>
</tr>
<tr>
<td>(Na^{+} + H_2O \rightleftharpoons NaOH + H^+)</td>
<td>(K_{NaOH} = \frac{[NaOH][H^+]}{[Na^+][H_2O]} )</td>
<td>(-0.95)</td>
</tr>
<tr>
<td>(Na^{+} + 2H_2O \rightleftharpoons NaOH + H_2O)</td>
<td>(K_{NaOH} = \frac{[NaOH]}{[Na^+][H_2O]} )</td>
<td>(-20.01)</td>
</tr>
<tr>
<td>(Ni^{2+} + 2H_2O \rightleftharpoons NiOH + H_2O)</td>
<td>(K_{NiOH} = \frac{[NiOH]}{[Ni^{2+}][H_2O]} )</td>
<td>(-10.5)</td>
</tr>
<tr>
<td>(Ni^{2+} + Ni^{2+} \rightleftharpoons NiNi^{2+})</td>
<td>(K_{NiNi^{2+}} = \frac{[NiNi^{2+}]}{[Ni^{2+}]^2} )</td>
<td>(-2.73)</td>
</tr>
<tr>
<td>(Li^+ + SO_4^{2-} \rightleftharpoons LiSO_4)</td>
<td>(K_{LiSO_4} = \frac{[LiSO_4]}{[Li^+][SO_4^{2-}]} )</td>
<td>(-2.29)</td>
</tr>
<tr>
<td>(Li^+ + H_2O \rightleftharpoons LiOH + H^+)</td>
<td>(K_{LiOH} = \frac{[LiOH][H^+]}{[Li^+][H_2O]} )</td>
<td>(-0.5)</td>
</tr>
<tr>
<td>(Li^+ + Li^{+} \rightleftharpoons LiLi^+)</td>
<td>(K_{LiLi^+} = \frac{[LiLi^+]}{[Li^+][Li^{+}]} )</td>
<td>(-0.7)</td>
</tr>
<tr>
<td>(H^+ + H_2O \rightleftharpoons H_2O)</td>
<td>(K_{H_2O} = \frac{[H_2O]}{[H^+][H_2O]} )</td>
<td>(-9.237)</td>
</tr>
<tr>
<td>(H_2O \rightleftharpoons H^+ + OH^-)</td>
<td>(K_{H_2O} = \frac{[H^+][OH^-]}{[H_2O]} )</td>
<td>(-14)</td>
</tr>
</tbody>
</table>

The extended Debye–Hückel model, Eq. (19), was used herein to calculate activity coefficients for the aqueous phase species. A discussion on the model is presented elsewhere [24,25,32]. The activity coefficient γ relates the activity a to a measured molar concentration of the species in the aqueous phase: a = γc. Activity coefficients of the species in the organic phase were assumed unity.
2.2. Numerical methods

The model for the liquid–liquid extraction equilibrium of Co, Ni, and Li consists of nonlinear algebraic equations for the equilibrium constants of all the aqueous speciation reactions (Eqs. (23), (25), (27), (29), (31), (34), (36)). In the same manner, the model for the liquid–liquid distribution equilibrium of ammonia consists of equations for the aqueous speciation reactions (Eqs. (37)–(40)), and the reactions in the assumed extraction mechanism (Eqs. (20) and (35)).

In order to study the extraction equilibrium of ammonia in the pH 2–10 range, the aqueous speciation reactions shown in Table 2 were considered, following the approach presented by Inoue et al. [30]. The value of the dissociation constant of ammonium nitrate was taken from Mozurkevich (1993) [35], whereas the rest of the constants were taken from the database of Medusa software [31].

Table 2

Aquous speciation reactions in the liquid–liquid extraction from an ammonium nitrate solution [31,35]

<table>
<thead>
<tr>
<th>Chemical reaction</th>
<th>Equation for equilibrium constant ( \log K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_4^+ + \text{NO}_3^- \leftrightarrow \text{NH}_4\text{NO}_3 )</td>
<td>(-1.63 ) (37)</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{NO}_3^- \leftrightarrow \text{HNO}_3 )</td>
<td>(-1.283 ) (38)</td>
</tr>
<tr>
<td>( \text{H}^+ + \text{NH}_4^+ \leftrightarrow \text{NH}_4\text{H} )</td>
<td>9.237 (39)</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} + \text{H}^+ + \text{OH}^- )</td>
<td>(-14 ) (40)</td>
</tr>
</tbody>
</table>

The reaction in Eq. (32) is actually obtained by combining the reactions in Eqs. (20) and (35). Therefore, Eq. (32) represents the net extraction reaction, whereas Eqs. (20) and (35) describe the extraction in detail, and enable the mechanistic modeling of the extraction process.

In order to study the extraction equilibrium of ammonia in the pH 2–10 range, the aqueous speciation reactions shown in Table 2 were considered, following the approach presented by Inoue et al. [30]. The value of the dissociation constant of ammonium nitrate was taken from Mozurkevich (1993) [35], whereas the rest of the constants were taken from the database of Medusa software [31].

2.2. Numerical methods

The model for the liquid–liquid extraction equilibrium of Co, Ni, and Li consists of nonlinear algebraic equations for the equilibrium constants of all the aqueous speciation reactions (Eqs. (20)–(35)), and the reactions in the assumed extraction mechanism (Eqs. (23), (25), (27), (29), (31), (34), (36)). In the same manner, the model for the liquid–liquid distribution equilibrium of ammonia consists of equations for the aqueous speciation reactions (Eqs. (37)–(40)), and the reactions in the assumed extraction mechanism (Eqs. (34) and (36)). In addition, the mass balance and electrical charge balance equations are needed to solve the systems of nonlinear algebraic equations for the extraction equilibrium phase composition. The set of equations can be solved since it is possible to formulate the same number of independent equations as there are variables (species). However, a good initial guess is required, since otherwise erroneous or inaccurate results can be obtained. Therefore, a rate-based approach, described in the following section, is used herein as an alternative.

Solution of the phase equilibrium model

A rate-based approach [24,25,36] was used herein to solve the model equations, since the approach was found to be more efficient in comparison to the solution of a system of nonlinear algebraic equations using, for example, a Newton-Raphson method. The rate-based approach implies conversion of the nonlinear algebraic equations of the equilibrium constants and linear balance equations into the system of ordinary differential equations (ODEs). Since reversible chemical reactions proceed until an equilibrium is reached, the solution of a system of ODEs at plateau gives the same result as the solution of the respective system of nonlinear algebraic equations. Therefore, the element balance equations for the aqueous phase species, Eqs. (41), and the total mass balance equations, Eq. (42), for the heterogeneous two-phase reactions in a batch reactor can be used to calculate the composition of the process phases at equilibrium.

\[
\frac{d\text{NH}_4^+}{dt} = - \sum_{j=1}^{n} \text{R}_j \frac{d\text{R}_j}{dt} \quad (41)
\]

\[
\frac{d\text{NH}_4\text{NO}_3}{dt} = \text{R}_j \frac{d\text{R}_j}{dt} \quad (42)
\]

where \( \text{V}_{\text{aq}} \) and \( \text{V}_{\text{org}} \) are the volumes of the aqueous and organic phases.
respectively, $t$ is the time, $i$ is the index of species in the aqueous phase, $k$ is the index of the corresponding species in the organic phase, $S$ is the index of equilibrium reactions, $m$ is the number of reactions in the system, $k$ is the stoichiometric coefficient of the species and $R$ is the rate of an elementary reaction. For an elementary reaction, Eq. (43), a reaction rate equation, Eq. (44), is formed directly from the reaction stoichiometry, in agreement with the mass action law. The reaction equilibrium constant, Eq. (45), gives a relationship between the forward and backward parts of the reversible reactions. The forward reaction rate constant can be assigned the value $k_f \approx 1000$. It can be the same for all the reactions, since it does not affect equilibrium but the time required to reach it.

\[ nA + mB + \ldots \rightarrow cC + dD + \ldots \]

\[ k_f = \frac{[C][D]^d}{[A][B]^c} \]  

\[ k_b = \frac{[A]^m}{[B]^n} \]

where $k_f$ and $k_b$ are the reaction rate constants of the forward and backward reactions, respectively, $K$ is the equilibrium constant.

The ODEs in Eqs. (46) and (47) can be solved simultaneously as an initial value problem by integration. In such a way, the model can be solved faster, at the same time the accuracy of the solution can be easily controlled by solver settings. The model was solved numerically with ode15s solver in Matlab.

**Estimation of parameter values**

All modelling in the current study was done in Matlab. An open source MCMC code package, developed by Laine [37,38], was used to estimate the reliability of the modeling results. The model developed for the liquid-liquid extraction equilibrium of Co, Ni, and Li was calibrated with the data presented by Virialainen et al. [16]. The unknown model parameters, i.e. the extraction reaction constants (Eqs. (23), (25), (27), (29), (31)), were estimated by nonlinear regression fitting of the experimentally measured extent of extraction of the metals, minimizing the sum of the squared residuals (Eq. (46)).

\[ SSR = \sum_{j=1}^n \sum_{i=1}^N \left( \log(\text{LLXNH}_i)_{\text{exp}} - \log(\text{LLXNH}_i)_{\text{mod}} \right)^2 \]  

where SSR is the sum of the squared residuals, $E$ is the extent of metal extraction, $j$ is the index of an experimental data point, $N$ is the total number of experimental points, $m$ is the number of a metal, and $T$ is the total number of metals.

The model for the liquid-liquid extraction equilibrium of Co, Ni, and Li contains equilibrium constants for the ammonia liquid–liquid equilibrium distribution (Eqs. (34) and (36)). The constants were estimated separately, from independent data retrieved from Inoue et al. [30]. The extraction equilibrium constants (Eqs. (34) and (36)) were estimated by nonlinear regression fitting of logarithmic total concentration of ammonia in the organic phase, minimizing the sum of the squared residuals (Eq. (47)).

\[ SSR_f = \sum_{j=1}^n \left( \log(\text{LLXNH}_j)_{\text{exp}} - \log(\text{LLXNH}_j)_{\text{mod}} \right)^2 \]

where $j$ is the index of experimental points, and $N$ is the total number of experimental points.

**Process simulation**

The process simulations were done using a sequential modular simulation approach. In the approach, the process step models are solved in the sequence in which the steps appear in the process under the condition, that the inlet stream compositions and concentrations of the species in the organic phase are the same as the outlet stream compositions and concentrations of the species in the aqueous phase. The process simulations were done using a sequential modular simulation approach. In the approach, the process step models are solved iteratively, until the mass balance over the entire process converges. The model developed in Section 2.1 is used to simulate loading, scrubbing and stripping stages in a continuous counter-current liquid–liquid extraction process.

**3. Results and discussion**

The model for the liquid–liquid extraction equilibrium of Co, Ni, and Li from a sulfate solution, developed in the current study, accounts for the extraction of ammonium along with the extraction of the metals. The models for ammonium equilibrium distribution and extraction of Co, Ni, and Li is first calibrated and then validated below. Finally, the main task, analysis of the separation process operation with different leachates is presented.

**3.1. Model calibration**

**3.1.1. Ammonia equilibrium distribution**

The extraction reaction equilibrium constants for ammonium shown in Eqs. (34) and (36), $K_{LLXNH_{4A}^{+}}$ and $K_{LLXNH_{4}^{-}}$, were fitted against the data retrieved from Inoue et al. [30] minimizing the sum of the squared residuals in Eq. (47). The estimated values of the model parameters are presented in Table 3. The estimated value of $K_{LLXNH_{4A}^{+}}$ differs from the value estimated by Inoue et al. [30]. This difference may result from the different approaches used for parameter estimation. The nonlinear regression modeling used herein is considered superior to linear regression, since linearization alters the error structure of the data.

The model developed in the current study shows an excellent fit (Fig. 2a) to the experimental data presented by Inoue et al. [30]. In comparison to the model of Inoue et al. [30], the model developed herein explains well the extraction behaviour from acidic to basic solutions (pH 2–10).

**3.1.2. Extraction equilibrium of Co, Ni, and Li**

The model for calculating the compositions at phase equilibrium in the liquid–liquid extraction of Co, Ni, and Li from a sulfate solution using Cyanex 272 extractant was developed as described in Section 2.1. The parameters were fitted against the pH-extraction isotherms from Virialainen et al. [6] minimizing the sum of the squared residuals in Eq. (46). The composition of the sulfate leachate was 14.4 g/L Co, 0.5 g/L Ni, and 2.8 g/L Li. The estimated values of the model parameters, extraction equilibrium constants for Co, Ni, and Li, are presented in Table 3. The values of the model parameters were estimated for 1 M Cyanex 272 modified with 5% v/v trietylamine (TOA). The modifier was used for decreasing organic-phase viscosity and preventing third phase formation at high loading. The goodness of fit presented in Fig. 2b indicates a good correlation of the experimental data with the developed model.

The results of the MCMC analysis of the model parameters are presented in Fig. 3, which shows two-dimensional posterior distributions. The density of the dots in each subfigure represents the

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Estimated values of the parameters in the models for ammonia equilibrium distribution and extraction of Co, Ni, and Li.</th>
<th>log $K_{LLXNH_{4A}^{+}}$</th>
<th>log $K_{LLXNH_{4}^{-}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{LLXNH_{4A}^{+}}$</td>
<td>$-14.20$</td>
<td>$-14.66$</td>
<td></td>
</tr>
<tr>
<td>$K_{LLXNH_{4}^{-}}$</td>
<td>$-6.43$</td>
<td>$-7.11$</td>
<td></td>
</tr>
<tr>
<td>$K_{LLX_{12}^{+}}$</td>
<td>$-6.71$</td>
<td>$-6.92$</td>
<td></td>
</tr>
<tr>
<td>$K_{LLX_{12}^{+}}$</td>
<td>$-2.28$</td>
<td>$-2.46$</td>
<td></td>
</tr>
<tr>
<td>$K_{LLX_{12}^{+}}$</td>
<td>$-0.72$</td>
<td>$-0.88$</td>
<td></td>
</tr>
</tbody>
</table>

* The standard deviation of the parameter estimates was estimated using the Markov chain Monte Carlo method.
probability that the true values of the parameters lie in that region, and the two circles represent the 95% and 90% probability regions of the parameters. It can be seen from the banana-shaped distribution in Fig. 3 that parameters $K_{LLXNi1}$ and $K_{LLXNi2}$ are slightly correlated. Such a correlation results from the small number of data points on the extraction isotherm for Ni in between pH 6 and 7, as the corresponding pair of parameters for Co does not correlate. All of the other parameters are well determined, as shown by the well-centered probability distributions, and the sharp peaks in the one-dimensional distributions. In addition, despite the correlation, the model with the fitted parameters explains the extraction of Co, Ni, and Li well, as can be seen in Fig. 2b.

Fig. 2. (a) Extraction of ammonia with Cyanex 272. Total monomeric extractant concentration $= 1.45$ M, $x = 0.657$ M, $\bullet = 0.340$ M. Experimental data from Inoue et al.[30]. Solid lines: prediction of the model from the current study, dashed lines: model from Inoue et al. [30]. (b) Dependence of metal extraction from the simulated sulfate leachate of Li-ion battery waste on the equilibrium pH. Symbols: circles = Co, triangles = Ni, squares = Li. Lines: model from the current study. Experimental data from Virolainen et al. [6].

Fig. 3. Two-dimensional posterior distributions for the model parameters fitted with the data for the modified extractant. The 50% and 95% confidence regions (black lines), and the one-dimensional marginal densities (red lines), were calculated based on the density estimation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
3.2. Model validation

Once the equilibrium model parameters were estimated from the pH—extraction isotherms, the model was validated against experimental data on loading and stripping of the metals from Virolainen et al. [6]. The organic phase contained 1 M Cyanex 272 modified with 5% v/v TOA, and 48% pre-neutralized with ammonia, as presented by Virolainen et al. [6]. As can be seen in Figs. 4 and 5, the fitted model predicts well the loading and stripping equilibria.

From the excellent results of the predicted loading and stripping steps of the liquid – liquid extraction of Co, Ni, and Li, it was inferred that the model is also capable of predicting the scrubbing step in the process.

3.3. Separation process operation with different leachates

The model developed and validated above can be employed to design and analyze a continuous counter-current process for the separation of metals from Li-ion battery leachate. The common approach is to extract Co and Ni in separate liquid extraction circuits, whereas Li remains in the final raffinate after Ni extraction. For instance, such a process has been suggested in which both Co and Ni were produced as 99.9%, and Li as 99.8%, pure, using 2-ethylhexyl hydrogen(2-ethyl-hexy)phosphonate (PC-88A) extractant [21,22]. Recently, Virolainen et al. [6] argued that keeping pH at around 6.5 in the scrubbing step, the de-sired purity of Li (> 99%) in the raffinate is not achievable if the scrubbing product is recycled back to the loading feed. Instead, additional purification must be carried out by e.g. precipitation of lithium carbonate [7,39] or lithium phosphate [11,14]. Therefore, a pure Li product can be achieved with the suggested liquid – liquid extraction process. Otherwise, pH around 7.5 can be adjusted by varying the O/A ratio in the second loading stage to increase Li purity in the raffinate, since concentrations of Co and Ni in the aqueous phase in this stage are such low that they are not precipitated. Fig. 7c demonstrates that operating the process at pH between 6.5 and 7.5 in the second extraction stage provides a pure mixture of Co and Ni in the scrubbed loaded organic phase.

Virolainen et al. [6] kept pH at around 6.5 in the scrubbing step provides complete scrubbing of Li leaving Ni and Co in the scrubbed loaded organic phase. The simulations of the interconnected loading and scrubbing steps, however, show (Fig. 7d) that the influence of phase ratios on the performance of the inter-connected loading (two stages) and scrubbing steps, with given feed composition and flow rate of the leachate, is presented in Fig. 7. Only the operation with O/A (scrubbing) < O/A (loading) is feasible here, due to the mass balance of the process streams. Fig. 7a shows the equilibrium pH in the second loading stage. It can be seen that the desired pH of around 7 is achievable within a narrow region only under the conditions studied. This requires a very stable process operation. The region where the pH is between 6.5 and 7.5 is marked in Fig. 7b–d with cyan and magenta lines. Fig. 7b shows that, when the process is operated such that pH 7 is maintained in the second loading step, the desired purity of Li (> 99%) in the raffinate is not achievable if the scrubbing product is recycled back to the loading feed. Instead, additional purification must be carried out by e.g. precipitation of lithium carbonate [7,39] or lithium phosphate [11,14]. Therefore, a pure Li product can be achieved with the suggested liquid – liquid extraction process. The simulations show that the effect is minor and is mainly seen in Ni recovery. Using a single stage would yield low Li recovery and lower purity of Co and Ni in the loaded organic. Addition of the second loading stage resolved these issues. However, addition of a third stage makes the performance worse, since purity of Li in raffinate and recovery of Ni slightly drop. The cause of this drop is that the saponified extractant is consumed according to Eq. (20) in the last loading stages, whereas the extraction proceeds according to Eq. (32) in the first stage, where pH decreases, decreasing Ni extraction. The number of loading stages does not affect the Li recovery or its purity in the raffinate very much. Two loading stages appear to be the optimal process configuration, providing high recovery of Li, and loaded organic with high purity of Co and Ni. This result agrees well with the conclusion based on the experimental studies [6].

The model developed and validated above can be employed to design and analyze a continuous counter-current process for the separation of metals from Li-ion battery leachate. The common approach is to extract Co and Ni in separate liquid extraction circuits, whereas Li remains in the final raffinate after Ni extraction. For instance, such a process has been suggested in which both Co and Ni were produced as 99.9%, and Li as 99.8%, pure, using 2-ethylhexyl hydrogen(2-ethyl-hexy)phosphonate (PC-88A) extractant [21,22]. Recently, Virolainen et al. [6] argued that keeping pH at around 6.5 in the scrubbing step, the desired purity of Li (> 99%) in the raffinate is not achievable if the scrubbing product is recycled back to the loading feed. Instead, additional purification must be carried out by e.g. precipitation of lithium carbonate [7,39] or lithium phosphate [11,14]. Therefore, a pure Li product can be achieved with the suggested liquid – liquid extraction process. Otherwise, pH around 7.5 can be adjusted by varying the O/A ratio in the second loading stage to increase Li purity in the raffinate, since concentrations of Co and Ni in the aqueous phase in this stage are such low that they are not precipitated. Fig. 7c demonstrates that operating the process at pH between 6.5 and 7.5 in the second extraction stage provides a pure mixture of Co and Ni in the scrubbed loaded organic phase.
this process scheme does not allow maintaining the equilibrium pH > 6 in the scrubbing stage, when pH is between 6.5 and 7.5 in the last loading stage. As a result, Ni is partially scrubbed along with Li. Therefore, some amount of Ni always circulates between the loading and scrubbing stages, decreasing the efficiency of extractant utilization.

The low recovery of Ni (< 93%) in the simulations presented in Table 4 is explained by the same reason.

The recovery of Ni in the two-stage process can be improved by dosing a base to the first loading stage, which can decrease the required degree of neutralization of the PNO to the second loading stage. Even though part of the Ni is lost to the raffinate in the two-stage process in Table 4, the purity of the Li in the raffinate is very high (99.54%). This is due to the low concentration of Ni in the leachate (0.5 g/L) and the high equilibrium pH of 7.5 in the second loading stage. Low amounts of Co and Ni in the raffinate also decrease the risk of precipitation.

The performance (simulation results) of the interconnected loading and scrubbing stages of the processes with varying leachate composition is presented in Table 5. The O/A ratio in the scrubbing was set to 1 in all simulations, while the O/A in the two-stage loading step was adjusted so that the equilibrium pH of 7.5 is maintained in the second loading stage. The same scrubbing solution (0.3 g/L Ni and pH 1.4) was used in all the processes. The simulations show very good performance of the processes with different leachate compositions when the equilibrium pH of 7.5 is maintained in the last loading stage by adjustment of

<table>
<thead>
<tr>
<th>Loading Stages</th>
<th>( \Delta R_{\text{Li}} ), %</th>
<th>( \Delta R_{\text{Co}} ), %</th>
<th>( \Delta R_{\text{Ni}} ), %</th>
<th>( \Delta R_{\text{Li}} ), %</th>
<th>( \Delta R_{\text{Co}} ), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.72</td>
<td>99.86</td>
<td>99.78</td>
<td>100.00</td>
<td>92.76</td>
</tr>
<tr>
<td>2</td>
<td>99.54</td>
<td>99.99</td>
<td>99.99</td>
<td>100.00</td>
<td>88.06</td>
</tr>
<tr>
<td>3</td>
<td>99.42</td>
<td>99.99</td>
<td>99.99</td>
<td>100.00</td>
<td>84.55</td>
</tr>
</tbody>
</table>

O/A phase ratios in the loading and scrubbing stages. Co is recovered completely from the leachates into the LO, and most of the Li (> 99%) is left in the raffinate. At the same time, complete recovery of Ni is not achieved (due to low pH in the first loading stage as discussed above) with the highest recovery corresponding to the leachates II and III that have the highest Ni concentration. The higher recovery of Ni is followed by the lower purity of Li in the raffinate. However, the underlying reason is the higher Ni concentration in the leachates. It is thus concluded that higher Ni content of leachate impedes pure Li recovery in the process.

The performance of the separation process with the different leachate compositions in Table 5 is shown in Fig. 8. As seen in the figure, a purity of > 99% of Li in the raffinate is achieved with different O/A ratios for different leachates. Also the location of the feasible operating window (cyan and magenta lines) depends on the leachate composition.
The leachates with higher total concentration of Co and Ni (Leachate II, III, and IV), require higher O/A ratio in the loading stage for the same O/A ratio in scrubbing.

Performance of the two-stage stripping of Ni from the loaded organic phases corresponding to the four cases in Table 5 is shown in Fig. 9. The loaded organic phase contains 11 g/L Co, O/A = 1. The stripping efficiency increases with increasing strip liquor acidity. The complete stripping of Ni is possible only at the cost of co-stripping of Co and, consequently, reduced Ni purity. The achievable Ni purity in the loaded strip liquor increases with the Ni concentration in the LO. If the Ni concentration in the LO is lower than 2 g/L, which is the case in Leachate I and Leachate IV, it is not possible to reach high Ni purity (> 99%) in strip liquor. Therefore, Leachates II and III with higher Ni concentrations are particularly well suited for this process since the product strip liquor with high Ni purity can be produced. Complete stripping of Co from the loaded organic after Ni stripping can be easily accomplished in one stage, for example, with a strip feed of 10 g/L Co and 25 g/L H₂SO₄ [29].

4. Conclusions

The influence of leachate composition on operation and performance of solvent extraction circuits for recovery and purification of Li, Co, and Ni from spent Li-ion battery leachates was studied by numerical simulations. For this purpose, a new model for the equilibrium of the liquid–liquid extraction of these metals from a sulfuric acid solution with bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272 extractant) was developed and validated. The model accounts for the aqueous phase speciation of the species present in the sulfate solution, and explains the extraction of the metal ions with Cyanex 272 by interfacial

| Leachate | Co, g/L | Ni, g/L | Li, g/L | Source | O/A loading | $\Delta H^{eq}$, % | $\Delta R^{eq}$, % | $\Delta P_{Li}^{eq}$, % | $\Delta P_{Co}^{eq}$, % | $\Delta P_{Ni}^{eq}$, % | $\Delta P_{Cu}, g/L$
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>14.0</td>
<td>0.5</td>
<td>3.8</td>
<td>[6]</td>
<td>0.57</td>
<td>99.57</td>
<td>99.99</td>
<td>99.98</td>
<td>100</td>
<td>88.39</td>
<td>0.62</td>
</tr>
<tr>
<td>II</td>
<td>16.7</td>
<td>11.0</td>
<td>1.4</td>
<td>[26]</td>
<td>0.72</td>
<td>98.48</td>
<td>99.95</td>
<td>99.98</td>
<td>100</td>
<td>96.45</td>
<td>4.59</td>
</tr>
<tr>
<td>III</td>
<td>11.3</td>
<td>11.5</td>
<td>1.8</td>
<td>[27]</td>
<td>0.67</td>
<td>98.98</td>
<td>99.94</td>
<td>99.96</td>
<td>100</td>
<td>96.73</td>
<td>5.76</td>
</tr>
<tr>
<td>IV</td>
<td>25.1</td>
<td>2.5</td>
<td>6.2</td>
<td>[21]</td>
<td>0.72</td>
<td>99.65</td>
<td>99.98</td>
<td>99.96</td>
<td>100</td>
<td>94.27</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 5 Performance (simulation results) of the interconnected loading and scrubbing stages of the processes with varying leachate composition.
competitive ion exchange reactions of different stoichiometries. In addition, ammonium equilibrium distribution in the extraction system was modeled to enable prediction of the metal extraction with the pre-neutralized extractant.

The process flowsheet, in which Co and Ni are recovered together from the leachate in the loading step, leaving Li in the raffinate, and subsequently, Co and Ni are separated and purified in the selective stripping step, was found to be very flexible. The process was shown to be applicable to separate Co, Ni, and Li from leachates of different composition. The process can be tuned for treatment of different leachates by adjustment of O/A phase ratios in the loading and scrubbing stages. It was found that high Ni content of the leachate impedes pure Li recovery in the process. The higher the Ni concentration in the leachate, the higher purity of Ni is obtained in the stripped fraction. The process scheme allows adjusting the process performance to the changing market value of the metals.

References

Publication IV

Vasilyev, F., Virolainen, S., Sainio, T.

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Hydrometallurgy
Vol 153, pp. 121-133, 2018
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Synthesis of hydrometallurgical processes for valorization of secondary raw materials using ant colony optimization and key performance indicators

Fedor Vasilyev, Sami Virolainen, Tuomo Sainio *

Lappeenranta University of Technology, Laboratory of Separation Technology, Skinnarilankatu 34, FI-53850 Lappeenranta, Finland

** Abstract **

An algorithm-based method for synthesis of hydrometallurgical processes using limited amounts of experimental data is presented. The method enables simultaneous selection and sequencing of unit operations and optimization of operating parameters. An ant colony optimization (ACO) based algorithm is used to identify the most economic process alternative in an iterative manner. Key performance indicators are used for comparison of candidate processes: a purification performance index measures purity improvement and a separation cost indicator is used as an objective function in process optimization. Computational times were reduced significantly with the suggested method compared to an algorithm which evaluates all the possible process options. The practical applicability of the method to hydrometallurgy is demonstrated by investigating zinc recovery from argon oxygen decarburization dust with two alternative leaching methods and recovery of lanthanides from nickel metal hydride (NiMH) batteries. In the first zinc recovery process, 150 min normal batch leaching with 0.5 M H₂SO₄ is used, and in the other one 270 min batch leaching with H₂SO₄ is done by controlling the pH (<3.0). In both cases the leachate is extracted with D₂EHPA at pH 4.27, and stripped with circulating solution from zinc electrolysis. For lanthanides recovery the algorithm suggested a process in which the raw material is leached with 1.3 M HCl, the leachate is extracted with D₂EHPA at pH 2.2, organic phase is stripped with 2.0 M HCl and 99% pure Ln-oxalates are precipitated with oxalic acid at pH 0.6. Compared to previously suggested process for the same raw material, the algorithm suggests operating the leaching step such that higher selectivity is achieved by sacrificing some yield.

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** Abbreviations **

ACO ant colony optimization
AOD argon oxygen decarburization
CPU central processing unit
EDR energy dissipation rate
IRR internal rate of return
KPI key performance indicator
SCI separation cost indicator

** Notation **

A flow rate, m³/s
c_i concentration of contaminants, kg/m³
E concentration of extractant, m³/m³
K specific cost of expenses, €/kg
k_specific cost of a leaching step, €/kg
h specific cost of a purification step, €/kg
L probability
M number of components in a chemical system
N number of ants in a colony
n number of process steps
P number of discrete values of operating parameters
SL solvent loss in solvent extraction
T concentration of a target metal in the system, kg/m³
t_b batch time in leaching, s
U number of unit operations
V_l volume of leaching vessel, m³
X purity
Y yield

Greek symbols
ɑ the degree of importance of the pheromones
ξ parameter used to control the scale of the global updating of the pheromone
τ amount of pheromone in a cell
ρ pheromone decay factor

* Corresponding author.
1. Introduction

Hydrometallurgical process development usually starts with analysis of the raw materials to be treated, i.e., chemical composition, mineralogy, state, particle size, volume etc. (Forseth and Anumaa, 2013). The process itself typically consists of three consecutive main steps: leaching, concentration, and purification, and final product recovery. Several alternative unit operations are available for each process step. For instance solvent extraction, ion exchange, and/or selective precipitation can be employed for purification and concentration, and final product recovery. Several alternative unit operations are available for each process step. For instance solvent extraction, ion exchange, and/or selective precipitation can be employed for purification and concentration, and final product recovery. Moreover each unit operation can be run under a wide range of operating conditions (pH, pressure, phase ratio, solvent type, etc.). A key to successful and efficient hydrometallurgical purification is identification of the most suitable sequence of unit operations and the most effective combination of operating parameters to obtain the desired purification and yield with minimum (economic) effort.

Cisternas (1999) identified lack of works devoted to design of complete process due to complexity of the problem and great number of variables and restrictions to consider in its extensive review on synthesis of processes in extractive metallurgy and inorganic chemistry. To decrease the size of the problem process steps are usually designed individually (Cisternas, 1999), so that there are many methods and techniques available for design of each process step (Galvez et al., 2004; Alonso et al., 2001; Trujillo et al., 2014). However, synthesis of complete processes is potentially more efficient since process step interactions are taken into account (Angira and Babu, 2006; Cisternas, 1999).

When a new hydrometallurgical process is being developed, comparison between process alternatives and process optimization is usually done based on the experience of scientists and engineers, as well as on extensive experimentation (Rintala et al., 2011). Over-expenditure on reagents, experimental biases, complicated data processing and the complexity of considering several process parameters simultaneously prolong the course of hydrometallurgical process development at its early stages and contribute to inefficiency. Hydrometallurgical purification process development is usually based on scale-up of processes established on a laboratory or pilot scale. Conceptual design or process synthesis in the early stage is thus viewed as the most important stage of process development (Criner et al., 2005). Major decisions affecting the lifecycle of the process are made during development of the first process flowsheet.

Experience-based process synthesis can often result in overall suboptimal processes with inefficient utilization of energy and auxiliary materials (Nfor et al., 2009). Therefore, systematic process development based on identification of justified optima is essential for efficient utilization of time and resources.

Nfor et al. (2009) identified four types of process synthesis strategies applicable to chemical industries: heuristics or knowledge-based strategies (Criner et al., 2005), optimization-based strategies (Steimel et al., 2013; Grossmann and Daichendt, 1996), high-throughput experimentation strategies (Bhambure et al., 2011; Schuldt and Schmoeckler, 2013) and a combination of the aforementioned strategies (Ahamed et al., 2006). Each approach has strengths and weaknesses as discussed elsewhere (Nfor et al., 2009). Mathematical optimization based method can offer significant advantages to hydrometallurgical process development: clarification of interactions between unit operations, utilization of validated models for process optimization, user-independence after formulation of the search space, and the ability to identify the optimal process meeting the set criteria (Nfor et al., 2009). Application of mathematical optimization requires a superstructure of process alternatives and the availability of useful objective functions. Numerical measures for assessment of process performance are required for efficient application of optimization based method. The measures have to reflect the main features of the alternative unit operations and form a reliable base for comparison. The main criteria for decisions on process synthesis in extractive metallurgy are technical feasibility and economic potential, along with environmental, safety and other aspects (Linninger, 2002; Chakraborty et al., 2004). It is desirable to base process synthesis decisions upon costs over the complete process. However, at the very beginning of process development, before process concepts are available, such information is not available and the profitability of a process or its internal rate of return (IRR) cannot be precisely estimated. The use of the key performance indicators (KPIs) introduced by Wielenhupfer and Schmoeckler (2010) offers a potentially effective approach to address this problem. The KPIs were developed for rating purification and cost-efficiency on the basis of single step purity improvement, yield and specific costs. The indicators do not require complete mass and energy balances and can be applied from the beginning of experimental investigation. Although the KPIs were first introduced for evaluation of pharmaceutical bio-separation processes, they are equally valid for hydrometallurgy.

Solution of an optimization problem requires a suitable and efficient algorithm that is capable of identifying the minimum value of the target function and the corresponding sequence of unit operations and their operating parameters. Mathematical programming algorithms and methods available for synthesis of chemical processes have been the subject of a number of reviews (Grossmann and Daichendt, 1996; Grossmann et al., 1999; Arev et al. and Piskopoulou, 1998). Algorithms based on extensive searches for the optimal solution are computationally not preferred due to the high computational efforts required (Raæesi et al., 2008). However, the problem can be addressed in a more efficient manner by using meta-heuristics to find approximate solutions (Raæesi et al., 2008; Biswas et al., 2009). The stochastic meta-heuristic ant colony optimization (ACO) algorithm has been found to be promising for efficient synthesis and optimization of processes (Raæesi et al., 2008; Chuanfeng and Xin, 2002).

The objective of this research was development of an algorithm-based method for synthesis of hydrometallurgical processes using experimental data. Key theoretical aspects of in silico hydrometallurgical process development using ant colony optimization (ACO) and key performance indicators (KPIs) are discussed and the developed method and algorithm are presented. The efficiency of the algorithm is demonstrated, and utilization of the method is examined based on two case studies, namely recovery of Zn from argon oxygen decarburization (AOD) dust, and extraction of lanthanides from spent nickel metal hydride (NiMH) batteries.
2. Methods

The proposed method for design and optimization of hydrometallurgical purification processes consists of five steps:

- feed characterization and product specification,
- preselection of unit operations and the mass separation agents,
- collection of data (experiments or literature search for missing data),
- automated process synthesis,
- verification and validation of the constructed process.

In the first step, the specific characteristics of the purification process are set, e.g., the composition of the raw material, target purity, target concentration and other constraints. Based on these, a number of promising separation unit operations and corresponding mass separation agents are preselected. The latter are experimentally investigated by data collection experiments (construction of ad- and desorption isotherms, concentrations in leaching versus time or pH, step yields, changes of concentrations, etc.). The missing data can be also collected using literature search. The acquired data are used for simultaneous design and optimization of a purification process by means of a developed ACO-based algorithm and the synthesized process is then studied and developed further.

A hydrometallurgical process chain is built of individual unit operations: leaching, solvent extraction, stripping, chemical precipitation, etc. However, in general the unit operations are considered in the ACO-based algorithm as black boxes with inputs and outputs, and could just as well be continuous (e.g. SX) and even consist of multiple stages. An output from a unit operation is an input for the next one in the constructed process chain, i.e., the yield from one unit operation affects the feed composition of the next one. A model for each unit operation constructed are present there. Also the matrix containing pheromone values is created of the same size. Every hypothetical ant travels through the collected experimental data and all the processes that can be constructed are present there. Also the matrix containing pheromone values is created of the same size. Every hypothetical ant travels through the graph selecting one cell on each layer consequently creating a process. In each iteration, N hypothetical ants travel from the start point to the end point of the graph. Each iteration starts from launching the first ant and ends by updating the pheromone matrix in compliance with the evaluation of solutions constructed by the hypothetical ant colony in the iteration. On the initialization step a three-dimensional matrix corresponding to ACO search network (Fig. 1) is created. It contains the collected experimental data and all the processes that can be constructed are present there. Also the matrix containing pheromone values is created of the same size. Every hypothetical ant travels through the graph selecting one cell on each layer consequently creating a process route. All the process routes from the superstructure are being evaluated and the best one is

![Graphical representation of the ACO search in the form of a multi-layered structure, with n process steps, U unit operations and P discrete values of operating parameters for each unit operation.](image-url)
As the raw materials are solids in the cases considered in this paper, prior to the first iteration the pheromone is uniformly distributed over the search domain in such a way that only leaching can be chosen as a unit operation of the first layer. In addition, heuristics and a phase selection rule are applied in the ACO-based algorithm to govern the selection of successive unit operation. The former one renders the logic of hydrometallurgical process synthesis and determines, for example, that only solvent extraction or precipitation can follow the leaching step and not stripping. The later one postulates that the phase with yield of target element more than 50% is subject- ed for further treatment. The heuristics and the rule are realized by respective pheromone redistribution for each hypothetical ant before it makes a decision on the next layer.

After each iteration, the pheromone value of each cell is updated according to the pheromone updating rule Eq. (2) (Rao, 1996). One iteration is a complete cycle involving the ant’s movement, pheromone evaporation and pheromone deposition. The goal of the pheromone update is to increase the pheromone value associated with good or promising paths

$$\tau_{l,u,p} = \left(1 - \rho \right) \tau_{l,u,p} + \sum_{k} \Delta \tau_{l,u,p}^{k}$$

where $\Delta \tau_{l,u,p}^{k}$ is the amount of pheromone deposited on cell $l,u,p$ by the best ant, $\rho$ is the pheromone decay factor. The decrease in pheromone intensity favors the exploration of different paths during the search process, which assists elimination of poor choices made previously. Furthermore, it helps in binding the maximum value attained by the pheromone trails.

At the end of an iteration, when each ant has chosen a cell on each layer, i.e., after construction of the solutions’ superstructure, the constructed processes have to be evaluated and compared to identify the best one. SCI function, which represents dependence of specific costs of final product on composition of raw materials and unit operation parameters, is used as an objective function for optimization. The pheromone deposited on cell $l,u,p$ by the best ant $k$ is taken as (Rao, 1996)

$$\Delta \tau_{l,u,p}^{k} = \begin{cases} \frac{\xi \cdot SCI_{l,u,p}^{k}}{SCI_{worst}} & \text{if } k \in \text{global best path} \\ 0 & \text{otherwise} \end{cases}$$

where $SCI_{worst}$ is the worst value and $SCI_{best}$ is the best value of the objective function among the paths taken by the $N$ ants, and $\xi$ is a parameter used to control the scale of the global updating of the pheromone. The larger the value of $\xi$, the more pheromone is deposited on the global best path, and the better the exploitation ability.

The pheromone decay factor $\rho$, the global updating scale parameter $\xi$ and the population of the ant colony $N$ are the principal parameters of the ACO algorithm. Values of these parameters may slightly change depending on the problem size and complexity. The values $\rho = 0.1$ and $N = 2$ - $U$ - $P$, where $U$ and $P$ were used, as Ranesi et al. (2008) showed that for a non-linear combinatorial problem ACO algorithm finds the optimal solution with minimal computational effort with these values. The global updating scale parameter $\xi$ was varied for each particular problem depending on scale of difference between $SCI_{worst}$ and $SCI_{best}$. An empirically adjusted typical value was 1.5.

2.2. Key performance indicators (KPIs)

In order to evaluate the suitability of different process alternatives in the early stages of process development, selectivity and estimated relative costs or KPIs introduced by Winkelmüller and Schenbecke (2010) are applied. KPIs are suitable for initial stages of purification process design, where not enough data for rigorous optimization is available.
2.2.1. Purification rating

Purity, defined as the fraction of the target product in a mixture with contaminants, is an essential concept in description of performance and can be described by Eq. (4) (Winkelnkemper and Schenbecker, 2010), where $T$ is the concentration of a target metal in the system, $c_i$ is the concentration of contaminant $i$, and $M$ is the number of metals in the system:

$$x = \frac{T}{T + \sum_{i=1}^{M} c_i} = \frac{1}{1 + \sum_{i=1}^{M} \frac{c_i}{T}}$$ (4)

For assessment of the purification of one step as a percentage of the purification of the total process to be designed, the purity of the initial mixture $x_i$ and the target purity $x$ must be considered as given boundaries of the $x_i$ (0, 1) process. The purificational performance index ($PPI$) is defined as (Winkelnkemper and Schenbecker, 2010):

$$PPI_i = \frac{\log \left( \frac{1}{x} - \frac{1}{x_i} \right)}{\log \left( \frac{1}{x_i} - \frac{1}{x} \right)}$$ (5)

Due to high nonlinearity of arctangent function, $PPI$ is a balanced measure of purity over the whole purity range of a purification process. It evenly rates purification process steps, when high purity improvement requires moderate effort, and conversion and recovery steps, when small purity improvement requires great effort. Thus $PPI$ can be used to connect the purification performance with the projected effort. As the purity $x$ is defined by the concentrations of all contaminants $i$ ($c_i$) and the target substance ($T$) Eq. (4), $PPI$ can be rearranged and expressed with the concentrations (Winkelnkemper and Schenbecker, 2010):

$$PPI_i = \frac{\log \left( \frac{1}{x} - \frac{1}{x_i} \right)}{\log \left( \frac{1}{x_i} - \frac{1}{x} \right)} = \log \left( \frac{1}{x_i} - \frac{1}{x} \right) / \log \left( \frac{1}{x} - \frac{1}{x_i} \right)$$ (6)

Eq. (6) shows that $PPI$ reflects changes in contaminant-to-target ratios.

2.2.2. Cost-estimation

As soon as a complete process scheme is established, the influence of single purification steps on total process costs is readily quantifiable using a separation cost indicator (SCI). The separation cost indicator depends only on the normalized purification rating, yield ($Y$), and the specific costs (Winkelnkemper and Schenbecker, 2010). In the present case, the specific costs are leaching cost, $k_{lep}$, and the specific cost of purification steps, $k_{per}$:

$$SCI = Y^2 \cdot \left( \frac{k_{lep} \cdot \left( \frac{1 - x}{1 - x_{lep}} \right)}{1 - Y} \right)$$ (7)

Both $PPI$ and $Y$ are used as decimal fractions in Eq. (7) and the SCI function is determined for $Y \in [0, 1]$ and $PPI \in [0, 1]$. A major challenge is quantification of specific costs for the leaching and purification steps, since comparison of the process alternatives using SCI is only as reliable as the degree of precision of the estimation of these specific costs.

The optimization task of the purification process synthesis is minimization of total specific production costs for the process. Therefore, the sum of specific costs of the process steps is taken as the target function. The specific costs of the whole process are equal to the sum of step-specific costs of all purification steps within the process:

$$SCI_{tot} = \sum_{i=1}^{M} SCI_i$$ (8)

2.2.3. Determination of SCI for leaching and purification

For comparison purposes, the costs of alternative leaching processes, $K_c$, can be calculated using operational costs (Streikman and Tyagi, 1996):

$$K_c = \sum K_{eq} + \sum K_{chem} + \sum K_{extr} + \sum K_{el}$$ (9)

Only the chemical costs and the costs of electricity required for mixing are here taken into account in estimation of specific costs of leaching steps. Chemical costs are calculated based on the quantity of each chemical required for the process and its unit price. The quantity of acid needed is calculated from the process chemistry, the composition of the solids and its consumption in the process. The costs of mixing accounts electricity needed for slurry mixing. Both chemical and electricity costs are calculated per unit mass of target metal in the leachate:

$$K_c = K_{eq} + K_{chem}$$ (10)

For simplification and generalization, operating costs of solvent extraction are here assumed to result from the introduction of the organic phase to the process stream, stripping by aqueous solution and power consumed in mixing and pumping of the phases. The function for calculation of the operating costs resulting from losses of the target compound and solvent, for both solvent extraction and stripping stages, is (Robinson and Paynter, 1971):

$$K_{per} = A \cdot K_{extr} \cdot \frac{E}{T} + SL \cdot A \cdot K_{el} - \left( 1 - T \right) \cdot K_{el}$$ (11)

where $A$ is the feed rate of the aqueous phase, $m^3/s$; $K_i$ is the price of target element, €/kg; $E$ is the concentration of the target element in the raffinate, kg/m$^3$; SL is the solvent loss per unit volume, $m^3/m^3$; $E$ is the volume concentration of extractant, $m^3/m^3$; $K_{extr}$ is the cost of extraction, €/m$^3$ and $K_{el}$ is the cost of diluents, €/m$^3$.

Pumping and mixing costs can be estimated from their ratio with reagent costs, as the operating costs of solvent extraction are stated as consisting of 89.8% reagents and 10.1% electricity (US Bureau of Mines, 2009). Therefore, dividing the operating costs by the final concentration of the target metal $T$, the specific costs for the solvent extraction and stripping steps are:

$$K_{per} = A_{org} \cdot K_{org} \cdot T^2 + 1.11 \cdot SL \cdot A_{org} \cdot K_{el} - \left( 1 - T \right) \cdot K_{el}$$ (12)

where $A_{org}$ is the raffinate flow rate, $m^3/s$; $A_{org}$ is the flow rate of organic phase, $m^3/s$ and $A$ is the flow rate of the phase containing major amount of the target metal, $m^3/s$. 

The ACO-based algorithm was implemented in Matlab. In order to demonstrate the efficiency of the method, calculation times were compared with an enumeration algorithm also implemented in Matlab. The latter constructs all possible combinations of process alternatives and operating parameters and finds the one with the lowest specific production costs for the target component using the SCI function. Arbitrary purity and yield data were used as inputs, and the number of process steps and operating conditions were varied to vary the total number of process alternatives.

As seen in Fig. 3, the ACO-based algorithm is significantly faster when the number of process alternatives is large. Typically, the solution is obtained with a few seconds, even when enumeration takes tens of minutes. For very small problems, the difference is not significant and enumeration can be faster.

The efficiency of the ACO-based algorithm in process synthesis originates from the fact that it identifies the best combination of process steps without evaluation of all possible process combinations. Instead, it performs selection of the best process options in an iterative manner, discarding the worst unit operations or operating parameters at the very beginning. Hence, it is possible to evaluate many processes and select the best one in a reasonably short time. The difference in calculation times would be even more critical if the computational effort required to evaluate the PPI and SCI on each layer was considerable. This is the case if dynamic simulations are involved or iterative solutions of sets of algebraic equations are required.

3. Results and discussion

In order to evaluate the proposed method and algorithm from hydrometallurgical point of view, two case studies are presented.

3.1. Zinc recovery from AOD dust

Argon oxygen decarburization (AOD) dust is generated in stainless steel production processes, and contains valuable heavy metals. Its composition is presented in Table 1. Based on previous work by Viralainen et al. (2013), Zn was chosen as the target component for recovery.

The most common way to produce metallic Zn in hydrometallurgy is by electrolysis of ZnSO4 solutions (Habashi, 1997). The chemical composition of the electrolyte in the process has a significant influence on process performance and economics. The electrolyte is to contain 50–90 g/L of Zn and 120–200 g/L of H2SO4 (Tsakiridis et al., 2010), and typical impurity content of industrial electrolytes is: Fe 20–50 mg/L, Ni 0.1–0.5 mg/L, Mn < 10 g/L, Na < 10 g/L, Mg < 10 g/L, and other metals < 20 mg/L (Marchenko, 2009). Using these limitations, the target purity of Zn can be calculated, according to Eq. (1), as 99.6%.

The process was constructed utilizing H2SO4 as the lixiviation agent. H2SO4 in low and moderate concentrations shows high yield and selectivity for Zn over Fe (Starwalski, 2010), and in high H2SO4 concentrations yields are even higher but some of the undesired Fe is also leached. Thus two routes were examined separately; a route in which the dust was leached directly in batch reactor with 0.5 M H2SO4, and a route in which the dust was leached by controlling the pH with H2SO4 to be close to, but not below 3.0. Three extrants were selected for purification of the AOD leachate: 25% v/v Di-(2-ethylhexyl)phosphoric acid (D2EHPA) in kerosene, 10% v/v carboxylic acid Versatic 10 in n-heptane and 20% v/v hydroxynitrone LIX 984 in xylene (Extraction data only for Zn, Ni, Fe and Pb were found in the Rodriguez de San Miguel et al. (1997). Extraction of other metals from the leach solution by extrant LIX 984 was assumed to be negligible). Phase ratio was 1:1 for all the extractants. Stripping of the loaded organic phase was done by spent electrolyte. Its metal content is presented in Table 1 (Perreira et al., 2007).

Table 1

<table>
<thead>
<tr>
<th>Composition of the raw material (AOD) and aqueous solutions in the recovery process of Zn from AOD dust. The raw material contains 31.5% of other elements (mainly oxygen) not listed here. The concentration of H2SO4 in Zn stripping solution is 18.1 g/L.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Composition of the raw material (Viralainen et al., 2013), %</td>
</tr>
<tr>
<td>Composition of Zn stripping solution (Perreira et al., 2007), mg/L</td>
</tr>
<tr>
<td>Composition of the final purified solution in the process with direct leaching and D2EHPA extraction, mg/L</td>
</tr>
<tr>
<td>Composition of the final purified solution in the process with pH-controlled leaching and D2EHPA extraction, mg/L</td>
</tr>
</tbody>
</table>
Experimental data on leaching of AOD dust and solvent extraction were taken from literature (Virvilainen et al., 2013; Rodríguez de San Miguel et al., 1997; Preston, 1985) and are presented in Appendix A. The available leaching data represent two modes of leaching: direct leaching with H$_2$SO$_4$ (Fig. A1), and leaching with controlled pH of leachate above 3.0 to prevent dissolution of Fe (Fig. A2). The data are expressed as concentrations of metals and pH, depending on leaching time in a batch process. Therefore, the task is to find the optimal time to dissolve Zn in the most economical way. For solvent extraction and stripping steps, the data represent dependence of metals extraction on pH of aqueous phase, and the task is to identify the most economical pH using yield and purity improvement as target quantities. For calculation of stripping step, the same equilibrium data sets were used as for extraction step. The solvent extraction data for D2EHPA, hydroxylamine LIX 984 and Versatic 10 acid are respectively presented in Figs. A1, A4 and A5.

The developed ACO-based algorithm was used for simultaneous process design and optimization, i.e., for selection of the most economical sequence of unit operations and its operating parameters. A separation costs for the leaching (k$_l$) and purification (k$_{pur}$) steps are required for calculation of SCI. The values can be calculated according to Eq. (10) and Eq. (12).

Consumption of H$_2$SO$_4$ in the leaching can be estimated based on dissolution chemistry. The Zn dissolution reactions are the following (Havlik et al., 2005):

\[
\text{ZnO} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4^+ + \text{H}_2\text{O} \quad (13)
\]

\[
\text{ZnFe}_2\text{O}_4 + 4\text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4^+ + \text{Fe}_2\text{SO}_4^{3–} + 4\text{H}_2\text{O} \quad (14)
\]

\[
\text{ZnFe}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4^+ + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad (15)
\]

\[
\text{CaO} + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} \quad (16)
\]

Reaction (16) is assumed to go to completion. The leaching of Zn from its minerals is slower than formation of CaSO$_4$, so the consumption of H$_2$SO$_4$ depends on desired concentration of Zn in the leachate. In absence of other knowledge, it is assumed that zincate and franklinite are present in ratio of 1.2 in the AOD dust and thus six moles of H$_2$SO$_4$ are required for dissolution of three moles of Zn. Therefore, the concentration of H$_2$SO$_4$ (in units of g/L) needed is three times the desired final concentration of Zn in the leachate (M$_{\text{Zn}}$/M$_{\text{CaO}}$ = 1.5). A considerable amount of H$_2$SO$_4$ is consumed also in reaction (16) as the dust contains 7% CaO. Consequently, the total amount of H$_2$SO$_4$ required is:

\[
m_{\text{H}_2\text{SO}_4} = \frac{0.07 \times m_{\text{CaO}} \times M_{\text{Zn}}}{M_{\text{CaO}}} + 3 \times c_{\text{Zn}_{\text{leach}}} \times V_\text{L} \quad (17)
\]

The specific cost of chemicals is then calculated as:

\[
k_{\text{chem}} = \frac{K_{\text{chem}}}{c_{\text{Zn}_{\text{leach}}} \times V_\text{L}} (0.07 \times m_{\text{CaO}} \times M_{\text{Zn}} + 3 \times c_{\text{Zn}_{\text{leach}}} \times V_\text{L}) \quad (18)
\]

A value of 0.145 €/kg was used for the price of leaching acid, k$_{\text{chem}}$, the volume of leaching vessel, V$_\text{L}$ was 5 L, and the mass of the AOD dust was 0.8 kg. The concentration of Zn in the leachate, c$_{\text{Zn}_{\text{leach}}}$ is a time dependent variable and changes as leaching progresses.

We assume complete particle suspension in a severe agitation operation with energy dissipation rate (power input/unit mass) EDR = 1 W/kg slurry (Niemiow, 1997). The specific costs of mixing (electricity) in leaching are:

\[
k_{\text{mix}} = \frac{\text{EDR} \times \rho_{\text{slurry}} \times t_\text{lech}}{60 \times c_{\text{elec}}} \quad (19)
\]

where \(\rho_{\text{slurry}}\) is the slurry density, kg/m$^3$, \(t_\text{lech}\) is the batch time in minutes and \(c_{\text{elec}}\) is the concentration of target metal in the slurry, kg/m$^3$.

Eq. (12) is used for calculation of the specific costs of the purification steps for both solvent extraction and stripping. In the case of Zn solvent extraction from leachate of AOD the equation takes the form:

\[
k_{\text{SX}} = \frac{K_{\text{SX}} \times c_{\text{Zn}_{\text{leach}}} \times c_{\text{Zn}_{\text{extr}}} + 1.11 \times SL \times R_{\text{SX}} \times (E \times K_{\text{extr}} + (1-E) \times K_{\text{slurry}})}{R_{\text{SX}} \times c_{\text{Zn}_{\text{leach}}}^\text{org}} \quad (20)
\]

where R$_{\text{SX}}$ is the organic to aqueous phase ratio in solvent extraction, c$_{\text{Zn}_{\text{leach}}}^\text{org}$ is the concentration of Zn in raffinate, kg/m$^3$ and c$_{\text{Zn}_{\text{leach}}}^\text{org}$ is the concentration of Zn in organic phase, kg/m$^3$.

In the stripping stage, the costs for neutralization of stripping electrolyte with NaOH to the certain pH are taken into account, and thus Eq. (10) for the stripping of loaded organic phase takes the form:

\[
k_{\text{str}} = \frac{K_{\text{str}} \times c_{\text{Zn}_{\text{leach}}}^\text{org} + 1.11 \times \text{SL} \times (E \times K_{\text{extra}} + (1-E) \times K_{\text{slurry}})}{c_{\text{Zn}_{\text{leach}}}^\text{org}} \quad (21)
\]

where R$_{\text{str}}$ is the organic to aqueous phase ratio in stripping; c$_{\text{Zn}_{\text{leach}}}^\text{org}$ is the concentration of Zn in the aqueous phase after stripping, kg/m$^3$; m$_{\text{NaOH}}$ is the mass of NaOH needed for neutralization of the electrolyte, kg; and K$_{\text{slurry}}$ and K$_{\text{extr}}$ in the price of NaOH, €/kg.

The price of Zn is assumed to be 1.39 €/kg (LME spot price March, 2014), the prices of D2EHPA and kerosene are assumed to be 2.32 €/L and 0.74 €/L (U.S. Energy Information Administration, 2014), the prices of Versatic 10 and xylene are assumed to be 1.59 €/L and 5.03 €/L, and prices of LIX 984 and n-heptane are assumed to be 7.89 €/L and 4.12 €/L. The solvent loss per unit volume is set to be 100 ppm (Cytec, 2006). The price of NaOH is assumed to be 0.34 €/kg. The price of electricity is taken as 0.087 €/kWh (Statistics Finland, 2014). Eq. (18)-(21)
are implemented in the algorithm for calculation of the SCI function according to Eq. (7).

The hydrometallurgical processes for the recovery of Zn from AOD dust constructed by the ACO-based algorithm are presented in Table 2. The design space (see graph in Fig. 1) consisted of 3 process steps, 8 unit operations and 30 levels of operating parameters for each step (linear interpolation of data was used). The number of alternative processes and operating parameter combinations is approximately 1.4 · 10^7 but, with ACO-based method, the CPU time was only 13 s. The short computational time to solve the current process-synthesis problem can be explained by simplicity of the model, as only algebraic calculus is used, and by efficiency of the ACO in solving combinatorial optimization problems (Raeesi et al., 2008; Chunfeng and Xin, 2002).

The process constructed by the ACO-based algorithm for the direct leaching method consists of three steps. The time for leaching step with H_2SO_4 is 150 min (corresponding pH of leachate is 3.0). The second step is solvent extraction with D2EHPA at pH 4.27. Final purification stage is stripping with the electrolyte without neutralization. The initially specified final purity of Zn is 99.6% in the electrolyte is not achieved (96.3%) that is also indicated from the total recovery of Zn. The PPI value was 68.5%. The PPI should normally be equal to 100% when the specified target purity is reached. The composition of the final purified solution is presented in Table 2.

The concentrations of the contaminating elements in the final solution are higher than the required limits, though the calculated concentration of Zn in the purified solution is higher than initially specified (86.5 g/L). The impurities that are more electronegative than Zn, e.g. K, Na, Ca, Mg and Mn, do not directly interfere with the electrolytic process and can be tolerated up to 60 g/L. The impurities that are more electropositive than Zn, e.g. Fe, Ni, Cr and Pb lead to a reduction in the overvoltage, decrease in the current yield and deterioration of cathode purity (Habashi, 1997). For this reason, the maximum tolerable concentrations of these impurities are very low. Although the selected extractant for purification of the AOD leachate, D2EHPA, is characterized by its high capacity and selectivity for Zn over a wide range of common metals (Tsakiridis et al., 2010), the concentrations of Fe and Ni exceed the specified limits, and consequently the obtained electrolyte cannot be readily used in the electrolysis of Zn.

From the data for direct method (Fig. A1 in Appendix A) it can be seen that Fe would eventually precipitate away from the solution as the pH increases over 3, but there was still 1000 mg/L left after one day. Thus a similar process, but the first step is the previously introduced controlled leaching, was also optimized. Leaching time was optimized to be 270 min, and the solvent extraction and stripping steps are exactly the same as in the process with the direct leaching. This process with controlled leaching is characterized by higher specific costs (controlled leaching 5.06 €/kg, direct leaching 3.61 €/kg) resulting from lower leaching yield, but it provides the electrolyte with permissible concentrations of impurities although the overall purity target was not reached. Though this case study clearly reveals the power of the constructed ACO-based algorithm in the hydrometallurgical process design, the previous discussion shows that the algorithm needs to be modified to use values of individual impurity components as boundary conditions if needed.

The most important characteristics for process performance of the constructed purification sequence for direct leaching process are presented in Table 3. It is worth noting that the values of the enrichment factors for solvent extraction with D2EHPA indicate considerable purification of Zn during the one step solvent extraction stage of the process. In practice, solvent extraction is carried out in cascades of two or more stages. The algorithm able to handle also such multiple process steps in one unit process layer, and calculation of the PPI values could even involve dynamic simulations.

The calculated specific production cost (5.06 €/kg), is higher than the market price of Zn (1.94 €/kg according to LME). It should be borne in mind, however, that the separation cost indicator is as such not intended for calculation of production costs but rather as a fast tool for comparison of process alternatives during the process concept synthesis stage of process development (Winkelnkemper and Schrenkbecker, 2010).

### Table 3

<table>
<thead>
<tr>
<th>Element</th>
<th>Zn</th>
<th>Ni</th>
<th>Fe</th>
<th>Cu</th>
<th>Cr</th>
<th>K</th>
<th>Mn</th>
<th>Mg</th>
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<td>Enrichment factor for Zn over metal</td>
<td>1.38</td>
<td>0.01</td>
<td>0.01</td>
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<td>0.05</td>
<td>0.05</td>
<td>5.25</td>
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<td>Load extraction</td>
<td>1</td>
<td>85</td>
<td>1</td>
<td>1.3</td>
<td>19</td>
<td>20</td>
<td>1.2</td>
<td>5</td>
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<td>Back extraction</td>
<td>632</td>
<td>10</td>
<td>0.1</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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### Table 4

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<th>Ni</th>
<th>Fe</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>La</th>
<th>Co</th>
<th>Pr</th>
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<td>Raw material, %</td>
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<td>4.8</td>
<td>7.7</td>
<td>2.4</td>
<td>1.1</td>
<td>2.7</td>
<td>9.2</td>
<td>0.8</td>
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</tr>
<tr>
<td>Product material, %</td>
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<td>-5.01</td>
<td>-5.01</td>
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<td>-5.01</td>
<td>-5.01</td>
<td>-5.01</td>
<td>-5.01</td>
<td>-5.01</td>
</tr>
<tr>
<td>Al</td>
<td>3.4</td>
<td>3.4</td>
<td>3.4</td>
<td>3.4</td>
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<td>3.4</td>
<td>3.4</td>
<td>3.4</td>
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</tr>
<tr>
<td>Mn</td>
<td>10.2</td>
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<td>10.2</td>
<td>10.2</td>
<td>10.2</td>
<td>10.2</td>
<td>10.2</td>
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</tr>
</tbody>
</table>

3.2. Recovery of lanthanides from nickel metal hydride (NiMH) batteries

Present-day NiMH batteries contain multicomponent alloys such as La_2Ni_5Fe_5Al_6, La_2Ni_5Fe_5Co_5Al_6, MnNi_2Co_5Fe_5Al_6 and MnNi_2Co_5Fe_5Al_6 (where Mn refers to rare earth mischmetal) as the cathode and Ni(OH)_2 as the anode. In a recent comprehensive review of research on recycling of spent NiMH batteries (Binnemans et al., 2013), composition of the spent batteries is given as 36–42% Ni, 3–4% Co and 8–10% mischmetal containing La, Cr, Pr and Nd. The composition of raw material considered here is presented in Table 4. Lanthanides were chosen as target metals for their high value and relatively high content in the raw material. The target purity was set at 95% and the target phase as a solid precipitate.

The aim of this case study was to investigate the feasibility of the presented method to identify what should be the targets of each process.
The recovery of lanthanides from nickel metal hydride batteries is presented in Table 5. The spent nickel metal hydride batteries. Characteristics of the process steps are presented in Fig. 4. The organic phase is mostly loaded with lanthanides, Fe and Zn. The raffinate after solvent extraction contains mostly Ni, Co, Fe and Mn.

The constructed process resembles the conceptual flowsheet presented by Zhang et al. (1998). The difference in the values of the leaching acidity can be explained by the fact that the strategy of Zhang et al. (1998) was to maximize the leaching yield for all the metals. Here the ACO-based algorithm suggests optimizing leaching conditions towards selective leaching of lanthanides. Here single stage batch unit operations are exclusively used in the constructed processes, whereas multi-stage counter-current solvent extraction was explored experimentally by Zhang et al. (1998). The different operational modes thus explain the difference in operating parameters for solvent extraction and stripping. In addition, in this study, the economic factor was taken into account when comparing different schemes for interconnecting unit operations, because it is important to consider the economics of a designed process from the early stages of the process development.

### Table 5
Synthesized process for recovery of lanthanides from nickel metal hydride batteries using ACO-based algorithm. A stands for aqueous, O for organic and S for solid.

<table>
<thead>
<tr>
<th>Unit operation</th>
<th>pH</th>
<th>Target phase</th>
<th>c_{HCl}, mol/L</th>
<th>O/A</th>
<th>Yield, %</th>
<th>PPI, %</th>
<th>SCI, %</th>
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</thead>
<tbody>
<tr>
<td>Leaching</td>
<td>A</td>
<td>1.3</td>
<td>0.05</td>
<td>1</td>
<td>95.4</td>
<td>31.5</td>
<td>2.63</td>
</tr>
<tr>
<td>Stripping</td>
<td>O</td>
<td>2.0</td>
<td>-</td>
<td>1</td>
<td>99.89</td>
<td>18.7</td>
<td>2.81</td>
</tr>
<tr>
<td>Precipitation</td>
<td>O/S</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>98.2</td>
<td>1.33</td>
</tr>
<tr>
<td>Total process</td>
<td></td>
<td>1.1</td>
<td>0.005</td>
<td>1.1</td>
<td>90.0</td>
<td>3.3</td>
<td>57.7</td>
</tr>
</tbody>
</table>

![Fig. 4](image)

**Fig. 4.** Changes in metal purities in the constructed process for lanthanides recovery from spent nickel metal hydride batteries. Characteristics of the process steps are presented in Table 5.
Appendix A. Experimental data for case of Zn recovery from AOD dust

The experimental data used as an input in the ant colony optimization algorithm for the case of Zn recovery from AOD dust is presented in Figs. A1 to A5. The data were interpolated such that for each unit operation there were 30 levels of operating parameters. The pH isotherms for solvent extraction (Figs. A3–A5) are used for both extraction and stripping unit processes. The data produced by the research group of the current authors (the AOD case), have been presented in appendices both as figures and in tabular form (Figs. A1 to A3, Tables A1 to A3). The data obtained from literature have been presented as they appear in the references.

Fig. A1. Direct leaching of AOD dust with 0.5 M H₂SO₄, L/S ratio = 5 L (L/kg), T = 30 °C. (For more details an interested reader is referred to Virolainen et al., 2013.)

Fig. A2. Leaching of AOD dust with H₂SO₄, and controlled pH of the solution by keeping the pH close to, but above, 3.0 with 96% H₂SO₄, L/S ratio = 5 L (L/kg), T = 30 °C. (For more details an interested reader is referred to Virolainen et al., 2013.)

Fig. A3. Solvent extraction of metals with D2EHPA from solution obtained from 0.5 M H₂SO₄ leaching of AOD dust. T = 30 °C, O/A = 1:1. (For more details an interested reader is referred to Virolainen et al., 2013.)

Fig. A4. Percent of extraction of 20 ppm of metal ions as a function of the equilibrium pH of the aqueous phase with 0.3 M hydroxyoxime LIX 984 at T = 25 °C. (For more details an interested reader is referred to Rodríguez de San Miguel et al., 1997.)

Fig. A5. Solvent extraction of some metals with 0.50 M solution of Versatic 10 acid in xylene at 20 °C. (For more details an interested reader is referred to Preston, 1985.)
Table A2
Leaching of AOD dust with 0.5 M H2SO4 and controlled pH of the solution by keeping the pH close to, but above, 3.0 with 96% H2SO4. L/S ratio = 5:1 (L/kg), T = 30 °C. (For more details an interested reader is referred to Virolainen et al., 2013.)

<table>
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<tr>
<th>Time, min</th>
<th>pH</th>
<th>Zn</th>
<th>Ni</th>
<th>Fe</th>
<th>Ca</th>
<th>Cr</th>
<th>K</th>
<th>Mn</th>
<th>Mg</th>
<th>Pb</th>
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<tr>
<td>0</td>
<td>3.00</td>
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<tr>
<td>15</td>
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<td>30</td>
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<td>12812.89</td>
<td>46.38</td>
<td>2051.00</td>
<td>599.01</td>
<td>452.78</td>
<td>1348.70</td>
<td>846.24</td>
<td>1755.74</td>
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<td>45</td>
<td>2.62</td>
<td>13032.74</td>
<td>56.05</td>
<td>1900.02</td>
<td>593.00</td>
<td>455.16</td>
<td>1450.32</td>
<td>910.42</td>
<td>1846.68</td>
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<td>60</td>
<td>2.7</td>
<td>13428.79</td>
<td>57.89</td>
<td>1830.70</td>
<td>610.40</td>
<td>450.56</td>
<td>1462.17</td>
<td>936.30</td>
<td>1862.25</td>
<td>17.09</td>
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<td>90</td>
<td>2.76</td>
<td>13494.78</td>
<td>55.95</td>
<td>1651.62</td>
<td>595.05</td>
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<td>1353.75</td>
<td>887.80</td>
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<td>120</td>
<td>2.80</td>
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<td>61.22</td>
<td>1590.54</td>
<td>595.03</td>
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<td>1378.18</td>
<td>907.49</td>
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<td>150</td>
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<td>67.70</td>
<td>1577.77</td>
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<td>1385.37</td>
<td>984.09</td>
<td>1983.09</td>
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<td>300</td>
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<td>1385.87</td>
<td>982.18</td>
<td>1952.12</td>
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<td>573.10</td>
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<td>4.17</td>
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<td>1013.18</td>
<td>2004.87</td>
<td>16.59</td>
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Table A3
Solvent extraction of metals with D2EHPA from solution obtained from 0.5 M H2SO4 leaching of AOD dust. T = 30 °C, O/A = 1:1. (For more details an interested reader is referred to Virolainen et al., 2013.)

<table>
<thead>
<tr>
<th>pH</th>
<th>Metals remaining in the raffinate, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>Ni</td>
</tr>
<tr>
<td>0.01</td>
<td>99.90</td>
</tr>
<tr>
<td>0.50</td>
<td>78.94</td>
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<tr>
<td>3.52</td>
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<td>4.08</td>
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<td>5.51</td>
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<td>7.56</td>
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</table>
Appendix B. Experimental data for the case of lanthanides recovery from spent NiMH batteries

The experimental data was used as an input in the ant colony optimization algorithm for the case of lanthanides recovery from spent NiMH batteries is presented in Tables B1 to B2 and Figs. B1 to B2. The data were interpolated such that for each unit operation there were 8 levels of operating parameters.

### Table B1

| Effect of HCl concentration and O:A phase ratio on stripping of some metals from DEHPA at 25 °C. Solvent loading (g L−1): [RE] = 2.45, [Ni] = 0.34, [Zn] = 0.22, [Al] = 0.15, [Fe] = 1.15. (For more details an interested reader is referred to Zhang et al., 1998.)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
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<td>Ni</td>
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<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Co</td>
<td>0.01</td>
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</table>

### Table B2

| Effects of pH on precipitation of some metals as oxalates by addition of 0.3 mol L−1 (NH4)2C2O4 at 60 °C, under stirring (200 rpm). (For more details an interested reader is referred to Fernandes et al., 2013.)

<table>
<thead>
<tr>
<th>pH</th>
<th>Ni%</th>
<th>Co%</th>
<th>Al%</th>
<th>Fe%</th>
<th>Mn%</th>
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<td>0</td>
<td>0.27</td>
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### References

- D2EHPA in kerosene at O:A = 1 and at 25 °C. (For more details an interested reader is referred to Zhang et al., 1998.)

**Fig. B1.** Solvent extraction of metals from the leachate of spent NiMH batteries with 25% DEHPA in kerosene at O:A = 1 and at 25 °C. (For more details an interested reader is referred to Zhang et al., 1998.)
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Acta Universitatis Lappeenrantaensis 818

ISBN 978-952-335-281-0 (PDF)
ISSN-L 1456-4491
ISSN 1456-4491
Lappeenranta 2018