

Simulation based life cycle assessment method for evaluation of hydrometallurgical cyanide-free gold processes

Heini Elomaa

Simulation based life cycle assessment method for evaluation of hydrometallurgical cyanide-free gold processes

Heini Elomaa

The public defense is available via remote technology.

Join Zoom Meeting: <https://aalto.zoom.us/j/650442383>

Meeting ID: 650 442 383

Zoom Quick Guide: <https://www.aalto.fi/en/services/zoom-quick-guide>

A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Chemical Engineering, at a public examination held at the lecture hall Auditorium C100 of the school on 3 April 2020 at 12.

**Aalto University
School of Chemical Engineering
Department of Chemical and Metallurgical Engineering
Hydrometallurgy and Corrosion**

Supervising professor

Assistant Professor Mari Lundström, Aalto University, Finland

Thesis advisors

Docent Jari Aromaa, Aalto University, Finland

D.Sc. Lotta Rintala, VTT, Finland

Preliminary examiners

Professor Jacques Eksteen, Future Battery Industries Cooperative Research Centre, Australia

Professor Hylke J. Glass, Camborne School of Mines, University of Exeter, United Kingdom

Opponent

Professor Jan Cilliers, Imperial College London, United Kingdom

Aalto University publication series

DOCTORAL DISSERTATIONS 42/2020

© 2020 Heini Elomaa

ISBN 978-952-60-3805-6 (printed)

ISBN 978-952-60-3806-3 (pdf)

ISSN 1799-4934 (printed)

ISSN 1799-4942 (pdf)

<http://urn.fi/URN:ISBN:978-952-60-3806-3>

Unigrafia Oy

Helsinki 2020

Finland



Author

Heini Elomaa

Name of the doctoral dissertation

Simulation based life cycle assessment method for evaluation of hydrometallurgical cyanide-free gold processes

Publisher School of Chemical Engineering

Unit Department of Chemical and Metallurgical Engineering

Series Aalto University publication series DOCTORAL DISSERTATIONS 42/2020

Field of research Processing of Materials

Manuscript submitted 5 December 2019

Date of the defence 3 April 2020

Permission for public defence granted (date) 12 February 2020

Language English

Monograph

Article dissertation

Essay dissertation

Abstract

In this doctoral dissertation simulation based life cycle assessment was adapted in evaluation of process performance and environmental impacts of cyanide-free gold leaching. This methodology enables the evaluation of industrial scale process operation combined with early stage estimation of environmental impacts of the processes. The simulations are based on hydrometallurgical expertise, and can be adjusted according to experimental data. Adapting such a methodology in to evaluation of hydrometallurgical gold processes, is relevant for two reasons. Firstly, the challenges in up-scaling the metallurgical processes from laboratory to industrial scale require that the new technologies are assessed already in development stage, for both process performance and environmental impacts. Secondly, this is extremely timely in gold production, where cyanidation is the dominant processing method and faces several challenges as the gold ore grades diminish and mineralogy of the ores become increasingly complicated, in addition to health and safety risks related to cyanide. Gold production should utilize the best available technology, due to which the research has started to focus on more environmentally friendly alternatives in order to replace cyanidation.

In the current study the simulations have been constructed using HSC-Sim, linked to GaBi software. HSC-Sim enables flowsheet simulation of hydrometallurgical processes to create accurate life cycle inventory data that can be used in life cycle assessment. This study presents simulation of six gold extraction processes, including pressure oxidation, cyanidation, chlorination, halogen leaching and cupric chloride leaching. The main challenges for cyanide-free chloride based processes are water balance, in situ method for recovery of gold, and improved gold recovery. However, the faster leaching kinetics, and the simultaneous oxidation of sulfide mineral and gold extraction could offer competitive edge for chloride processes. The estimated environmental impact categories in this work include global warming, acidification and eutrophication potential as well as water resource depletion. Cyanidation shows lowest indicator values in all categories, however by optimization of the chloride processes and improved recovery the indicator values can be brought to same level.

The simulation based life cycle assessment was found to be a suitable methodology for evaluation of critical points in development stage processes and estimation of their early stage environmental indicator values. This work does not only contribute to research of cyanide-free processing of gold, but also critically evaluates the existing data and provides more accurate inventory data for other life cycle assessment researchers. Finally, the methodology utilized can provide the supportive information necessary to introduce more sustainable processing methods, not only for gold industry but to any metallurgical processing.

Keywords cyanide-free gold leaching, HSC-Sim, GaBi, process simulation

ISBN (printed) 978-952-60-3805-6

ISBN (pdf) 978-952-60-3806-3

ISSN (printed) 1799-4934

ISSN (pdf) 1799-4942

Location of publisher Helsinki

Location of printing Helsinki **Year** 2020

Pages 177

urn <http://urn.fi/URN:ISBN:978-952-60-3806-3>

Tekijä

Heini Elomaa

Väitöskirjan nimi

Hydrometallurgisten syanidivapaiden kultaprosessien arvioiminen simulaatioon perustuvalla elinkaarianalyysillä

Julkaisija Kemian tekniikan korkeakoulu**Yksikkö** Kemian tekniikan ja metallurgian laitos**Sarja** Aalto University publication series DOCTORAL DISSERTATIONS 42/2020**Tutkimusala** Materiaalien prosessointi**Käsikirjoituksen pvm** 05.12.2019**Väitöspäivä** 03.04.2020**Väittelyluvan myöntämispäivä** 12.02.2020**Kieli** Englanti **Monografia** **Artikkeliväitöskirja** **Esseeväitöskirja****Tiivistelmä**

Tässä väitöskirjatutkimuksessa käytettiin simulaatioon perustuvaa elinkaarianalyysia syanidivapaan kullan prosessoinnin suorituskyvyn ja ympäristövaikutusten arviointiin. Tämä menetelmä mahdollistaa kehitysvaiheessa olevien teollisen mittakaavan prosessien arvioinnin yhdistettynä ympäristövaikutusten arviointiin. Simulaatiot perustuvat hydrometallurgiseen asiantuntemukseen, ja niitä voidaan säätää kokeellisten tietojen perusteella. Tällaisen metodologian soveltaminen hydrometallurgisten kultaprosessien arviointiin on olennaista kahdesta syystä. Ensinnäkin metallurgisten prosessien teollisen mittakaavan käyttöönotto voi olla haasteellista jonka vuoksi kehityksen alla olevia prosessien toimintaa ja ympäristövaikutuksia on arvioitava jo aikaisessa vaiheessa Toiseksi, syanidivapaat prosessivaihtoehdot ovat ajankohtaista kullantuotannossa, jossa syanidointi on hallitseva prosessointimenetelmä. Syanidaatioon liittyy useita haasteita, kun tarve prosessoida köyhiä ja vaikeasti liuotettavia malmeja kasvaa, ja syanidin käyttöön liittyy terveys- ja turvallisuusriskejä. Kullantuotannossa olisi käytettävä parasta käytettävissä olevaa tekniikkaa, minkä seurauksena tutkimus on keskittynyt ympäristöystävällisempiin prosessivaihtoehtoihin syanidin korvaamiseksi.

Tässä väitöskirjatutkimuksessa simulaatiot on rakennettu käyttämällä HSC-Simiä, joka on yhteensopiva GaBi -ohjelmiston kanssa. HSC-Sim mahdollistaa hydrometallurgisten prosessien vuokaavioiden simuloimisen, jotta saadaan tarkka inventaarioanalyysi käytettäväksi elinkaarianalyysissä. Tässä väitöskirjatutkimuksessa simuloitiin kuusi prosessia, mukaan lukien refraktorisen kultaalmin painehapetus, syanidaatio (CIP/CIL), klorinaatio, halogeeniliuotus ja kuparikloridiliuotus. Syanidivapaiden kloridiprosessien päähaasteet ovat vesitasapaino, in situ-menetelmä kullan talteenottamiseksi ja talteenoton parantaminen. Kloridiprosessin nopeampi liuotuskinetiikka ja sulfdimineraalien hapetus ja kullan liuottaminen samanaikaisesti voivat tarjota kilpailuedun verrattuna syanidaatioon. Arvioituihin ympäristövaikutusluokkiin kuuluvat ilmaston lämpenemis-, happamoitumis- ja rehevöitymispotentiaali sekä vesivarojen ehtyminen. Syanidaation indikaattoriarvot ovat kaikissa kategorioissa alhaisimmat, mutta optimoimalla kloridiprosesseja ja parantamalla talteenottoa indikaattoriarvot voidaan saattaa samaan tasoon. Simulaatioon perustuva elinkaarianalyysi on todettu sopivaksi menetelmäksi kehitysvaiheen prosessien kriittisten pisteiden arvioimiseksi ja vertailukelpoisten ympäristöindikaattorien arvojen tuottamiseksi. Tässä työssä on kullan syanidivapaan prosessoinnin tutkimuksen ohella tuotettu tarkempaa inventaarioanalyysidataa, jota muut elinkaarianalyysi-tutkijat voivat hyödyntää. Lisäksi käytetty metodologia tuottaa tietoa, joka mahdollistaa kestävämpien prosessien kehittämisen niin kullantuotantoon kuin mihin tahansa metallurgiseen prosessointiin.

Avainsanat syanidivapaa kullan liuotus, HSC-Sim, GaBi, prosessisimulaatio**ISBN (painettu)** 978-952-60-3805-6**ISBN (pdf)** 978-952-60-3806-3**ISSN (painettu)** 1799-4934**ISSN (pdf)** 1799-4942**Julkaisupaikka** Helsinki**Painopaikka** Helsinki**Vuosi** 2020**Sivumäärä** 177**urn** <http://urn.fi/URN:ISBN:978-952-60-3806-3>

Acknowledgements

The research presented in this doctoral thesis was carried out at Aalto University School of Chemical Engineering within the research group of Hydrometallurgy and Corrosion during the years 2016- 2019. A six month research visit to University of Witwatersrand, Johannesburg, South Africa took place from January to June in the year 2018. Main funding was provided by Emil Aaltonen foundation project grant through the Sustainable Gold -project. Finnish Foundation for Technology Promotion is greatly acknowledged for funding the research in the year 2019. Metallinjalostajat ry, Magnus Ehrnrooth Foundation, Walter Ahlström Foundation and Goldtail (Finnish Academy, grant nr. 31969) are greatly acknowledged for their financial support.

I would like to express my gratitude to Professor Mari Lundström for her support during my doctoral studies. Her endless enthusiasm for hydrometallurgy and research is an inspiration to us all. I am deeply grateful to my advisor Docent Jari Aroma. Thank you for all the discussions and input to my work. I will never stop admiring your ability to see the essence of research. I would also like to thank Professor Emeritus Olof Forsén for support and advice, especially during the writing process of this thesis. I wish to express my sincere thanks to Professor Herman Potgieter for giving me the opportunity to undertake research exchange in the University of the Witwatersrand. I hope it was the beginning of a long and fruitful collaboration between Aalto and Wits.

There are no words to describe how grateful I am for our KULTA-team. Lotta and Maria, you have made this a golden journey. Thank you for all the support and let us keep each other shining in the future!

I want to express thanks to my colleagues in the laboratory of Hydrometallurgy and Corrosion. Especially my thanks go to my colleagues and friends Joseph Hamuyuni, Pyry Hannula, Arif Aji, Riina Ahtiainen, Petteri Halli, Antti Porvali, Pia Sinisalo and Sipi Seisko.

I wish to thank my parents for all support and tools in life to complete this work. I want to thank my mother Paula for introducing us to the academic life early on and providing advice to me not only as her daughter but a fellow researcher. I want to thank my brothers, Olli and Tapio, in the team HOT for much needed sarcastic humor. Nyt väitöskirja lepää!

Finally, I would like to thank my friends for supporting me during making of this thesis. My sincere thanks to Olli Halminen for sharing the struggles of doctoral studies. Thank you, Posse, for almost 20 years together in which we have

grown and accomplished so many wonderful milestones. I hope we continue to have many celebrations for years to come! I also wish to express my sincere thanks to three amazing women: Elina, Sanna and Saira.

Most of all, Erno, I wish to thank you for all the patience and understanding during these years. Thank you for always listening, encouraging me and letting me follow my dreams to wherever in the world.

Pori, February, 2020

Heini Elomaa

Contents

Acknowledgements	I
List of abbreviations and symbols	V
List of Publications	VI
Author's Contribution	VII
1. Introduction	1
1.1 Background	1
1.2 Objective of this thesis	3
1.3 New scientific contribution.....	5
1.4 Structure of this thesis	6
2. Theoretical foundation	7
2.1 Life cycle assessment (LCA)	7
2.1.1 Environmental impact categories.....	8
2.2 Adaptation of simulation based life cycle assessment.....	9
2.3 Classification of gold ores	10
2.3.1 Free-milling gold	11
2.3.2 Refractory gold materials.....	11
2.4 Effect of mineralogy on process performance	12
2.5 Extractive gold processes.....	13
2.5.1 Pressure oxidation.....	13
2.5.2 Cyanidation	14
2.5.3 Chlorination and hypochloride leaching	15
2.5.4 Halide/halogen leaching process.....	16
2.5.5 Cupric chloride leaching process	17
2.6 Process selection	18
3. Simulation methodology	23
3.1 Ore composition used in simulation	23
3.2 Electrochemical methods to produce kinetic data for simulation	24
3.3 Process simulation	25

3.3.1	Example of simulation method.....	25
4.	Results	31
4.1	Process performance comparison	31
4.1.1	Preliminary studies	31
4.1.2	Leaching.....	32
4.1.3	Gold recovery.....	33
4.1.4	Water balance.....	36
4.1.5	Mass balances.....	37
4.2	Environmental indicators of processes	40
4.2.1	Global warming potential.....	41
4.2.2	Acidification potential.....	44
4.2.3	Eutrophication potential.....	45
4.2.4	Water depletion	46
4.2.5	Environmental implication of produced waste streams	47
5.	Discussion	51
5.1	Limitations of the research	52
5.2	Recommendations for further work.....	53
6.	Conclusions	55
	References	57
	Appendices	69

List of abbreviations and symbols

Abbreviations

AP	Acidification Potential
BAT	Best Available Technology
EP	Eutrophication Potential
CCD	Counter-Current-Decantation
CIL	Carbon-in-leach
CIP	Carbon-in-pulp
GWP	Global Warming Potential
HSC-Sim	HSC Sim, HSC Chemistry software
HTP	Human Toxicity Potential
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
ORP	Oxidation-Reduction Potential
PCB	Printed Circuit Board
PLS	Pregnant-Leach-Solution
POX	Pressure Oxidation
REE	Rare Earth Elements
SMBS	Sodium metabisulfite
SX	Solvent Extraction
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
WEEE	Waste Electric and Electronic Equipment

Symbols

L	liter	
M	molarity	(mol/L)
m-%	mass percentage	
t	tonne	
<i>T</i>	temperature	(°C)
<i>V</i>	voltage	(mV)
wt-%	weight percentage	

List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their Roman numerals.

I Elomaa, Heini; Rintala, Lotta; Lundström, Mari. 2017. Process simulation and environmental footprint of gold chlorination and cyanidation processes. In: Proceedings of European Metallurgical Conference 2017, Volume 3, pages 1293-1310. ISBN 978-3-940276-74-2.

II Elomaa, Heini; Sinisalo, Pia; Rintala, Lotta; Aromaa, Jari; Lundström, Mari. 2019. Process simulation and gate-to-gate life cycle assessment of hydrometallurgical refractory gold concentrate processing. International Journal of Life Cycle Assessment. Accepted. DOI: 10.1007/s11367-019-01723-6

III Elomaa, Heini; Rintala, Lotta; Aromaa, Jari; Lundström, Mari. 2018. Open circuit potential and leaching rate of pyrite in cupric chloride solution. Canadian Metallurgical Quarterly, volume 57, issue 4, pages 416-421 DOI: 10.1080/00084433.2018.1477652

IV Elomaa, Heini; Rintala, Lotta; Aromaa, Jari; Lundström, Mari. 2020. Process simulation based life cycle assessment of cyanide-free refractory gold concentrate processing - Case study: cupric chloride leaching. Submitted to Minerals Engineering, 1/2020.

Author's Contribution

Publication I: “Process simulation and environmental footprint of gold chlorination and cyanidation processes”

H.E. carried out the literature survey of gold chlorination and cyanidation processes, simulated the processes using HSC-Sim, and constructed the LCA models of the simulations with GaBi LCA software. H.E. wrote the manuscript under supervision of L.R. and M.L..

Publication II: “Process simulation and gate-to-gate life cycle assessment of hydrometallurgical refractory gold concentrate processing”

H.E. carried out the literature survey of cyanidation and halide/halogen leaching and simulated the cyanidation and halogen leaching processes. P.S. simulated the pressure oxidation process. H.E. conducted the LCA assessment of the processes using Gabi software. H.E. wrote the manuscript under supervision of L.R., J.A. and M.L.. P.S. critically reviewed the results and conclusions.

Publication III: “Open circuit potential and leaching rate of pyrite in cupric chloride solution”

H.E. was responsible for the experimental design together with the co-authors, conducted the experiments, analyzed the data and built the regression model. H.E. wrote the manuscript under supervision of L.R., J.A. and M.L..

Publication IV: “Process simulation based life cycle assessment of cyanide-free refractory gold concentrate processing - Case study: cupric chloride leaching”

H.E. carried out the literature survey of gold cupric chloride leaching and simulated the process using HSC-Sim. H.E. conducted the LCA estimations of the process using Gabi software. H.E. wrote the manuscript under supervision of L.R., J.A. and M.L..

1. Introduction

Despite of the toxicity of cyanide, and the high risk of environmental catastrophes, cyanidation maintains its position as the primary gold leaching method. This leads to the question: What is still required in the development of cyanide-free processing of gold for it to compete with cyanidation?

Firstly, the process has to at least offer stable metallurgical performance to provide feasible operation. Secondly, the cyanide-free process has to also provide an economically competitive option, with reasonable operation costs through resource consumptions. Finally, the produced waste streams such as gaseous emission, waste waters and solid wastes, have to be environmentally benign and easily disposable or re-usable (Laitos, 2012a). Therefore, this thesis aims to investigate both the performance of selected cyanide-free processes, and their environmental impacts.

1.1 Background

The industrial revolution was an era of fast progress in manufacturing processes including those related to metallurgy. The turn of the 18th century witnessed major developments in metallurgical processes, especially related to iron production. The industrial revolution also expanded gold production from simple panning for gold to extraction of gold from minerals. Over the following centuries, several unit processes including gravity concentration, amalgamation, cyanide leaching, chlorination, zinc precipitation and carbon/charcoal absorption, have been adapted to gold processing. These unit processes still form the basis of most flowsheets designed for gold recovery (Marsden & House, 2006).

Chlorine was discovered in 1774, and was soon available for commercial usage. However, it took almost a hundred years before the first chlorine based process for treatment of gold ores was proposed by Plattner in 1848. In this process, chlorine gas was passed through the crushed ore producing gold chloride complexes, which are water soluble and can be precipitated later on by ferrous sulfate (FeSO_4), hydrogen sulfide (H_2S) or charcoal (Rose, 1898). First commercial process of chlorination was used in 1858 (Schnabel, 1921; Marsden & House, 2006). From United States, the chlorination process spread to Australia and South Africa (Schnabel, 1921). Meanwhile, in 1783 the solubility of gold in cyanide was recognized. Eventually, in 1846 Elsner reported the dissolution of gold in aerated cyanide solutions and in 1889 MacArthur *et al.* patented the cyanidation process. During mid-1900s, the cyanidation process was investigated in Witwatersrand ores, which had lower grades than those previously handled, and gold associated as fine grains in hard rock. The

timing of cyanidation and exploitation of Witwatersrand ores, in addition to the releasing of gold price from the rigid constraints of 35\$/oz gold (Fleming, 1992) was beneficial in commercializing cyanidation and improving gold production in South Africa (Marsden & House, 2006). Consequently, the era of major technological development beginning in the 1970s focused especially on cyanidation, which overpowered other processing methods, and remains to dominate the gold production until the present day.

Gold has been of interest to humans throughout the history, as seen from the various processes developed for extraction of gold. Gold is inert at ambient temperature and pressure, which is why there are very few naturally occurring compounds of gold (Marsden & House, 2006). Hence, gold presents itself in nature either as native gold, or compounded with silver as electrum, or in gold tellurides and associated with sulfides. The type of “invisible” gold, associated with sulfide minerals is called refractory gold. Refractory means that the gold is “locked” in the sulfide minerals matrix and needs to be liberated prior to gold leaching. In addition, the term “refractory” can also be used to describe gold ores and concentrates that are carbonaceous, rich in tellurides, having high copper content or other properties that make gold unavailable for cyanidation without pre-processing (Marsden & House, 2006). As the free-milling gold deposits on earth are almost fully consumed, the treatment of lower grade, more complex and refractory type ores has become essential for gold production. Further, the interest in recycling secondary raw materials with high gold content, such as electrical and electronic equipment, printed circuit boards (PCBs) and low grade secondary materials such as tailings, has increased (Syed, 2012). The need for treating increasingly complex ores and raw materials affects the economics of gold extraction processes, and further encourages the development of alternative cyanide free methods to challenge state-of-the-art cyanidation.

In addition to the change in mineralogy and complexity of future sources of gold, the development of cyanide-free alternative is also driven by environmental concerns. Cyanide is a toxic compound, and provides many risks in plant operation for environment and human health. There have been several environmental disasters in the past, such as the cyanide spill in Baia Mare in 2000 (Cunningham, 2005; UNEP, 2000) and a number of spillages in Argentina and earlier in Colorado 1992, Montana 1997, Nevada in 1989 and 1990, Kyrgystan 1998 and Guyana 1995 (Hilson & Monhemius, 2006; Moran, 1998). Additionally, almost 30 spillages have been reported, and have led to the banning of cyanidation in several countries such as Czech Republic, Germany, Hungary, Turkey and certain provinces of Argentina. Mudder & Botz (2004) report the major mining-related environmental incidents from 1975 to 2003. The states of Montana, Wisconsin, Colorado and South Dakota have banned usage of cyanide in mining industry (Laitos, 2012a) and approval of new cyanidation plants is very unlikely in these parts of world (Aylmore, 2016a). Such events have led to strict legislation related to the handling of cyanide.

There is critical debate regarding the real environmental impacts of cyanidation (Laitos, 2012a; Laitos 2012b; Mudder & Botz, 2004). The primary causes of major cyanide accidents are pipeline ruptures and accidents related to shipments and transportation of cyanide. (Mudder & Botz, 2004). It should be pointed out, that in order to critically review the challenges in cyanidation as well as alternative processes, many

different aspects should be considered. Gold production should utilize the best available technology (BAT), defined as the most efficient way to reach generally high level of environmental protection using industrial level technology, which can be adapted in an economically and technically profitable way. Alternative methods can possibly reach this definition in future, and consequently compete with cyanidation. Especially, considering the changing nature of future gold raw materials, the definition of BAT may not be fulfilled by cyanidation processes. Cyanidation has overpowered the gold industry mainly due its technical simplicity and economical reasons. In other words, cyanide is a cheap chemical and the cyanidation process performance is easy to control. As the industry and environmental policies require more environmentally benign processes, it becomes essential to evaluate the environmental impacts of development stage processes.

Digitalization and computers have changed the view of industrial process design by integration of process simulation. Simulations can be used to optimize or predict the performance of individual units, systems or even complete flowsheets. Simulation is nowadays a widely used method in designing new processes.

Simulation can be combined with life cycle assessment (LCA), which is a standardized method to evaluate the environmental impacts of a process, product or activity (ISO 14040, 2006). LCA has previously been adapted as an individual methodology to evaluate metallurgical processes. Process simulations combined with LCA can give exact information on the environmental impacts of metallurgical processes. This methodology can be adapted already in the early stages of process development, as a complementary and supportive tool, to predict the environmental impacts of a development stage process. Simulation based LCA has recently been adapted to different metallurgical processes (Pell *et al.*, 2019; Ghodrati *et al.*, 2017; Reuter *et al.*, 2015; Kotiranta *et al.*, 2015), however the method has not yet been adapted to the evaluation of gold leaching processes.

1.2 Objective of this thesis

Cyanidation is currently the dominating gold leaching process worldwide. However, cyanidation struggles with challenges related to treating low-grade refractory type materials that form the bulk of raw materials for gold nowadays. Furthermore, increasingly strict environmental legislations have resulted in banning the use of cyanide in operations. This thesis investigates the alternative development stage cyanide-free processes by experimental methods, process simulations and LCA. Alternative leaching methods include for example thiosulfate, thiourea, glycine and halide lixivants, of which the halide systems are the focus of this thesis. This thesis focuses on the following questions: What are the problems and challenges of refractory gold concentrate cyanide-free processing? Can the halide processes be environmentally benign compared to cyanidation?

Thus the specific objectives of this thesis are:

1. to simulate cyanidation and cyanide-free gold leaching processes while gaining more knowledge about challenges related to process performance
2. to perform life cycle assessment of cyanidation and cyanide-free gold leaching processes in order to compare their environmental impacts

A literature survey of the cyanide-free processes was conducted in order to gather data for the simulations of selected processes. Experimental work was carried out to investigate the phenomenon of selected cyanide-free process. Process simulation provides information on the material flows and balances, as well as data for the sizing of the process equipment, enabling also the estimation of the corresponding electricity consumption. LCA of the hydrometallurgical process was built based on the process simulation, in order to evaluate the process performance and environmental impacts. The challenges and advantages in cyanide-free gold leaching processes are discussed based on the simulation models. Existing technical solutions already have an impact on environmental performance of the processes and future development, and are evaluated accordingly. The environmental impacts of alternative cyanide-free gold processes are investigated and compared to the environmental impacts of the predominant cyanidation process. The structure of research conducted in this thesis is presented in Figure 1.

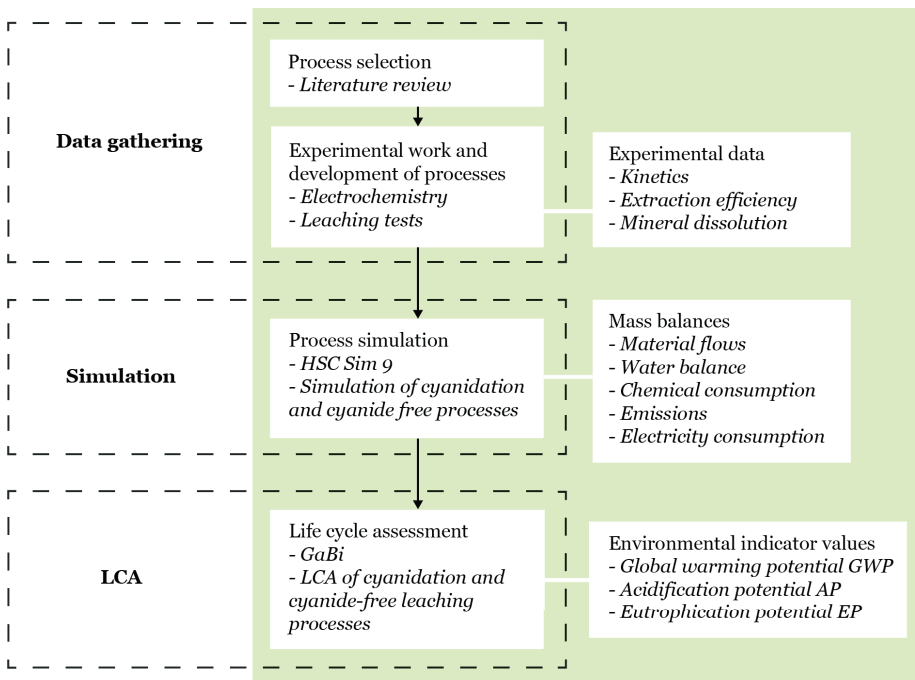


Figure 1. The structure of research conducted in this study and the achieved parameters from each sub-category.

The results obtained in this research are included in the original publications (I- IV). Figure 2 presents the logic in the structure and connection of articles and the compendium section.

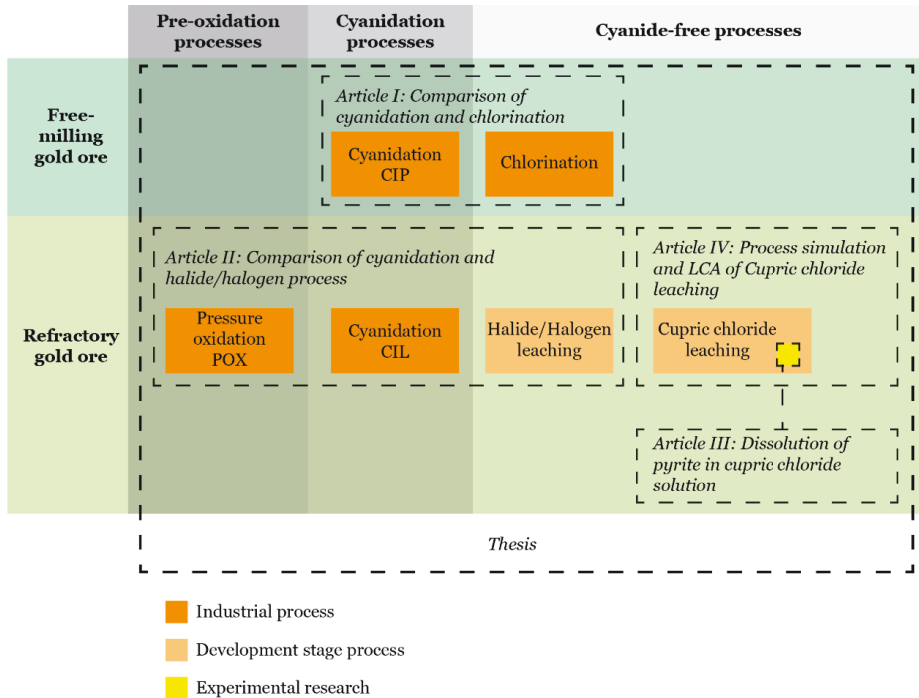


Figure 2. The logical structure and connection of publications (I-IV) and the compendium section.

1.3 New scientific contribution

This study contributes to new scientific knowledge regarding the cyanide-free leaching of gold. Chosen development stage cyanide-free processes are compared to cyanidation process by using simulation based LCA. Issues related to process performance are highlighted based on the results obtained with simulations. Process simulation is used as a tool to build up life cycle inventories (LCI) of the processes, used in subsequent LCA. This is in contrast to the past evaluations of development stage processes that were conducted in the interest of economic performance. The environmental indicators of cyanidation and selected cyanide-free processes are estimated. Simulation based LCA has been adapted for the first time to evaluate development stage cyanide-free gold leaching processes.

1.4 Structure of this thesis

This thesis consists of one peer-reviewed conference publication [I], one scientific peer-reviewed journal publications [III], two submitted manuscripts to peer-reviewed journals [II, IV] and the compendium section. The publications are attached as appendices attached to the thesis.

Chapter 2 in the compendium section introduces the theoretical foundation of the research by presenting the LCA methodology and theory behind the simulation as a tool for LCI creation. Furthermore, the basic gold raw materials are reviewed along with their processing in different leaching methods. Finally, the aspects of mineralogy, and their effect on the chosen processing methods are highlighted. A review of cyanide-free gold processes is also presented, and the selection of simulated processes is justified. Chapter 3 presents an example of simulation based LCA, adapted for research in I, II and IV. Process comparison, e.g. effect of leaching kinetics [III], recovery methods, and results of estimated environmental indicators are presented in Chapter 4. Discussions and recommendations for future research are given in Chapter 5. Finally, the conclusions are presented in Chapter 6.

2. Theoretical foundation

Environmental considerations have become an important and mandatory step for process selection, development and exploitation of mineral resources. Process selection needs to take into account the environmental impacts that unit processes have for example on water and air quality, land degradation, flora and fauna, sustainability and social development. The specific aspects in metallurgical processing are degree of alteration of minerals and metals by the process, process water balance, discharge need and methods for waste disposal and treatment (Marsden & House, 2006). From an environmental point of view, the aspects include type and amount of solid, liquid and gas wastes produced as well as short- and long-term stability of waste products. As stated previously, gold production should utilize the Best Available Technology (BAT). In order to evaluate the probability of new cyanide-free processes in challenging the widely used cyanidation alternative, environmental indicators of the processes should be evaluated and compared. The common method to produce indicator values of selected impact categories is life cycle assessment (LCA).

2.1 Life cycle assessment (LCA)

LCA is a standardized method, used structurally and comprehensively to evaluate the environmental impacts of products, processes and activities (ISO 14040, 2006; ISO 14044, 2006). With LCA, the environmental impacts can be objectively assessed throughout the entire life cycle of the product, process or activity. Additionally, LCA helps in quantifying and characterizing the material flows to specific environmental impacts. Furthermore, it identifies problems in the life span of the studied systems. Thus, comparative solutions and improvements can be suggested. LCA is also a powerful tool for decision making in different fields of society, industry, and in government or non-government organizations. The use of LCA in marketing increases all the time, as consumers and actors in industry require knowledge of sustainable production.

LCA can be divided into 4 stages (ISO 14040, 2006):

- Defining goal and scope
- Defining Life Cycle Inventory (LCI)
- Calculating impact assessment
- Interpretation of the results

In the first stage, the goal, system boundary and level of detail are defined, which affects the depth of LCA. In the second stage, the LCI of the process is defined, indicating the inputs and outputs data of the studied system. In the third stage, the LCI is used to estimate the specific environmental indicators of selected impact categories, and in the final stage the results are discussed, recommendations are derived and data for decision-making is provided. The interconnection of LCA stages and interpretation of results is shown in Figure 3.

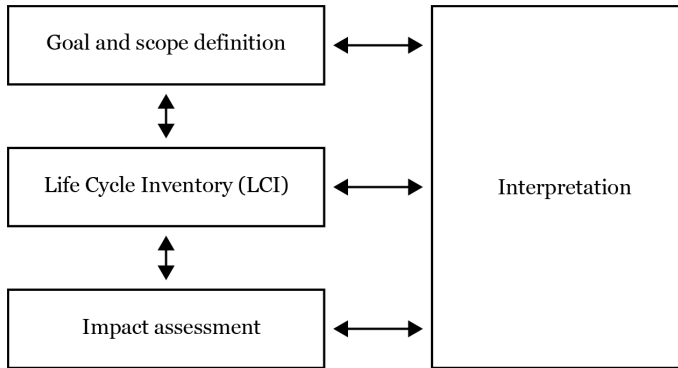


Figure 3 . The interconnections of LCA stages.

The inventory data and the assumptions made in the study will affect and set the basis of any LCA study and therefore, the results will depend on these factors (Norgate & Haque, 2012). Reuter (1998) stated that the inventory analyses used for metallurgical processes are often simplified to black-boxes, and do not express the complicated connections and systems of processing, which are unique for each metal processing plant. He proposes the use of simulations as the basis for creating reliable inventory data.

2.1.1 Environmental impact categories

The impact to environment is classified into different impact categories. The common impact categories are Global Warming Potential, (GWP), Human Toxicity (HT), Ecotoxicity, Acidification potential (AP) and Eutrophication Potential (EP). Many categories are expressed as equivalents of several emissions contributing to the same impact category. Thus, the produced numerical estimations i.e. indicators in LCA are describing an impact category. For example, impact category global warming potential is described with the indicator CO₂-equivalent (Curran, 2012).

For hydrometallurgical processing, the interesting categories are AP, EP, GWP and from the point of resource consumption, water depletion. In brief, AP describes the ability of a certain substance to release H⁺ ions, which decreases the pH of soil and water. EP describes the over enrichment of nutrients to aquatic or terrestrial locations, resulting in oxygen depletion. GWP presents the heat trapped by greenhouse

gases in the atmosphere, reflecting on the increase of global temperature. Water depletion describes the amount of reduced water resources, which is evidently important in water scarce areas. (Klöpffer & Grahl, 2014; Curran, 2012)

2.2 Adaptation of simulation based life cycle assessment

Reuter (1998) presented the principle of the simulation methodology to produce life cycle inventories, in order to provide accurate and detailed data about metallurgical processes. Various databases provide data for environmental impacts of metals processing (Althaus & Classen, 2005), however an aggregated form is often used to present LCI data (Ghodrat *et al.*, 2017). Furthermore, a recent review investigating LCA studies in mining and metallurgical industry concludes that most of the studies use generic databases and average values available in LCA software (Segura-Salazar *et al.*, 2019). Consequently, it is challenging to make effective comparison or take co-production into account. The synergistic advantage of process simulation and LCA help to generate more detailed LCI inventories and open the “black-box” of metallurgical processes (Segura-Salazar *et al.*, 2019). In addition, geographic locations and country specific legislation will have an impact on the performance and optimization of metallurgical processes. Generalized database values for metals processing do not take these facts into account. The methodology adapted to this study has been comprehensively described by Reuter *et al.* (2015) and illustrated through two case studies.

Simulation is already used as a part of classic process design in the metallurgy industry. Although reporting of environmental indicators is rapidly becoming a necessity for producers, reporting of environmental indicator estimations of developing processes is not yet a normality. Extending the design of processes to include early-stage environmental impact estimations through simulation based LCA should be considered as a future methodology.

Through simulation, plant specific information can be produced, followed by more specific environmental impact estimations. This methodology would provide a more detailed picture of the investigated technologies in order to improve the environmental performance. Simulation is required for the optimization of material flows in metallurgical plants. Thus, the addition of environmental indicator estimation produces important information, which can provide more transparent process evaluations for professionals, experts, industry, society, decision-makers and the common public. (Reuter, 1998)

The gold mining industry in particular, suffers from a bad reputation of possible environmental catastrophes related to cyanidation process. The recent cyanide spills and wildlife death events, as well as the human and ecotoxicity of cyanide, have led to increasing resistance from stakeholders towards the cyanide leaching process (Greenwald & Bateman, 2016). For a cyanide-free alternative to replace cyanidation, better metallurgical performance of the alternative process is required, in addition to economic advantages as well as proven reductions in environmental burden.

The ISO 14044 (2006) states that a critical review of the LCA study can be carried out by internal or external experts, but he or she has to be independent from the LCA study. Additionally, the outside reviewer, rather than the commercial process

provider, should provide information about the cyanide-free process performance. To produce a simulation of a metallurgical process requires significant knowledge about the unit processes used in extractive metallurgy and process understanding. Simulating metallurgical processes requires data of process conditions and material specific characteristics. Such data, in sufficient amounts, can be found from published literature so that metallurgy experts and researchers can produce general flowsheets. Simulation software such as HSC-Sim of Outotec can be used to create accurate flowsheets of metallurgical processes to simulate mass and energy balances which can be applied as life cycle inventories of the processes.

The following Sections 2.3-2.6 present the principles of gold geometallurgy and extractive metallurgy. On this theoretical basis, the simulations can be supported and built to present the estimations of future cyanide-free processing of gold.

2.3 Classification of gold ores

Throughout the history, gold has been a highly valued precious metal due to its unique properties, and still remains to be the most valuable metal to be extracted from ores. Raw materials for gold extraction have shifted to more complex and lower grade ores, which has created new challenges for traditional cyanidation process. The characteristics of ore–mineralogy, gold speciation and liberation –define the processing methods, requirements and overall performance of the process. Thus, in order to maintain effective process performance, the metallurgist needs to understand the geometallurgical aspects of the deposit in question (Marsden & House, 2006).

Gold occurs predominantly as native metal due to its inert nature at ambient pressures and temperatures. However, gold can be found alloyed with (15%) silver or with tellurium, selenium, bismuth, mercury, copper, iron, rhodium and platinum. (Marsden & House, 2006)

Gold-bearing minerals are classified into primary and secondary materials, as listed in Table 1 (McQuiston & Shoemaker, 1975; Marsden & House, 2006). Generally, these materials can be further classified roughly into two categories, free-milling gold ores and refractory ores.

Table 1. The classification of gold materials to primary and secondary materials.

Primary ores	Secondary materials
- placers	- gravity concentrates
- free-milling ores	- flotation concentrates
- oxidized ores	- tailings
- silver-rich ores	- refinery materials
- iron sulfides	- recycled gold
- arsenic sulfides	- PCBs
- copper sulfides	- WEEE
- antimony sulfides	
- tellurides	
- carbonaceous ores	

2.3.1 Free-milling gold

The definition of free-milling gold ores is that, with direct cyanidation more than 90% of the gold is extracted from the ore. Free-milling gold ores can be divided into two sub-categories; namely paleoplacers and quartz vein gold ores. Gold is found in both of these ores within hard rock matrix. The most famous paleoplacer deposit is the Witwatersrand gold reef. Gold is unliberated in paleoplacers, and crushing/grinding is required for liberation (Marsden & House, 2006). The gold can move from paleoplacer host deposits and this type of ores are called placer ores. Placer ores are exceptions as they do not need any pretreatment (La Brooy *et al.*, 1994), and the gold is present in a liberated form unlike in paleoplacers. The hydrothermal circulation effect results in the formation of a variety of gold bearing quartz vein deposits found as replacement of wall rocks or open space filling along fractured zones (Henley, 1975).

2.3.2 Refractory gold materials

Gold can also be found as ultrafine solid solution inclusions in the sulfide mineral matrix (Marsden & House, 2006). This gold is referred to as “invisible” or “locked” and such materials are called refractory. The term refractoriness is defined by ore mineralogy based on the efficiency of extraction of gold from an ore by conventional cyanidation. Table 2 presents the classification of ore refractoriness according to the achieved recoveries of gold in cyanidation (La Brooy *et al.*, 1994).

Table 2. Classification of ore refractoriness based on recovery in direct cyanidation, modified from La Brooy *et al.* (1994).

< 50% recovery	Highly refractory
50-80% recovery	Moderately refractory
80-90% recovery	Mildly refractory
>90% recovery	Non-refractory (Free-milling)

The poor recoveries of gold from refractory ores are predominantly due to the following characteristics (Afenya, 1991; Fraser *et al.*, 1991, Haque, 1987):

1. The gold occurs as very small particles in intimate association with sulfide minerals and siliceous gangue as “locked gold”. Or in some orebodies, the gold is in the atomic lattice within other minerals as chemically bonded solid solutions and not as particulates.
2. The gold is associated with active carbonaceous matter. The carbonaceous material does not “lock-up” the gold but interferes with the chemistry of gold cyanidation and the subsequent recovery processes.

The minerals corresponding to the refractory type definition are: iron – pyrite and pyrrhotite; arsenic - arsenopyrite (most common), realgar and orpiment; copper – chalcopyrite and bornite; as well as carbonaceous matter (Fraser *et al.*, 1991). The most interesting minerals associated with refractory ores are arsenopyrite and carbonaceous material. According to Marsden & House (2006), the gold content in arsenopyrite can vary from <0.2 to 15 200 g/t. The gold content of other typical

sulfide minerals range from: <0.2 to 132 g/t in pyrite, <0.2 to 72 g/t in tetrahedrite and <0.2 to 7.7 g/t in chalcopyrite. Compared to pyrite, the amount of gold within the arsenopyrite matrix can be 40 times higher. This is significant in the sense that arsenopyrite can contain most of the gold found in the ore compared to pyrite (Fraser *et al.*, 1991).

The presence of naturally occurring carbonaceous material in the ore relates to the preg-robbing phenomenon, where the gold recovery is inhibited by the adsorption of gold on the carbonaceous material (Miller & Díaz, 2016). Traditionally, naturally occurring carbon has been eliminated by roasting (Fraser *et al.*, 1991). In cyanidation, carbon-in-leach (CIL) is preferred for preg-robbing materials rather than carbon-in-pulp (CIP) process. Preg-robbing phenomenon can be prevented with blinding agents such as kerosene or the amount of carbonaceous material in the ores can be decreased by oxidation (Miller & Díaz, 2016).

It has been reported since 1990 (Fraser *et al.*, 1991) that the ore bodies discovered then and in future (currently) will not be amenable to simple cyanidation, as most of the gold ore bodies being found were and are wholly or partially refractory. Low recoveries of gold from such ores using cyanidation have been indicated from metallurgical testwork. Therefore, processing methods more applicable for refractory type ores and concentrates are highly needed for gold extraction.

2.4 Effect of mineralogy on process performance

Ore mineralogy is a critical property having significant impact on gold recoveries and therefore has to be taken into account in process selection and parameter optimization. The mineralogy significantly affects the design of the process as gold tends to occur at least in two different forms in an ore (Zhou *et al.*, 2016), thus each gold deposit and material are unique. In order to design a feasible process, several variations need to be taken into account (Marsden & House, 2006; Harris, 1990; Henley, 1975):

- mineralogical mode of occurrence of gold
- gold grain size distribution
- host and gangue mineral type
- host and gangue mineral grain size distribution
- mineral associations
- mineral alterations
- variations of the above within deposit or with time

These characteristics of a gold deposit will affect the selection of mining methods, extractive process design and optimization, and the consequent performance.

Depending on the mineralogy, pretreatment processes may be needed for gold liberation. These include crushing and grinding for free-milling ores and oxidative pretreatments such as roasting, POX and bio-oxidation for refractory type gold ores.

Generally, some minerals and metals are considered as heavy cyanide consumers. Copper can be found in oxide ores as oxide copper minerals, and the dissolved copper is regarded as cyanide consumer. Copper forms copper-cyanide complexes prior to gold complex formation in cyanidation. It is known that silver also has similar

cyanide-consuming characteristics, when silver grade is high >10 g/t and/or gold is present as electrum. Moreover, the presence of impurity minerals significantly affect the process selection and operating conditions. For example, stibnite in aurostibnite acts as a cyanide consumer, and the presence of antimony results in poor dissolution of gold (Ubal dini *et al.*, 2000). Similarly, clay materials degrade the filtration performance. (Marsden & House, 2006) Such mineralogy related issues cannot be directly applied to cyanide-free processing of gold ores, and need to be further investigated. Moreover, there can be other mineralogy related problems in alternative lixivants. These issues require exact research and process simulation prior to advancing on industrial scale operation.

2.5 Extractive gold processes

Depending on the mineralogy, different processing of the various ores is required. Free-milling ores are simple to treat by gravity separation or direct cyanidation. Refractory type and complex materials are difficult to treat with these techniques, and require a pre-treatment prior to cyanidation to liberate the gold (La Brooy *et al.*, 1994; Afenya, 1991; Fraser *et al.*, 1991; Haque, 1987). Known pretreatment methods are roasting (Hammerschmidt *et al.*, 2016), POX (Thomas *et al.* 2016; Marchbank *et al.* 1996; Pangum & Browner, 1996; Mason *et al.*, 1985) and bioleaching (Brierley & Brierley, 2001; Iglesias & Carranza, 1994). In the following sections, the simplified chemistry of chosen pre-oxidation process (pressure oxidation), cyanidation, and the investigated halide processes are presented.

2.5.1 Pressure oxidation

POX is a process for pretreatment of refractory ore bodies for the liberation of recoverable metals such as gold. POX utilizes high temperature, high pressure, and the presence of oxygen to gain suitable processing conditions.

The preheated and preacidated slurry is subjected to a pressure oxidation autoclave. The applied temperature is between 180 °C and 225 °C, with a total pressure between 275 and 490 psia, and an oxygen partial pressure of at least 25 psia for 60 minutes (Thomas *et al.*, 1990). Pangum & Browner (1996) state that the conditions for complete sulfide mineral oxidation, i.e. gold bearing pyrite and arsenopyrite, are at temperatures between 170-200°C and oxygen pressures between 700-1000 kPa. These conditions can be described as aggressive, and high temperatures can lead to unreasonably expensive operational costs. However, lower temperatures are infeasible for efficient oxidation of sulfide minerals, and thus temperature is a critical parameter for the process. (Mason *et al.*, 1985) Typically, oxidation of sulfide sulfur is expected to be 50 to 95%. This is affected by the amount of sulfide sulfur, nature of sulfides in the ore, and distribution of gold.

The pyrite and arsenopyrite oxidation is suggested to happen through following Equations 1 and 2:

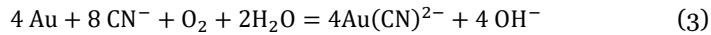


It can be observed that iron precipitates as jarosites and iron sulfate. Arsenic forms a stable precipitate with iron as ferric arsenate (Fleming, 1992; Haque, 1987). At its best, the POX process is self-sustaining in temperature and sulfuric acid concentration due to the exothermic reactions of sulfide minerals. In addition, counter-current-decantation (CCD) of the slurry enables removal of base metals, which can produce slimy hydroxides. Most of the acids generated in the autoclave can be subjected to neutralization, lowering lime consumption in the pH controlling step prior to cyanidation. Furthermore, the temperature can be dropped in the CCD circuit to a more suitable level for the cyanidation. The more detailed process description is presented in Publication II.

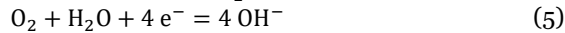
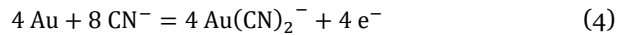
2.5.2 Cyanidation

In cyanidation process, the gold is oxidized by oxygen and then forms a complex with cyanate ion. Cyanide is introduced into the system mainly as sodium, calcium or potassium cyanide (Marsden & House, 2006). In aqueous alkaline solution, gold oxidizes and dissolves as Au(I) and complexes with CN^- to form $\text{Au}(\text{CN})_2^-$. According to the Eh-pH diagram presented by Marsden & House (2006), the Au(III) cyanide complex $\text{Au}(\text{CN})_4^-$ can also form, however it is not as stable as $\text{Au}(\text{CN})_2^-$ complex. The stability of dicyanoaurate ion ($\beta_2=1038$) is significant compared to other complexes.

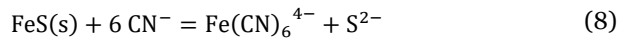
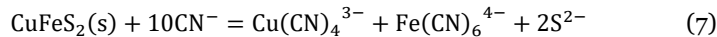
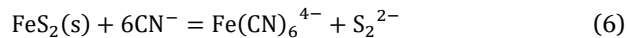
The overall dissolution reaction of gold in aerated, alkaline cyanide solutions proposed by Elsner (1846) is (Equation 3):



This reaction was further investigated by Kudryk & Kellogg (1954). They concluded that the dissolution of gold into cyanide is an electrochemical process. The reaction can be divided into partial reactions (Fleming, 1992): Equation 4 being the anodic reaction, and Equation 5 the cathodic reduction of oxygen.



During cyanidation minor amounts of sulfide minerals may dissolve. The dissolution reactions (Equations 6-8) of sulfide minerals are (Kianinia *et al.* 2018; Zhang *et al.*, 1997):



According to Zhang *et al.* (1997), due to oxidizing conditions in cyanidation, the formed S^{2-} can oxidize further to sulfate. Sulfide minerals thus increase the consumption of cyanide chemicals, and pretreatment is required to minimize the amount of the mineral (Hayes, 1985).

Cyanidation can be performed in different leaching systems such as agitation leaching, heap or dumb leaching, intensive cyanidation, vat leaching and *in situ* leaching.

The choice of the leaching method depends on the particle size and recovery, the dissolution rate and capital and operating costs. Generally, agitation leaching is suitable for most of ores. In steel tanks, the solids are kept in suspension by air or mechanical agitation. Usually, gold is recovered from the solution on activated carbon in CIP or CIL processes. The difference between these processes is that, in CIP the leaching and recovery of gold are conducted in separate reactor tanks. In adsorption, carbon flows counter current to the process slurry in generally five to six tanks, depending on tank sizes, carbon concentration and the amount of gold to be adsorbed. High carbon concentrations result in high gold adsorption, high carbon inventories, as well as increased fine carbon losses. The carbon concentration needs to be optimized to achieve optimal gold recovery, and to reduce operating risk of losing gold to tailings.

In CIL method, the leaching and recovery are conducted at the same reactors in counter current flow. CIL method is usually more efficient for refractory type materials, which can have preg-robbing characteristics (Fleming, 1992). The disadvantages of CIL are large carbon inventory leading to high in-plant gold lockup, and fine carbon particles due to carbon attrition. Thereby, associated gold losses are typically higher. Carbon loading is lower due to treatment of lower grade solutions, which increases the carbon transfer frequency as well as increases elution and reactivation requirements.

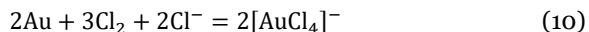
The loaded carbon is separated from the solution with screens, washed with hydrochloric acid to remove impurities, and subjected to elution process in order to obtain a small solution volume with high gold concentration. Gold is stripped from carbon by soaking in NaCN and NaOH combined solution, and washed with hot water. Then gold can be recovered by electrowinning from the enriched solution. The stripped carbon is subjected to reactivation process, where it is heated to 750 °C, after which it can be used again in the leaching units.

The cyanide slurry is subjected to tailings ponds, from where the solution is required to be treated for cyanide detoxification. According to Hewitt *et al.* (2012), the cyanide detoxification is conducted to meet the International Cyanide Management Institute (ICMI) code and/or regulatory, in order to release process waters from gold cyanidation plants. The most common oxidation process for CN is the sulfur dioxide assisted process, where Na₂SO₃ or Na₂S₂O₅ is used as a source of sulfur dioxide. A mixture of sulfur dioxide and air oxidizes the free cyanide in solution according to Equation 9 into a form in which it can be disposed of (Marsden & House, 2006):

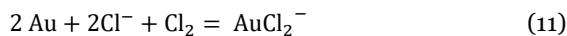


2.5.3 Chlorination and hypochloride leaching

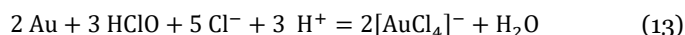
Chlorine has been known to dissolve gold from ores and concentrates since 1800s (Rose, 1989). There are various theories regarding the mechanism of gold dissolution in chlorine/chloride solutions (Nesbitt *et al.*, 1990). In the pure chloride systems, the possible oxidizing agent is chlorine gas or hypochlorite, depending on system pH. Depending on the stability of these oxidants, different mechanisms for gold leaching can be suggested. Gold will leach in the presence of chlorine gas and chloride ions to gold-chloro complexes [AuCl₄]⁻, when pH is less than 2, Equation 10 (Baghalha, 2007; Finkelstein *et al.*, 1966).



Nesbitt *et al.* (1990) have determined the mechanism of chlorination in aqueous solutions. First, the Au(I) complex AuCl_2^- is formed and is then rapidly oxidized to the Au(III) chloride complex AuCl_4^- . The mechanism for the dissolution of Au with excess chlorine is indicated in the Equations 11 and 12:



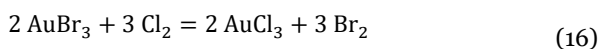
Another possible oxidizing agent is hypochlorite, HOCl , which is a strong oxidizing agent. Jeffrey *et al.* (2001) showed that gold dissolves in hypochlorous acid according to Equation 13 in the pH range 2.5-4.



The mechanism of gold dissolution in chloride solution occurs in three stages, first the Au(I)-chloride complex (AuCl) is formed on the surface of metallic gold, secondly AuCl complexes with chloride ion to AuCl_2^- and thirdly this complex moves to the solution and oxidizes with HClO to AuCl_4^- (Baghalha, 2007; Nicol, 1980). According to the Pourbaix diagrams presented by Nesbitt *et al.* (1990) in the Au-Cl- H_2O system, at low Cl^- concentrations, AuCl_4^- complex is the more stable soluble gold chloride species. AuCl_4^- complex is stable in the pH range of 0-6 and in a potential range greater than 0.9 V, depending on the concentration of gold and chloride ions. At higher concentrations of chloride ions, AuCl_2^- may be stable. The slower dissolution rate of Au would result in slower formation of AuCl_2^- complex, which is reduced to AuCl_4^- in diffusion limited chlorination.

2.5.4 Halide/halogen leaching process

Hypochlorides can be used to generate the chlorine gas *in situ* (Lalancette *et al.*, 2015a). According to Lemieux *et al.* (2014), if the solution of Br^- comes in contact with elemental Cl_2 , the Br^- will be oxidized to Br_2 and result in formation of corresponding amount of Cl^- . Br_2 attacks the gold and produce AuBr_3 , which in turn will be transformed to AuCl_3 (Equations 14-16).

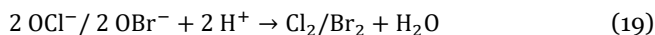


The Cl_2 and Br_2 gases will react with water forming hypohalides, according to Equations 17 and 18.



Lalancette *et al.* (2015a, 2015b) have patented a process for gold leaching from refractory gold ores using hypochlorite. The precious metals are recovered from a

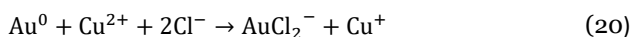
pregnant solution generated by the action of halogens or halogen derivatives on a precious metals-bearing ore. Simultaneously, the recycling of halogens from the resulting barren solution is facilitated. The redox potential of the solution has to be maintained at appropriate values, in the range of 800 mV vs. Ag/AgCl. The recovery of gold can be done with activated carbon. However, in the case of halogen leaching, particularly with bromine, the halogens have a tendency to form stable halogenated compounds with carbon. This disturbs the recycling of halogens and creates a disposal problem for halogenated carbon. Due to this, an alternative recovery method is proposed, by precipitation of gold on silica (Lalancette *et al.*, 2015a). Gold silicate product can be subjected to pyrometallurgical process to produce gold bullions. The process modelled in this study uses halogens for extraction of gold. In the process, halogens such as chlorine and bromine are used as free halogens for the extraction of precious metals. The halogens are recycled in the form of hypohalides by electrolysis of the barren solution. The liberation of free halogens from hypohalides follows Equation 19:



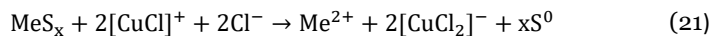
Excess halogens are scrubbed with sodium hydroxide. (Lalancette *et al.*, 2015a)

2.5.5 Cupric chloride leaching process

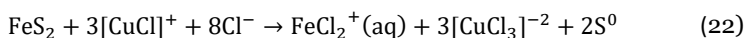
Chloride systems using redox couples as oxidants have been investigated early on. The most common system is using cuprous/cupric redox couple, and another option is ferrous/ferric redox couple. Seisko *et al.* (2019), Diaz *et al.* (1993), Frankenthal & Siconolfi (1982) and Nicol (1980) have investigated the mechanism and kinetics of gold leaching by cupric chloride. These studies have shown that gold dissolves in aurous form at lower oxidation potentials. In the conditions obtained for this study, the literature suggests (Seisko *et al.*, 2019) that majority of gold dissolves as AuCl_2^- . This reaction is reported by McDonald *et al.* (1987) as presented in Equation 20,



Equation 21 presents the general dissolution reaction for sulfide minerals, suggested by Lundström *et al.* (2005). The difference between Equation 20 and 21 is in the presentation form of copper species. It is well known that both cupric and cuprous ions can form a variety of chloride complex species (e.g Cu^{2+} , CuCl^+ , CuCl_2 (aq), CuCl_3^- , and CuCl_4^{2-} as well as Cu^+ , CuCl (aq), CuCl_2^- , CuCl_3^{2-} , $\text{Cu}_2\text{Cl}_4^{2-}$, and $\text{Cu}_3\text{Cl}_6^{3-}$, Zhao *et al.*, 2013). However, Equation 20 presents both cuprous and cupric ions in a simplified form, whereas Equation 21 presents the dominating cupric and cuprous complexes in the studied environment (Lundström *et al.*, 2005).



The pyrite oxidation has been studied in cupric chloride solutions and pyrite dissolution has shown enhanced results in higher cupric ion concentration and temperature. The dissolution has been suggested to follow Equation 22 [III].



The cupric and chloride ions are present in highly concentrated chloride solutions as different complexes (Lundström *et al.*, 2009a). Gold dissolution is suggested to proceed rapidly in chloride solutions; however the dissolution rates of pyrite and arsenopyrite are slow in cupric chloride solutions compared to pyrrhotite (Miettinen *et al.*, 2013). The pyrite dissolution in similar conditions has been shown to be minor compared to other sulfide minerals, chalcopyrite, bornite, sphalerite and covellite, during 2 hour leaching time. (Lundström *et al.*, 2009b).

Miettinen *et al.* (2016) describe an evaporation process in order to recover the chemicals in used chloride processing, to be re-used in leaching. The leaching is performed in cupric chloride solution at atmospheric pressure, and at temperatures close to 100 °C. Oxygen is provided to the system to regenerate the oxidant, i.e. oxidize cuprous ions to cupric, which provides the oxidative power to the system. It is possible that in these conditions arsenopyrite is oxidized, pyrite is oxidized to some degree and further gold is leached. The leaching residue is washed and solids are disposed to landfill, and the washing solutions are subjected to neutralization to produce pure and acid free solutions. The gold can be recovered in a solvent extraction process, where 2,2,4-trialkyl-1,3-pentanediol or 2-ethylhexanol is used as the organic extraction solution (Haapalainen, 2018; Paatero *et al.*, 2015). The gold is stripped from the organic solution to a weak NaCl solution from which it is reduced to metallic gold with sodium bisulfite (SMBS), Na_2SO_3 or $\text{Na}_2\text{S}_2\text{O}_5$. The usage of SMBS leads to the HCl reagent scrubbing procedure becoming unnecessary (Haapalainen, 2018). The gold is filtered out and solutions are directed to effluent treatment, where a hydroxide residue is produced and the required solution bleed is conducted. The depleted gold solution is subjected to neutralization process and evaporation process for recovering the chloride solution. The neutralization solids are also washed, producing an atacamite rich precipitate. More detailed description of the cupric chloride leaching process is found in Publication IV.

2.6 Process selection

Cyanidation has dominated the gold leaching industry from the 1970s. Through the decades, many alternative cyanide-free processes have been studied, for example halides, (Lampinen *et al.*, 2017; Yen *et al.*, 1990; Nicol, 1976), thiosulfate (Aylmore, 2016b; Dai *et al.*, 2013; Aylmore & Muir, 2001; Aylmore, 2001), thiourea (Li & Miller, 2006) or glycine (Oraby & Eksteen, 2015; Oraby & Eksteen, 2014). Furthermore, many reviews related to cyanide-free options have been published (Gökelma *et al.*, 2016; Konyratbekova *et al.*, 2015; Hilson & Monhemius, 2006; Senanayake, 2004; Tran *et al.*, 2001; Sparrow & Woodcock, 1995)

The reasons in favor of cyanide are the low price and stable process, which is considered easy to handle. Furthermore, activated carbon remains the default method for gold recovery from solution and upgrading. Other methods are only used when carbon is not shown an economic option. The disadvantages of using cyanide are the need for cyanide transportation, detoxification, management, monitoring, storage, as well as the risk of wildlife and human toxicity (Liddell, *et al.*, 2019). Nevertheless, the alternative processes have not yet challenged cyanidation in the industrial scale. All non-cyanide alternatives have diminishing factors. Because of their lower stability compared to cyanide-gold complex, they require more lixiviant to maintain the gold

in solution. However, as ore grades decline, the focus will transfer to non-cyanide heap and *in situ* leaching approaches, which would necessitate lixiviant systems that can withstand fairly large pH, Eh and dissolved oxygen gradients. Due to the risks of environmental hazards, and changes in mineralogy of available gold ores, the definition of BAT might no longer be fulfilled with cyanidation.

However, the uptake of any cyanide-free process ultimately requires assuring the decision-makers, financial partners and board of the company. Knowledge of process metallurgy should be developed at diverse levels throughout a mining company. Introducing a new technology is easier through incremental approach or if there are no other options available (Eksteen & Taylor, 2019).

Based on this predominant situation in gold industry, the available cyanide-free processes were assessed and chosen for more accurate investigation. The typical unit processes used in the gold industry are presented in Table 3, where the simulated processes selected for flowsheet designs in the current study (I, II, IV) are highlighted in bold text.

Within the investigated lixiviants, the halide processes show most potential as there is quite a variety of different methods already developed. The thiosulfate process of Barrick (Dai *et al.*, 2013) is used in industrial scale, and the scope of this study was limited to alternatives that have progressed to this stage. In addition, the organic lixiviants are challenging to be simulated with HSC-Sim due to database restrictions. Thus, the scope was limited to halide based processes. The available halide processes are presented in Table 4. From the halide processes, the Dundee process using *in situ* chlorine gas/hypohalide recycling for gold leaching, and the Outotec cupric chloride leaching process were chosen for the simulations in the current work. The simulated processes were compared to cyanidation process in the light of process performance and environmental impacts. In cupric chloride systems, simultaneous oxidation of sulfide minerals and leaching of gold is possible. Due to this, the pyrite dissolution was investigated by anodic polarization in cupric chloride solutions. A detailed approach of the experiments is given in corresponding Publication III.

Table 3. Typical unit processes used in gold industry, based on unit processes described by Marsden & House, 2006. The unit processes selected for simulation of the current study are highlighted in bold.

<i>Pre-oxidation</i>	<i>Leaching</i>	<i>Gold recovery and refining</i>	<i>Neutralization processes</i>
Roasting	Heap Leaching	Adsorptive material Activated carbon (CIP/CIL) Silica	Effluent treatment Precipitation
Bioleaching	Cyanide	Resins (RIP/RIL) Zinc precipitation	Cyanide Detoxification Dilution Natural Degradation Sulfur-dioxide-assisted oxidation Caro's acid
Pressure oxidation	Reactor Leaching	Precipitation	Iron-complexing Hydrogen peroxide Oxidation
Low-pressure oxidation	Cyanide Chlorination	Aluminium precipitation	
High-pressure acidic oxidation	Hypochlorite	Solvent extraction	
High-pressure nonacidic oxidation	Cupric Chloride	Ion Exchange	
Nitric acid oxidation	Ferric Chloride	Electrochemical methods	
Chlorine oxidation	Thiosulfate Thiocyanate Thiourea	Electrowinning Electrorefining Electro-deposition redox-replacement (EDRR)	
	Glycine Ionic Liquids	Smelting	

Table 4. The cyanide-free processes found in literature survey using halides. Modified from Forström, 2016, Lunström *et al.*, 2014 and Adams, 2016.

Process	Ore/Concentrate	Oxidant	Complexant	Recovery method	Additional information	Tested	Reference
Dundee Sustainable Technologies	Oxidized material	Cl ₂ / Br ₂	Cl ⁻ /Br ⁻	Silica adsorption	hypochlorite electrolysis	D	Lalancette <i>et al.</i> 2015a; Lalancette <i>et al.</i> 2015b
Intec	Sulfidic ores	Cu ²⁺ , Fe ³⁺	Cl ⁻ /Br ⁻	Carbon resin columns	Halex™	P	Moyes & Houllis, 2010
Nippon- N-Chlo	Cu-Au sulfidic ores	Cu ²⁺ , Fe ³⁺ , O ₂	Cl ⁻ /Br ⁻	Carbon/IX/EW/SX	low copper concentrate	D	Abe <i>et al.</i> 2008;
Neomet	Refractory carbonaceous ores	Fe ³⁺ , O ₂ , NO ₃	Cl ⁻	XAD-7	regeneration of oxidant and acids	P	Harris & White, 2014
Outotec Gold Chloride	Different patents for different feed materials	Cu ²⁺ , O ₂	Cl ⁻ /Br ⁻	SX (OT-307)		P	Lundström <i>et al.</i> 2019; Haapalainen, 2018; Haapalainen & Miettinen, 2016; Miettinen <i>et al.</i> 2016; Paatero <i>et al.</i> 2015; Miettinen <i>et al.</i> 2013; Leppinen <i>et al.</i> 2010
Platsol™	Au/PGM (base metals) ore	O ₂	Cl ⁻	Carbon/IX/reduction/precipitation(SO ₂ +N aHS)/ copper sementation		P, FS	Ferron <i>et al.</i> 2003; Fleming <i>et al.</i> 2001
Kell		Cl ₂	Cl ⁻	IX and precipitation	https://www.kellprocess.com/welcome	P, FS	Liddell <i>et al.</i> 2019; Liddell, 2003

3. Simulation methodology

In this study, the life cycle inventories (LCI) of the chosen processes were defined by simulating the processes using Sim module of HSC Chemistry software. First two stages of LCA were conducted with HSC-Sim (Outotec, 2019), deriving the information necessary to complete stages 3 and 4 in the GaBi software (thinkstep, 2019). This method provides an efficient tool to simulate and evaluate the environmental impacts of hydrometallurgical gold processes and produce comparable data for LCA. In addition, the previously listed particular aspects in metallurgical processing can be assessed from the produced simulation mass balances. Similar methods have been previously adapted in the environmental evaluation of other metallurgical processes (Pell *et al.*, 2019, Ghodrat *et al.*, 2017, Teir, *et al.*, 2016, Reuter *et al.*, 2015, Kotiranta *et al.*, 2015), and now to cyanide-free gold leaching processes [I-II, IV]. The simulations are based on existing literature data for cyanide-free gold leaching processes as well as current experimental research [III]. In this chapter, the material and process selections for simulations are described. This chapter also provides a summary of the research methodology (Figure 1) and the data gathered for simulated processes. Data was collected from literature such as scientific articles and patents. Additionally, known factors from industry were used.

3.1 Ore composition used in simulation

The free-milling gold ore composition was defined based on the published mineralogy (de Waal, 1982) of Witwatersrand gold ores located in South Africa. This deposit is a typical free-milling gold deposit, however, there can also be some gold associated with refractory or carbonaceous materials. For this research, the gold was determined to be free gold instead of refractory gold with only 1% of sulfides present. Additionally, it was assumed that copper was not present in the ore.

Table 5 shows the composition of synthesized free-milling gold ore used in the simulations.

The refractory gold ore composition was selected from a known Finnish deposit (Jaatinen, 2011). Based on the mineralogical and chemical analysis, a balanced composition of the material was calculated. The most similar minerals were found from the HSC database used in the simulation. Table 6 presents the balanced feed composition. As a final step the amount of pyrite was defined to be 32.05% based on the sulfur amount given in chemical analysis. According to these values, the amount of each mineral in the feed material was calculated as t/h, and these values were used as input for the process simulation.

Table 5. The mineralogy of free-milling gold concentrate used in simulation. (de Waal, 1982)

Mineral	Chemical Formula	Unit, m-%
Gold	Au	10 ppm
Silver	Ag	7.5 ppm
Uranium oxide	UO ₂	870 ppm
Quartz	SiO ₂	87.1
Chlorite	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	9
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	2.5
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	0.1
Zircon	ZrSiO ₄	0.1
Chromite	FeCr ₂ O ₄	0.15
Titanium oxide	TiO ₂	0.1
Pyrite	FeS ₂	1

Table 6. The balanced mineralogy calculated based on the chemical and mineralogical analysis. (Jaatinen, 2011)

Mineral	Value	Unit
FeAsS	13.8	%
Cu ₁₀ Fe ₂ Sb ₄ S ₁₃	0.34	%
C	1.95	%
FeS ₂	32	%
Fe ₂ O ₃	2.3	%
NiSb	0.23	%
PbS	0.06	%
Sb ₂ S ₃	0.19	%
FeO*TiO ₂	1.7	%
NaAlSi ₃ O ₈	4.8	%
KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	15.2	%
CaCO ₃	7.01	%
MgCO ₃	5.3	%
SiO ₂	15.0	%
Sum	100	%

3.2 Electrochemical methods to produce kinetic data for simulation

Voltammetry is one of the most diverse electrochemical methods, in which the changes of current through the system are investigated when the external voltage

changes. Within voltammetrical methods, anodic polarization is used to investigate the effect of temperature, solution concentrations on corrosion or dissolution behaviour. Polarization curves can be used to calculate the current density i.e. dissolution rate at open circuit potential (OCP) using Tafel method, based on Butler-Volmer Equation 23

$$\eta = a + b * \log (i) \quad (23)$$

in which a and b are Tafel coefficients. The current density can be used further to determine activation energy, which can indicate the rate controlling mechanism of the reaction as well as in shrinking core model to estimate the required leaching time. The methods are described in more detail in corresponding Publication III. These experimental methods provide essential information of the time perspective for electricity calculations included in LCI.

3.3 Process simulation

HSC Chemistry software is developed by Outotec Oy (Outotec, 2019) and can be used for metallurgical process design. The software includes multiples modules such as process simulation, reaction equations, heat and material balances, equilibrium calculations, electrochemical cell equilibriums and Eh-pH diagrams. HSC-Sim module is used for simulation of whole processes, including different process units. HSC-Sim can be used to draw graphical flowsheets, and further to simulate processes for chemistry, metallurgy, mineralogy, economics etc. The detailed parameters for construction of simulation models are given in corresponding publications [I-II, IV].

A literature survey on gold materials was conducted, and a typical material in the chosen era was used in simulations. Chlorination and cyanidation were compared for free-milling gold leaching [I]. For the development stage processes more refractory nature gold ore was chosen [II and IV]. If applicable, the mineralogical characteristics were taken into account in the flowsheet development, and selection of parameters for simulated process.

The process data for simulations was gathered based on literature, patents, known metallurgical data for unit processes and interviews with experts in industry. In addition, experimental work was conducted to validate some of the parameters used in simulation.

3.3.1 Example of simulation method

For each process a literature survey was conducted. Based on this a flowsheet was designed and drawn in HSC-Sim. As an example, the flowsheet for cupric chloride leaching of gold is presented in Figure 4. All process flowsheets used in this study are shown in Appendix 1. The chlorination and cyanidation (CIP) processes presented in Publication I were simplified compared to the more detailed process flowsheets developed for pressure oxidation, cyanidation (CIL), halide leaching and cupric chloride leaching [II, IV].

Parameters used in the simulations were gathered from literature. It was found that the literature reported parameter levels in halide and cupric chloride leaching varied

more compared to cyanide leaching. As an example, the parameter ranges found for cupric chloride are shown in Table 7. The parameters that are used to control conditions in the simulation are listed first, and the bottom half lists the parameters found for the processing but not effectively used to build the simulation. However, the simulation wizard parameters for thickeners and filters are also listed in this part, which are the conventional approximations of these unit processes. More scenario simulations were conducted for halide processes in order to evaluate the process conditions. The detailed descriptions of each simulation build-up can be found in corresponding Publications [I-II, IV]. All simulations were conducted using similar methods as described here.

In total, 6 processes were simulated and flowsheets were designed according to presented options in literature: POX (Fleming *et al.*, 2008), cyanidation (CIP) (Marsden & House, 2006), cyanidation (CIL) (Marsden & House, 2006), chlorination (Rose, 1898), halide leaching (Lalancette *et al.*, 2015a) and cupric chloride leaching (Miettinen *et al.*, 2016). Refractory concentrate was used as an input material for cyanidation (CIL), as well as halide and cupric chloride leaching, which are the mainly compared processes in this compendium part. Pressure oxidation was simulated as the pre-oxidation method.

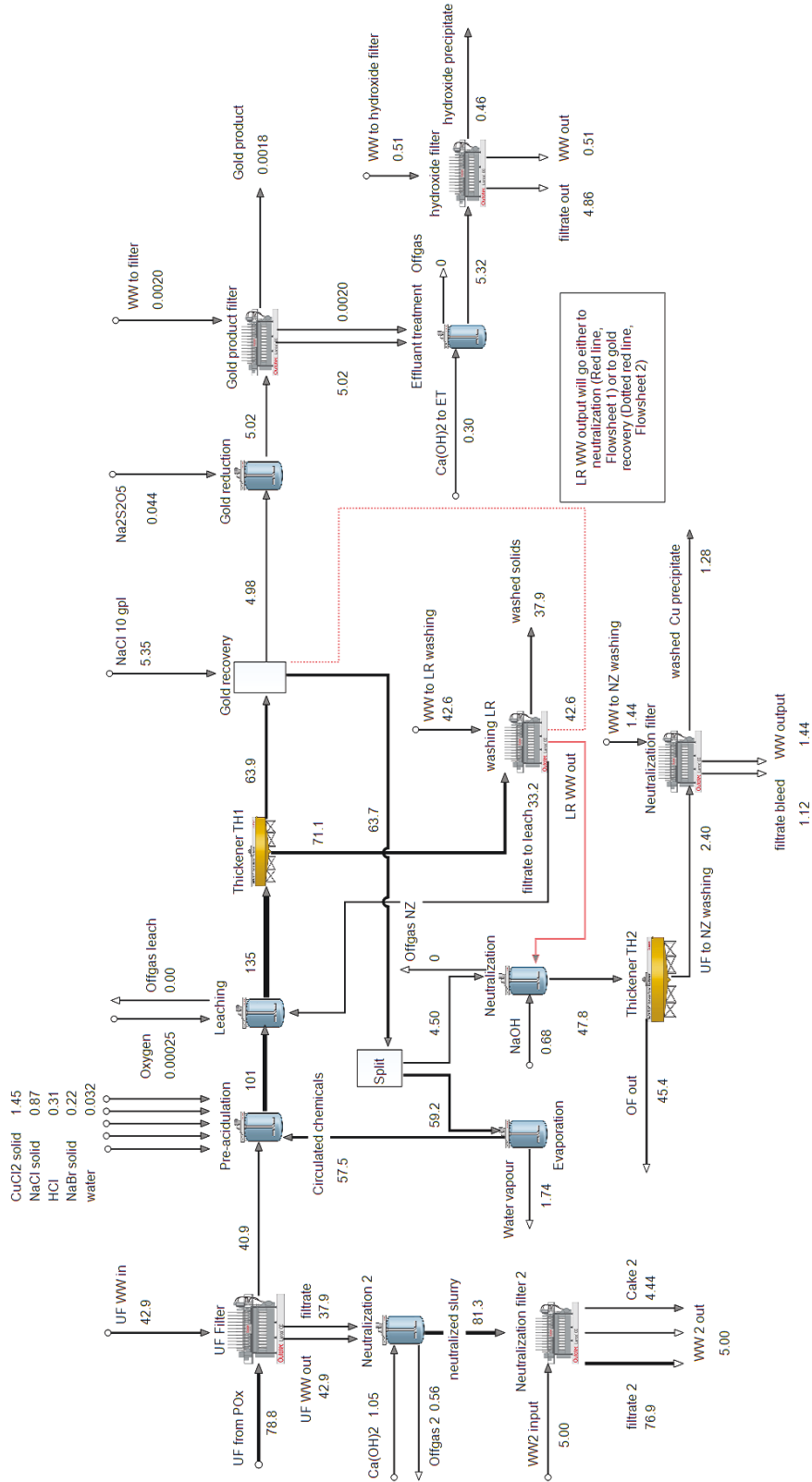


Figure 4. The flowsheet of simulated cupric chloride leaching process [IV], illustrated as t/h. The red line shows two options.

Table 7. The parameters reported in literature from which the studied cases are chosen and the unit, where certain parameters are monitored in the simulation [IV].

Unit process	Parameter Controlled Parameters	Value	Control Unit	Reference
Leaching	Cu ²⁺ conc.	1-110 g/L	Pre-acidulation	(Lundström <i>et al.</i> , 2019; Ahtiainen & Lundström, 2019; Miettinen <i>et al.</i> , 2016; Haavanlammi <i>et al.</i> , 2010; Leppinen <i>et al.</i> , 2010)
Leaching	Cl ⁻ conc.	10-330 g/L	Pre-acidulation	(Lundström <i>et al.</i> , 2019; Ahtiainen & Lundström, 2019; Miettinen <i>et al.</i> , 2016; Haavanlammi <i>et al.</i> , 2010; Leppinen <i>et al.</i> , 2010)
Leaching	Br ⁻ conc.	0-100 g/L	Pre-acidulation	(Ahtiainen & Lundström, 2019; Miettinen <i>et al.</i> , 2016; Haavanlammi <i>et al.</i> , 2010)
Leaching	HCl conc.	0.3-20 g/L	Pre-acidulation	(Ahtiainen & Lundström, 2019; Miettinen <i>et al.</i> , 2016)
Leaching	Solids conc.	150-380 g/L	Pre-acidulation	(Haapalainen & Miettinen, 2016; Miettinen <i>et al.</i> , 2016)
Gold stripping	NaCl conc.	10 g/L	Gold recovery	(Haapalainen, 2018)
Reduction of gold	Sodium bisulfite SMBS ratio	2-25 mol : 1 mol Au	Gold reduction	(Haapalainen, 2018)
Reduction of gold	Sodium bisulfite SMBS conc.	0.5 M / 95 g/L	Gold reduction	(Haapalainen, 2018)
Leaching	Other Parameters pH	0.5 < pH < 2.6		(Lundström <i>et al.</i> , 2019; Miettinen <i>et al.</i> , 2016; Haavanlammi <i>et al.</i> , 2010; Leppinen <i>et al.</i> , 2010; Lundström <i>et al.</i> , 2019; Miettinen <i>et al.</i> , 2016; Haavanlammi <i>et al.</i> , 2010; Leppinen <i>et al.</i> , 2010; Miettinen <i>et al.</i> , 2016)
Leaching	Oxidation potential	450-800 mV Pt vs. Ag/AgCl		(Lundström <i>et al.</i> , 2019; Miettinen <i>et al.</i> , 2010; Haavanlammi <i>et al.</i> , 2010; Leppinen <i>et al.</i> , 2010; Miettinen <i>et al.</i> , 2016)
Leaching	Atmospheric pressure			(Miettinen <i>et al.</i> , 2016)
Leaching	Temperature	80-100, used 95 °C		(Lundström <i>et al.</i> , 2019; Miettinen <i>et al.</i> , 2016; Haavanlammi <i>et al.</i> , 2010; Leppinen <i>et al.</i> , 2010; Miettinen <i>et al.</i> , 2016)
Leaching	Retention time	0.5 h		(Haapalainen & Miettinen, 2016)
Gold recovery	Gold concentration in organic solution	1-100, preferably 3-10 g/L		
Filtration	Filtration efficiency	96%		HSC Filter standard (Outotec, 2019)
Filtration	Filtration cake moisture	25%		HSC Filter standard (Outotec, 2019)
Filtration	Washing water amount	1.5 m ³ /t of solids		HSC Filter standard (Outotec, 2019)
Thickener	Solid conc. in underflow	40%		HSC Thickener standard (Outotec, 2019)
Neutralization	pH	>2.5		Estimation for atacamite precipitation

4. Results

This chapter presents the comparative results of chosen gold hydrometallurgical process simulations and their environmental indicators. In the preliminary study, the CIP process for free-milling concentrate was compared to the historically predominant chlorination [I]. The pressure oxidated refractory concentrate CIL process was compared to halogen/halide leaching in Publication II and to cupric chloride leaching in Publication IV. The electrochemical investigation of pyrite dissolution was conducted in Publication III. The estimated environmental indicators; global warming potential (GWP), acidification potential (AP), eutrophication potential (EP) and water depletion are presented [I, II, IV].

4.1 Process performance comparison

The following Sections summarize the results of simulated processes. The preliminary results of methodology [I] are presented first, then the results from leaching part of the simulations are highlighted and finally the observations from recovery processes are discussed [II-IV].

4.1.1 Preliminary studies

The simulation of chlorination and CIP processes [I] was a preliminary study to investigate the applicability of the simulation based LCA methodology on hydrometallurgical gold processes. The result from the study was that HSC-Sim and GaBi software provide an efficient tool to estimate the emissions of both current and development stage hydrometallurgical processes. The results suggested that the technological transformation from the historical chlorination to cyanidation was beneficial from the environmental point of view, as the main contributor to the GWP of chlorination was chlorine gas production. However, in the development stage processes, the use of chlorine gas is no longer applied, but an alternative oxidant is used, and the chloride ions necessary for complexation are supplied as salts.

Based on Publication I, the simulations were developed further to CIL process, and the development stage halogen leaching and cupric chloride leaching processes. These simulations were more complicated in nature, and provided an opportunity to more extensively assess the metallurgical performance. In following Sections, observations based on the simulations are summarized regarding the leaching and recovery processes.

4.1.2 Leaching

The steady-state simulation conducted with HSC-Sim does not take into account the residence time of slurry in reactors. However, with the mass balance and known residence time used in leaching stage, the number of needed reactors can be estimated. The number of reactors will have a direct effect on the electricity consumption for slurry mixing. In cyanidation, the leaching time can typically be around 24 h (Marsden & House, 2006), while in chloride leaching, the dissolution of liberated gold is extremely fast with a leaching time of only 2 hours (Aylmore, 2016a; Lalancette *et al.*, 2015a). The simulated mass balance for 40.2 t/h throughput in cyanidation with 24 h leaching time predicts the need for at least 6 reactors with effective volume of 269 m³. For the same throughput, halide leaching simulation estimated need for 6 reactors with effective volume of 131 m³, while for cupric chloride leaching only 2 reactors with effective volume of 131 m³ could be sufficient. This is due to the extremely fast kinetics in chloride processes. In agreement with the above estimations, de Andrade Lima & Hodouin (2005) reported a cyanidation reactor size of 412 m³ and Latva-Kokko *et al.* (2015) up to 5000 m³. In conclusion, the fast kinetics of chloride leaching enables shorter leaching times, which will consequently lead to a lower number of reactors and thereby reduce the consumed electricity required for mixing.

Cyanidation is an alkaline process, in which the pH is maintained around 10 to 11. On the contrary, chloride processes are acidic processes, and require pH as low as 1.5 to maintain the oxidant (cupric or ferric) soluble. In addition, the high chloride concentrations necessary to stabilize the Au complexes increase the corrosive nature of the leaching system. Whereas in cyanidation common steel reactors can be used for leaching, chloride processes require much more durable materials, such as titanium reactors or fiber-reinforced plastics (FRP), to work in corrosive conditions. However, refractory ores require a pretreatment process such pressure oxidation, which is usually also an acidic process. If such an ore is entering the cyanidation process after the acidic pretreatment, the pH needs to be increased using chemicals such as lime. This step is avoided if the subsequent leaching step would also be acidic, as in the case of chloride leaching. However, the bleed after gold leaching requires to be neutralized.

The best extraction and recovery rates of gold, based on laboratory test results found in literature, are anticipated in the simulations. For cyanidation, the high recoveries can be anticipated as the process is well known and widely used in the industry. Related to cyanide-free options, the recoveries are only estimations, and should be further verified in proper experimental work. For the free-milling concentrate high extraction rates are expected. As the refractory concentrate is pre-oxidized in POX simulation, and gold is fully liberated, the extractions in the subsequent cyanidation are also estimated to be close to 100%. Similarly, high extraction rates are estimated for halogen leaching and cupric chloride leaching for the pressure oxidated refractory concentrate.

It has been suggested that the cupric chloride lixiviant is capable of simultaneous oxidation of refractory sulfide minerals and leaching of gold in one unit process. Pyrite is one of the common sulfide minerals known to lock gold in its mineral matrix. In the current work, the dissolution of pyrite in cupric chloride solution was experimentally investigated by anodic polarization [III]. The measured corrosion current densities

corresponded to pyrite dissolution rates of 0.05-2.9 $\mu\text{m}/\text{h}$. Higher temperature and cupric ion concentration were shown to enhance the dissolution rate. Shrinking particle model can be used to estimate the leaching times and particle sizes of the feed, as the measured dissolution rate is known. Table 8 presents the estimations of pyrite conversion i.e. dissolution, based on shrinking core model (Levenspiel, 1999). The highest measured dissolution rate [III] is used to estimate the leaching time with varying particle sizes. For free-milling or pre-oxidated material, 2 hour leaching can be enough for complete gold dissolution. However, if refractory ore is subjected to direct cupric chloride leaching, the leaching time has to be increased significantly depending on particle size of the concentrate. According to industrial applications reviewed by Marsden & House (2006), the typical particle size in gold leaching is P80 > 75 μm . This implies that at least 15 hours leaching time is required, for direct cupric chloride leaching of refractory concentrate, to achieve around 60% conversion of pyrite. Complete conversion (>90%) of P80 particle size concentrate would require 22 hours. Nevertheless, the advantage is that, the use and therefore the capital and operational costs related to pressure oxidation process can be totally avoided.

Table 8. The effect of particle size on leaching time of pyrite and achieved conversion.

Particle size, μm	Leaching time, h	Conversion, %
40	2	13.9
40	15	83.4
75	2	7.4
75	15	59.6
105	2	5.3
105	15	39.7

4.1.3 Gold recovery

The common final recovery processes used in gold industry are (Table 3):

Gold enrichment into a second phase (followed by a consequent reduction step):

- Adsorptive material such as activated carbon, silica or resins
- Solvent extraction
- Ion exchange

Gold reduction into elemental form:

- Precipitation (or cementation) by zinc, aluminium, ferrous sulfate, hydrogen sulfide or charcoal
- Electrowinning, EDRR

Gold separation from less noble metals/impurities (from Au rich intermediates):

- Smelting

In this study, activated carbon and silica adsorption as well as solvent extraction unit processes were selected for gold recovery in the simulated flowsheets. The advantages and disadvantages of these processing methods are addressed below.

In cyanidation gold is recovered either by cyanidation in CIP or by CIL processes, where the activated carbon is pumped in counter-current to the slurry flow for adsorbing gold. The loaded carbon is gathered onto hoppers and treated in batch

process, by washing impurities out of the carbon, and subsequently by eluting gold to enriched cyanide solution. The main advantage in using activated carbon is the ability to recover gold simultaneously during leaching in cyanidation reactors. Furthermore, gold elution from activated carbon produces a small volume of highly concentrated gold solution, which means that the acid washing and elution columns, as well as the electrowinning cells, are in notably smaller scale compared to the reactor sizes used in leaching.

However, the gold recovery methods presented in the literature for cyanide-free gold processes (silica adsorption or solvent extraction, SX) require a solid/liquid separation stage between leaching and gold recovery unit processes, which introduces several streams with potential gold losses. In chloride leaching, the PLS and leach residue are separated first by thickening or filtering, and gold is recovered from resulting PLS. The disadvantage of this separation stage is the efficiency of thickeners or filters to subject all PLS to recovery stage. In addition, while pumping large volumes of PLS to recovery stage, some of the PLS, and therefore some of the soluble gold is lost in underflow of the thickener and thus to the leach residue. Even with all attempts to recover gold (PLS) from the leach residue along with filtrate recovery, some gold ends up to the washing waters of the leach residue. Consequently, either (i) gold is lost to water treatment or (ii) excessive amount of low chloride water is circulated back to gold recovery unit, challenging the water and chloride balance of the process. Both investigated chloride leaching processes were found to suffer from this problem. The gold recovery could be improved if the lost soluble gold can be recovered from the washing waters efficiently, or if the gold could be recovered during leaching by some method, similar to CIL. The former could be done by adding a separate recovery unit for the washing water output stream. Same or different gold recovery methods can be chosen for the additional recovery unit from the wash waters. In this study, the presented challenge was mitigated by adding a second silica adsorption stage for halide leaching. In the case of cupric chloride leaching the wash water stream was subjected to existing solvent extraction unit. However, this approach increased the amount of depleted solution to be circulated back to the leaching stage, creating the previously mentioned water accumulation problem. To summarize, in the current study, the cyanidation process benefits from the selected gold recovery process, i.e. gold recovery simultaneously during leaching on activated carbon (CIL). Whereas the halide processes were simulated to utilize silica adsorption or solvent extraction, as described in the literature (Lalancette *et al.*, 2015, Haapalainen, 2018). It is clear that the chloride based processes would benefit a suitable *in situ* gold recovery method.

Activated carbon could provide a possible recovery method for chloride systems but there are some restrictions. The halogens have a tendency to form stable halogenated compounds with carbon. This tendency disturbs the recycling of the halogens and creates a problem for the disposal of halogenated carbon (Lalancette *et al.*, 2015b). When using activated carbon as the adsorptive material in chloride leaching, the elution of the chloride complex from the activated carbon is also a problem. The cyanide-free elution of gold from carbon has not been widely investigated or published, in the existing literature. It has been verified that in chloride systems, gold complexes with activated carbon partially as gold chloride (Au(I)Cl) and partially as metallic gold (Parisien-La Salle, 2012; Sun & Yen, 1993; Hughes & Linge, 1989).

Elution of gold from these complexes can either be achieved by conventional cyanide process or by smelting. However, both of these options contradict partially with the original target of developing environmentally friendly cyanide-free gold processing. Either elimination of cyanide from the processing is forfeited or a pyrometallurgical processing step is added, in which carbonaceous material is incinerated, creating more CO₂ emissions.

In literature, silica adsorption process has been proposed for gold recovery. Lalancette *et al.* (2015b) suggest the use of silica, in the form of insoluble aluminosilicates, recycled glass or recycled slag, on to which gold is precipitated. In this alternative, the oxidation-reduction potential (ORP) of the PLS solution is lowered at ambient temperature and pressure. Sulfur dioxide (SO₂) or sodium sulfite (Na₂SO₃) as well as organic reducers such as formic acid, formaldehyde or oxalic can be used for the reduction of gold on silica. Sulfur dioxide can be circulated from oxidation of sulfide minerals, i.e. pretreatment by POX, if applicable. Total deposition of gold on the silica particles is claimed to be achieved in 30 to 60 minutes. The particles can load up to 30% of their weight of gold. The reported gold recovery values have been high; 99.98, 99.7 and 99.8% (Lalancette *et al.*, 2015b). However, when comparing silica adsorption to solvent extraction, it is clear that solvent extraction is already a state-of-the-art method in several base and rare-earth (REE) metals processes, whereas silica adsorption is only a development stage recovery method. Additionally, in the silica adsorption, the produced precipitate needs to be further subjected to smelting, and the adsorbent material is lost.

Haapalainen (2018) has patented a solvent extraction (SX) process for gold recovery from chloride complexed solutions. The process uses a gold extraction reagent combining 2,2,4-trialkyl-1,3-pentanediol and a long-chain alcohol such as 2-ethylhexanol. The main disadvantage of the SX process has been the use of expensive HCl as scrubbing chemical for organic phase. Some of the HCl can be co-extracted to organic phase during impurity stripping. This acid is lost during the process. However, Haapalainen (2018) suggests that the use of HCl can be eliminated by the use of weak NaCl. Gold can be stripped into this solution and recovered by reduction. Sodium metabisulfite (SMBS) can be used to reduce gold from the aqueous phase, thus impurities remain as soluble and exit the process with filtrate. The solvent extraction of gold from chloride solutions can be carried out in atmospheric temperature and pressure. Haapalainen (2018) reports reduction of gold to be 98.8% with short contact time and close to 100% (solution analysis below detection limit) with longer times.

However, there are some common challenges also with this technology. These are mainly related to solubility of phases in the form of: selectivity of organic phase to the extracted metal, stripping of metal from organic phase, stability of ligand, kinetics of the targeted metal separation, and separation of phases. Excessive crud formation is a general disadvantage of SX, which is caused by: properties of the feed solution, the solvent and its composition, the type of contactor selected, and the method of operation (Ritcey, 1980). The design of the process needs to enable an easy removal of crud from the circuit. Other problems can be the sulfate concentration originating from sulfide mineral dissolution, and calcium concentration is another concern of PLS compositions, as there is a risk of gypsum precipitation. In addition, many SX

processes use metallurgical-grade kerosene based solvents as diluents. Some of these have a low flash point and can be easily flammable. In addition, extractants used can be highly toxic (Han & Soderstrom, 2019). From simulation point of view, the solvent extraction is difficult to simulate due to lack of organic substances in HSC-Sim database. The size of SX unit for gold can be estimated by mass balance using simulation, however, the specific optimizations of the process operation need to be verified in experimental work. The simulation and estimation of environmental impacts for solvent extraction units require more research.

In conclusion, activated carbon is an efficient recovery process for cyanidation, but has some restrictions in chloride systems. The suggested process using adsorptive material in chloride leaching has been e.g. silica adsorption, in which however, solid-liquid separation is required before gold recovery unit, and the adsorptive material is lost in subsequent smelting of the gold silica product. Thus, solvent extraction can be adapted to chloride systems. However, the general problems related to this process remain. It is evident for a person skilled in this field, that more investigations are required to provide the best available technology for gold recovery from chloride solutions.

4.1.4 Water balance

Water balance can be challenging to optimize in hydrometallurgical processing. The geographical location of the process influences the disposal and management of water systems (/outputs) in the plant. In addition, the location also affects the availability of water.

The main inputs of water to pressure oxidation include water in preacidulation reactor and the cooling water required by the autoclave operation. In pressure oxidation process, the neutralized water can be utilized in washing of neutralization solids and in the CCD circuit. However, the simulation predicts a water bleed of 77.6 t/h out of the process [II]. The pressure oxidation produces a 35 wt-% slurry to be subjected to the following gold leaching process: cyanidation, halogen leaching or cupric chloride leaching. The 35 wt-% slurry concentration is typical for cyanidation process. Thus, according to the simulation, no additional water is required in for cyanidation. After gold leaching, the cyanide containing solution is subjected to cyanide detoxification, after which the tailings are deposited in ponds. The water can be pumped from the ponds back to the pressure oxidation process, if required.

In the chloride processes [II, IV], the aim is to circulate chloride containing solution back to leaching. This would enable the minimization of chemical consumption and chloride solution bleed out of the process. However, both chloride process simulations predicted that the accumulation of water and chloride occurs. In halogen leaching the problem was investigated in three scenarios [II]. First, a scenario was investigated where the leach residue was not washed. In this scenario, the accumulation of waters can be avoided but at the same time the gold present in PLS is lost to the tailings. In the second scenario, the leach residue is washed and the waters are circulated back to the process. This results in water accumulation, and consequently a bleed (92.2 t/h) is required to keep the water balance. In the final scenario, the PLS after gold recovery was used as the washing water for leach residue. An accumulation of water is observed also in this case, and a bleed of 56.9 t/h was needed out of the process.

Based on these observations and challenges in the water balance of halogen process, a more thickened slurry was subjected to cupric chloride leaching. In cupric chloride leaching, the raffinate is circulated back to the leaching reactors in order to recycle the cupric and chloride ions. According to Miettinen *et al.* (2016) the raffinate is split between an evaporation unit and neutralization. The evaporated solution with higher cupric and chloride concentrations is circulated to leaching. Evaporation is required in order manage the water balance, and to avoid dilution of the leaching stage. Evaporation allows to keep sufficient solid concentrations in leaching, as otherwise too much water would be circulated in the process. The cupric chloride leaching was investigated in two flowsheet options where in Flowsheet 1 the gold is not recovered from the washing waters, and in Flowsheet 2 the washing waters are subjected to solvent extraction in order to recover gold [IV]. The gold recovery can be significantly improved from 85% (in Flowsheet 1) to over 99% in Flowsheet 2, see Figure 4. However, this causes challenges in the water balance as more raffinate is created, which increases the amount of water needed to be evaporated. However, the required bleed from the process is decreased from around 46 t/h (Flowsheet 1) to 21 t/h.

The water balance of the chloride processes requires still further investigations, as water can be recovered from many processing streams to be used in the processes, as well as pumped from the tailings ponds back to processing. However, the pressure oxidation is very sensitive to chloride concentrations, which creates restrictions if circulating the treated waters to pressure oxidation.

4.1.5 Mass balances

The simplified flowsheets of studied processes are presented in Figure 5 -Figure 8, where the resource consumptions are normalized to produce 1 kg of Au, to emphasize the differences between the closed processing options. The comprehensive HSC-Sim flowsheets are shown in Appendix 1. The comparison of flows is summarized in Table 9.

It can be seen that more concentrate is required in chloride based processes to produce the aimed 1 kg of Au. In the cyanidation process, the estimated cyanide consumption is higher compared to reported values. More detailed descriptions of the mass balances are presented in Publications II and IV. These Figures indicate the previously described problematics of required S/L separation leading to gold lost in leach residue, and bleeds out of the effluent treatments. This shows that the chloride process in the presented for cannot yet compete with the state-of-the art cyanidation. However, the adaptation of the second gold recovery unit brings the obtained extractions to similar values as in cyanidation, which means that the normalized resource consumptions would decrease. The effect of this will be seen in following sections through environmental indicators.

Results

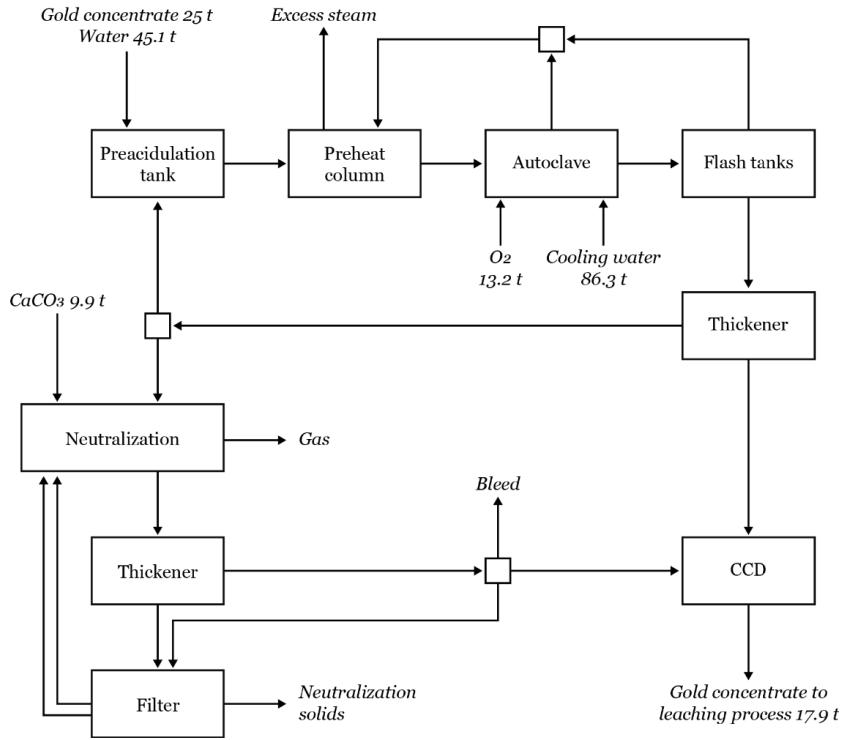


Figure 5. The pressure oxidation mass balance normalized to produce 1 kg of Au.

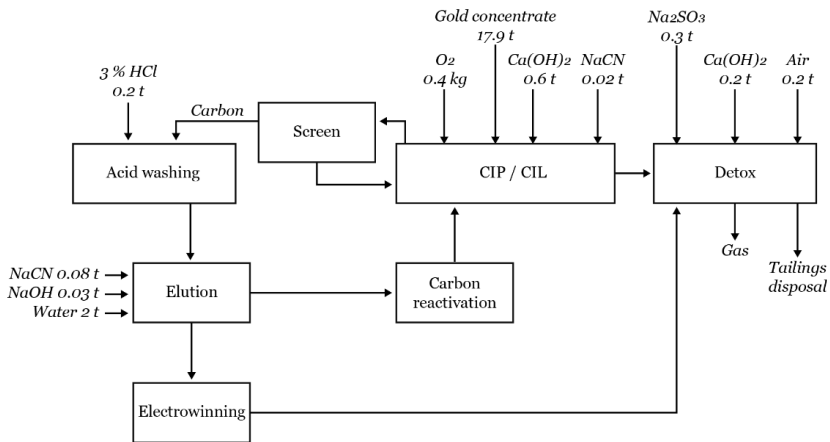


Figure 6. The cyanidation process mass balance normalized to produce 1 kg of Au.

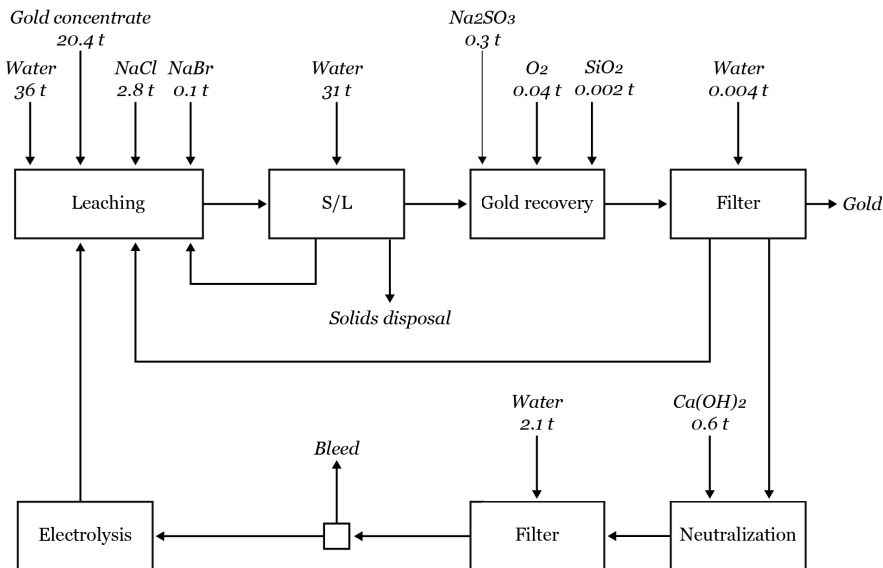


Figure 7. The halogen leaching process mass balance normalized to produce 1 kg of Au.

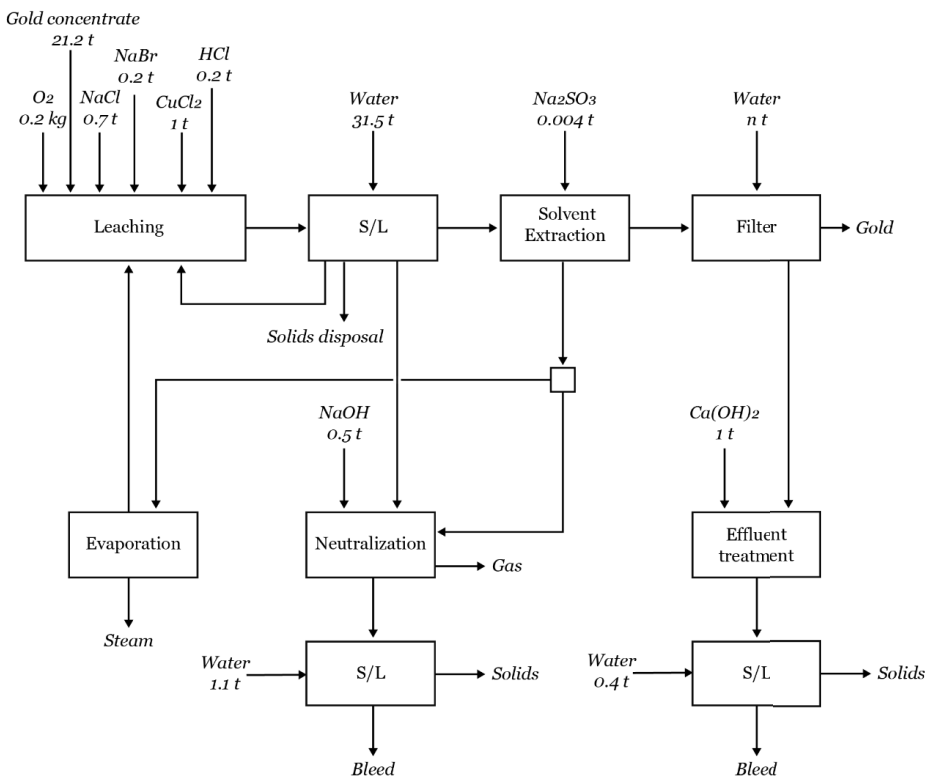


Figure 8. The cupric chloride leaching process mass balance normalized to produce 1 kg of Au.

Table 9. The masses of input streams normalized to production of 1 kg Au.

Streams	Cyanidation	Halogen leaching	Cupric Chloride leaching
Pressure oxidation			
Concentrate	25 t	28.5 t	29.6 t
Water	45.1 t	51.4 t	53.4 t
O ₂	13.2 t	15 t	15.6 t
Cooling water	86.3 t	98.4 t	102.2 t
Ca(OH) ₂	9.9 t	11.3 t	11.7 t
Produced concentrate to leaching	17.9 t	20.4 t	21.2 t
Leaching			
O ₂ /Air	0.4 kg	40 kg	0.2 kg
NaCN or CuCl ₂	0.02 t		1 t
NaOH	0.03 t		0.5 t
NaCl		2.8 t	0.9 t
NaBr		0.1 t	0.2 t
Ca(OH) ₂	0.8 t	0.6 t	1 t
3 % HCl	0.2 t		0.2 t
Na ₂ SO ₃	0.3 t	0.3 t	4 kg
SiO ₂		0.002 t	
Water	36.9 t	71.1 t	113 t

4.2 Environmental indicators of processes

Previously, the environmental impacts of gold processing have been studied by Norgate & Haque (2012), Haque & Norgate (2014) and Hagelüken & Meskers (2010). The comparison of results to other LCA studies is challenging as the system boundaries may vary significantly. Most of the published environmental indicator values are for cradle-to-gate system boundaries. In this study, the environmental indicators have been estimated for gate-to-gate scenarios of the selected gold processes. This compendium part presents the comparison of environmental indicators for pressure oxidation of refractory concentrate, and different leaching processes.

In this thesis, GaBi LCA software was used to estimate the environmental indicators for the processes. The corresponding inputs and outputs of the obtained HSC-Sim mass balances were searched from the GaBi database, as the HSC simulation produces a consistent mass balance of the process to be used as LCI (Llamas *et al.*, 2019; Scheidema *et al.*, 2016; Reuter *et al.*, 2015). The most electricity-consuming unit processes are taken into account for evaluation of the electricity consumption based on the mass balance and needed equipment. The functional unit of all simulated processes is 1 kg of produced gold. System boundaries in this thesis research are gate-to-gate approach for all processes. The specific characteristics of system boundaries and LCI data, as well as the cut-off flows and restrictions of database, are reported in corresponding Publication II and IV.

The results of this study are indicative, as the scales, conditions, technologies, and operation of the modelled processes are based on literature information, not on industrial process data. However, one significant result of this research is the set of process simulations constructed, which can be modified to specific operations for more detailed evaluation of specific gold plants.

The discussed scenarios of simulated processes in this compendium part are shown in Table 10. The detailed descriptions of the studied scenarios can be found in corresponding Publications II and IV. In the SCE 1 of both halogen and cupric chloride leaching the gold is lost to washing waters, as seen from the lower recovery percentage of gold, Table 10. This is improved by recovering the gold from the washing waters in SCE 2 of both processing options. In the SCE2 of cupric chloride leaching, exceptionally mild conditions are applied according to Ahtiainen & Lundström (2019). All the scenarios include the pretreatment POX process, thus high extraction of gold in leaching has been assumed as the gold is liberated. The differences between input masses of the processes and the concentrate amount required for cyanidation and SCE1 on both chloride processes to produce 1 kg of Au are seen in Table 9.

Table 10. The scenarios compared based on their environmental impact indicators.

<i>Cyanidation</i>	<i>Halogen leaching SCE1</i>	<i>Halogen leaching SCE2</i>	<i>Cupric chloride leaching SCE1</i>	<i>Cupric chloride leaching SCE2</i>
CIL recovery	NaCl 60 g/L	NaCl 60 g/L	Cu ²⁺ 40 g/L, Cl ⁻ 125 g/L	Cu ²⁺ 3 g/L, Cl ⁻ 50 g/L
	Silica adsorption	Silica adsorption, also from washing waters	Solvent extraction	Solvent extraction, also from washing waters
Gold recovery, 98.5%	Gold recovery 87.3%	Gold recovery 98.5%	Gold recovery 86.7%	Gold recovery, 99.1%

4.2.1 Global warming potential

Global warming potential (GWP) is a common impact category used in LCAs to present an estimate of heat trapped by greenhouse gases in the atmosphere. In other words, GWP is the cumulative radiative force of direct and indirect effects over specific time horizon resulting from the emission of a mass of greenhouse gas such as carbon dioxide, methane and CFCs, with respect to reference gas CO₂. (Klöppfer & Grahl, 2014) The short-wave radiation from the sun is partly adsorbed by earth's surface and partly reflected as infrared radiation. The reflected part is further adsorbed by greenhouse gases in atmosphere, and is re-radiated back to earth causing more warming effect to the earth. The activities of humankind will enhance the warming effect as we produce more greenhouse gases to the atmosphere. GWP is presented as carbon dioxide equivalent, meaning that an emission is referenced to CO₂ (Klöppfer & Grahl, 2014; Curran, 2012).

The GWP estimations of pressure oxidation followed by either cyanidation, halogen leaching or cupric chloride leaching of gold are presented in Figure 9. The total emission is divided into foreground and background processes contributing to the emission. As pressure oxidation has direct CO₂ emissions, it is the largest contributor to the GWP.

As stated in the Section 4.1.2, the chloride gold processes suffer from loss of gold to washing waters. The addition of a second recovery unit or subjecting the filtrate/washing water to gold recovery was investigated in Publication II and IV. For the cupric chloride leaching, exceptionally mild chloride leaching conditions (Ahtinen & Lundström, 2019) were also investigated in order to evaluate the chemical consumptions and the effect of leaching conditions to circulation of chloride solutions [IV]. As the environmental indicators are calculated per produced kg of gold, the improvement in recovery lowers the value of indicator per produced kg of Au, see Table 9 illustrating differences between masses to produce 1 kg of Au. The best-case scenario for halogen leaching is, improved recovery by adding a second recovery unit, SCE2. In cupric chloride leaching, the process operating at extremely mild conditions, and recovering gold from washing waters (SCE2), results in lowest GWP, Figure 9. The GWP value for cyanidation is 10600 kg CO₂-e/kg Au. The investigated chloride processes (SCE1) have higher values: 12600 kg CO₂-e/kg Au in halogen leaching and 12500 kg CO₂-e/kg Au in cupric chloride leaching. When the gold recovery is improved, the GWP can be lowered to 11500 kg CO₂-e/kg Au in halogen leaching and to 10600 kg CO₂-e/kg Au in cupric chloride leaching (SCE2). Thus, in the extremely mild conditions as described in Publication IV, the cupric chloride leaching can achieve a similar GWP value as cyanidation, suggesting a competitive cyanide-free method in terms of environmental emissions.

For free-milling ores, which do not require the preoxidation process, the GWP of the leaching process is significantly lower, as the direct CO₂ emissions from pressure oxidation can be avoided. However, due to the forecast of future ore deposits being mostly refractory, the removal of pre-oxidation process is highly unlikely. Only a processing method capable of simultaneous oxidation and leaching of refractory gold concentrate could make pretreatment methods (roasting, POX and bioleaching) unnecessary. As stated previously, sulfide mineral leaching e.g. in cupric chloride solutions, requires much higher leaching times compared to POX. However, the mixing of the slurry in atmospheric pressure will impact on energy consumption and consequently to the environmental indicator values. The major contributor to GWP is electricity consumption. In addition, the optimization of the chemical consumptions and recycling of the chemicals is essential.

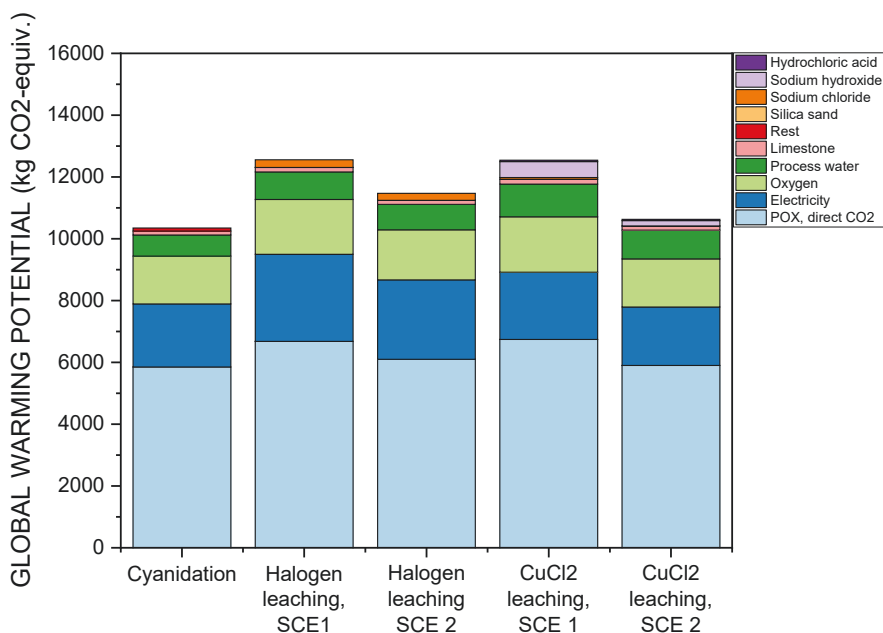


Figure 9. The estimations of Global Warming Potential (GWP) of pressure oxidation of refractory gold concentrate followed by cyanidation, halogen SCE1, and SCE2 or cupric chloride leaching, SCE1 and SCE2 as kg CO₂-e/kg Au.

The regional variations of the processing are mainly seen with the electricity consumption, due to differences in electricity grid mixes used in different countries. The countries producing most of the gold globally are Australia, South Africa, United States, and in Europe, Russia and Finland. However, the production amounts in Europe are marginal compared to other parts of world. In Table 11, the increase of GWP value is shown by changing the electricity grid mix region. The values in Figure 9 are referenced to European electricity grid mix. With electricity produced by Finnish grid mix, the GWP can be lowered to 9300 kg CO₂-e/kg Au in cyanidation, 11 000 kg CO₂-e/kg Au in halogen leaching SCE1 and 11 400 kg CO₂-e/kg Au in cupric chloride leaching SCE1. However, in China and Australia due to electricity production mostly using coal, the GWP is 35% higher than the Finnish value.

Table 11. The effect of electricity grid mix locality to benchmark (Finland) values as increment.

Country	GWP, CO ₂ -e		
	Cyanidation	Halogen leaching, SCE1	Cupric chloride leaching, SCE1
Finland (benchmark values)	9300	11100	11400
Australia	35.3%	38.7%	30.7%
USA	18.2%	21.6%	15.8%
China	35.3%	40.5%	30.7%

4.2.2 Acidification potential

Acidification potential describes the ability of certain substance to release H^+ ions, which decreases the pH of soil and water resources. These substances are, for example, sulfur dioxide and nitrogen oxide, which are air pollutants and transform to acids, H_2SO_4 and HNO_3 . The low pH causes damage to ecosystems as acids are deposited to soils and water. The effects of acidification are nutrients loss from soil and increase in metals solubility into soil. Thus, the regional effects of acidification can vary depending on whether the fresh water or seawater is close for transferring the acidic solutions to nature. (Klöpffer & Grahl, 2014)

Figure 10 presents the estimated acidification potential of pressure oxidated refractory gold concentrate in cyanide, halogen or cupric chloride leaching. The sodium chloride production and sodium hydroxide production are main differences when comparing cyanidation and chloride processes. In the mild conditions of chloride leaching, the impact of chemicals can be minimized and the overall impact brought to level of cyanidation, Figure 10. In practice, this requires efficient recycling of chloride chemicals in the processes in order to minimize the usage of fresh chemicals. In the simulations, efficient circulation of the chemicals was pursued and the input of fresh chemical amount contributing to indicator values is estimated. Similar to GWP, the main contributor to AP is the electricity consumption.

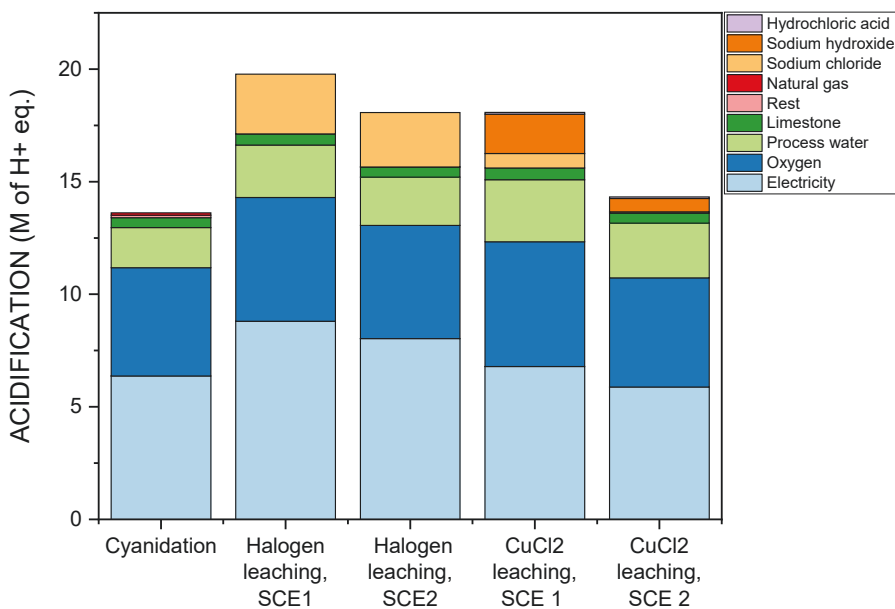


Figure 10. The acidification potential of pressure oxidated refractory gold concentrate followed by cyanidation, halogen leaching SCE1 and SCE2, or cupric chloride leaching SCE 1 and SCE2 as mol of H^+ -eq/kg Au.

4.2.3 Eutrophication potential

Eutrophication potential (EP) describes the enrichment of nutrients to certain place either aquatic or terrestrial (Klöpffer & Grahl, 2014). Common contributors to EP are air pollutants, waste water and fertilization in agriculture. Eutrophication as a phenomenon in aquatic systems results in accelerated algae growth, preventing sun light reaching lower depths of water systems. (Curran, 2012) Thus the decrease in photosynthesis and oxygen production occurs. Low oxygen concentrations in lakes lead to fish dying and anaerobic decomposition, producing hydrogen sulfide and methane. Eutrophicated soils suffer from increased susceptibility of plants to diseases and pests as well as degradation of plant stability. Enrichment of nitrate leads to increased nitrate content in groundwater, which can end up in drinking water. Nitrate at low levels is harmless; however, nitrite is toxic to humans and is a reaction product of nitrate.

Figure 11 presents the EP of pressure oxidated refractory gold concentrate in cyanide, halogen or cupric chloride leaching. Similar to AP, the main difference between cyanidation and chloride processes is the use of sodium chloride, which contributes on significantly to EP. Thus, to this impact category, it is essential to optimize the chemical consumption and minimize the obtained bleeds to environment. Also, sodium hydroxide contributes to EP. In cupric chloride leaching, sodium hydroxide was used in neutralization to precipitate atacamite, which could be recycled to leaching, as input chemical to suffice the cupric and chloride requirements. The alternative for NaOH would be lime, to be used in neutralization and cupric precipitation, and this topic requires further investigations to define which option would lead to the lowest eutrophication potential.

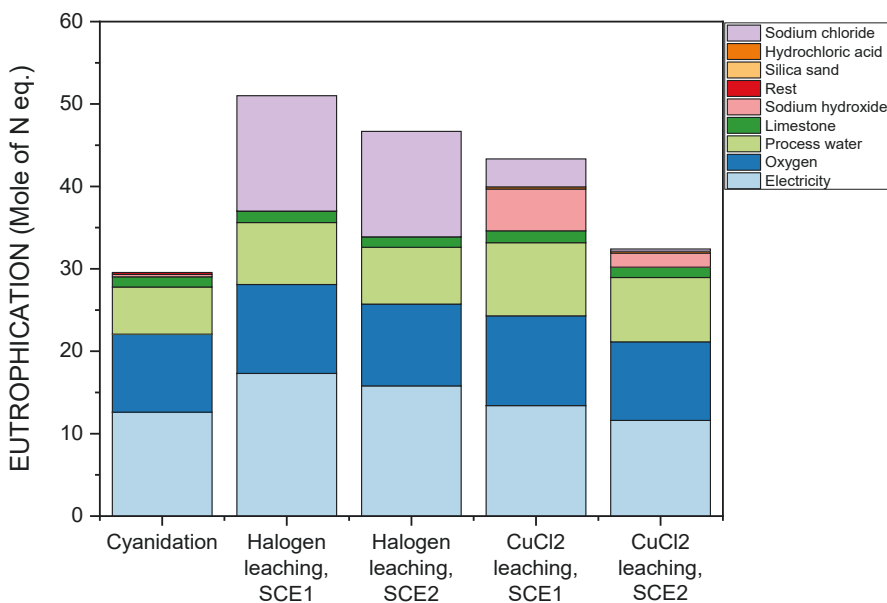


Figure 11. The eutrophication potential of pressure oxidated refractory gold concentrate followed by cyanidation, halogen leaching SCE1 and SCE2, or cupric chloride leaching SCE 1 and SCE2 as mol of N-eq/kg Au.

4.2.4 Water depletion

Water depletion describes the amount of water resources that is consumed. Obviously, in hydrometallurgical processing water is required in large quantities. The cupric chloride leaching shows generally the lowest indicator values in other impact categories, when optimized to extremely mild conditions. However, in water depletion impact category the challenges in water balance are shown. The water depletion is highest in cupric chloride leaching, and with the milder conditions the level can be brought down to same values as halogen leaching, see Figure 12. In cyanidation, the water depletion is 77 kg/kg Au, which is the lowest of all studied options. This relates to the fact that pressure oxidation produces quite optimized slurry for cyanidation, not requiring water addition to leaching, and consequently downsizing the processes in gold recovery i.e. acid washing, elution and electrowinning stages. The water depletion in halogen leaching SCE1 is 99 kg/kg Au and in cupric chloride leaching SCE1 is 105 kg/kg Au. The indicator value decreases in the SCE2 to 91 kg/kg Au (halogen leaching) and 89 kg/kg Au (cupric chloride leaching), as a result of improved gold recovery. However, the issue of large water volumes in process still remains. If the water balance can be optimized, it will definitely impact on the chemical consumptions and further to all impact categories.

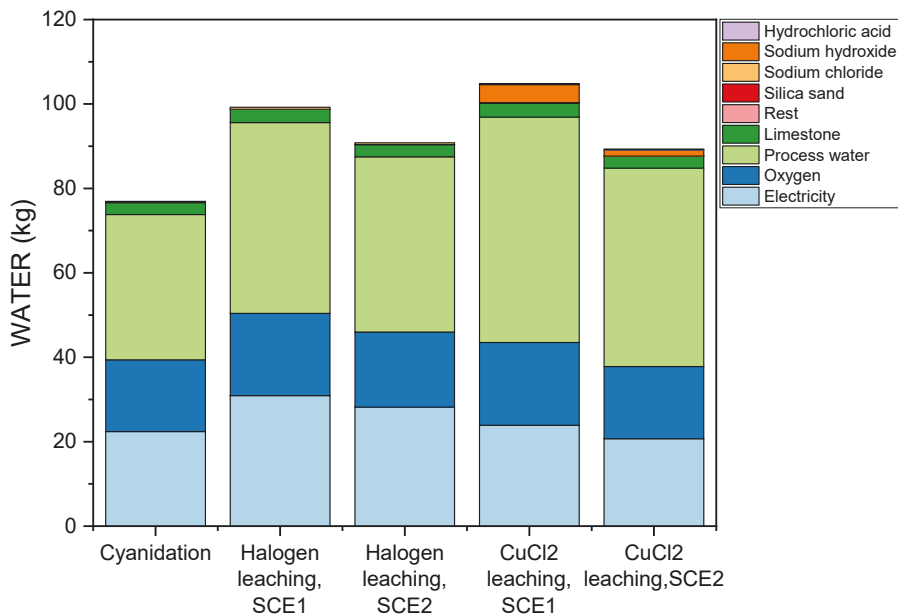


Figure 12. The water resource depletion of pressure oxidated refractory gold concentrate followed by cyanidation, halogen leaching SCE1 and SCE2 or cupric chloride leaching SCE2 and SCE2 as kg of H₂O/kg Au.

4.2.5 Environmental implication of produced waste streams

The simulations can predict the possible output streams of the processing. The treatment of these streams is outside of the system boundary of this study. However, these possible waste streams can be characterized and suitable suggestions can be made about the processing and disposal possibilities. The waste streams of hydrometallurgical processing are the solid wastes, gas discharges and waste waters. The aim of the processing is to produce: stable solid wastes that can be deposited, clean gases that can be let to the environment, and purified waste waters in which concentrations of hazardous elements are within the limits from environmental regulations. According to Beale (2016) following chemical parameters require monitoring in gold plants:

- physicochemical parameters (pH, electrical conductivity, total dissolved solids (TDS), temperature, dissolved oxygen, total suspended solids (TSS))
- dissolved metals (Al, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Zn)
- nutrients (NH_3 , NO_3 , NO_2 , PO_4)
- anions (Cl, SO_4 , hardness, alkalinity)
- organic parameters

In addition, the stability of toxic elements in tailings and suitable tailings disposal alternatives need to be assessed in gold plants, as well as the scrubbing of gas emissions. The composition of produced solid waste is affected by the mineralogy of the concentrate through unleached oxide and silica minerals and the produced neutralization precipitates. In this study, the refractory concentrate includes arsenopyrite, galena, tetrahedrite and breithauptite. These minerals have elements such as As, Pb and Sb, which are contaminants in natural environment. In addition, the leaching system will affect the composition of solids waste, through either the precipitated products or the moisture along solid waste. Thus, Cl, Cu and Fe are also important elements to be discussed. In the processing of sulfide minerals, obviously, sulfate concentration of disposable waters becomes an important parameter.

Arsenic

Because arsenic has several oxidation stages, its chemistry is complex leading also to complex disposal methods. In the simulations, As is predicted to be in As(III) form, whose toxicity is high. Prior to subjecting these waters to nature, the As(III) concentration needs to be lowered to acceptable safe levels of As(III), which in fresh water are $150\ \mu\text{g/L}$ (chronic) and $340\ \mu\text{g/L}$ (acute). (US EPA, 2019) Arsenic can be removed by chemical precipitation as ferric arsenate in low temperature or as scorodite at high temperatures (Ritcey, 2005). In the autoclave conditions, arsenopyrite dissolves as AsO_4^{3-} , thus the arsenic levels can be fixed by precipitating most of the AsO_4^{3-} as FeAsO_4 (scorodite). Better environmental management is achieved in this pre-oxidation method compared to for example roasting, where arsenic trioxide fumes are produced (Thomas & Pearson, 2016). Rest of the arsenic will be precipitated in neutralization as scorodite. The solubility of scorodite has been found to be low, less than $5\ \text{mg As/L}$. Scorodite is considered to be the most stable arsenate compound formed in nature and suitable for arsenic disposal purposes (Swash & Monhemius, 1998). Arsenic management will be one of the future

challenges as the ore grades decline and more arsenopyrite-bearing ores need to be treated (Asselin & Shaw, 2016).

Antimony

The principal antimony mineral found with gold is stibnite Sb_2S_3 (Rohner & Millard, 2016), which is present in the refractory concentrate chosen in this study. Antimony is chemically similar to arsenic and thus toxic (Multani *et al.*, 2016). Antimony minerals will also leach in pressure oxidation, and precipitate as $FeSbO_4$ (Tripuhyite). According to Multani *et al.* (2016), tripuhyite is an optimal form for antimony immobilization. The antimony concentration limits in Finland are for conventional landfill 0.7 ppm and for hazardous landfill 5 ppm (VNA, 202/2006).

Copper

In the cupric chloride leaching, evidently significant amounts of copper is end up in neutralization. The aim would be to efficiently circulate first the cupric containing solution back to the leaching reactors, and then precipitate the cupric ions in neutralization as possible compounds that can be utilized as leaching chemical. In the neutralization unit, Cu is precipitated with NaOH as atacamite. This residue, $Cu_2Cl(OH)_3$ is not subjected for landfilling, but can be used as leaching chemical to optimize cupric concentration in the process, which supports the precipitation of copper to this product instead of covellite, CuS.

Chloride

Chloride is essential for aquatic and terrestrial organisms, working as an extracellular anion in maintaining normal physiological functions. This however means, that in elevated concentrations chloride can cause disruption in osmoregulation, which leads to disturbances in reproduction, survival and growth (Nagpal *et al.*, 2013). As chloride is found in nature as NaCl and KCl salts, and most of the world's chloride is located in oceans, the acceptable chloride levels are higher compared to cyanide.

It is evident that chlorides are found in effluent discharges and solid residues of chloride based processes. The chloride concentration limits in Finland are: for inert landfill 300 ppm (Nyberg, 2019), conventional landfill 15 000 ppm and for hazardous landfill 25 000 ppm (Wahlström *et al.*, 2006). In halogen leaching the chloride concentrations in solid waste moisture correspond to 337-345 ppm, and in cupric chloride leaching 1080 ppm. These values suggest that the leach residue is suitable for conventional landfill.

The aim of the chloride based leaching processes has been to enable efficient recirculation of chloride chemicals and minimize the amount of effluents. The regulation value of chloride in drinking water is 230 mg/L (US EPA, 2019). The acute fresh water limit of chloride as NaCl is 600 mg/L (Nagpal *et al.*, 2013). The leaching conditions of the simulated chloride processes require high Cl^- concentrations, which means that similar concentrations can be found in the effluents. As there are no limits for chloride in mine waters (Kiipula, 2016), the levels of chloride need to be measured and monitored from the surrounding waters after effluent water discharges.

Cyanide

As discussed previously, the main concerns related to cyanide are in the use, storage and transport of the cyanide chemicals leading to potential contamination of surface and ground water. The primary concern of cyanide effluents is the concentration of

free cyanide, thiocyanate and metal-cyanide complexes. According to US EPA the limits for acute level of free cyanide in fresh water is 22 µg/L and chronic level is 5.2 µg/L. The toxicity of cyanide results from dissociation of metal complexes to form HCN, in lower pHs of 0-9 (Dobrosz-Gómez *et al.*, 2017; Marsden & House, 2006). According to Ritcey (2005), the permissible limit for free cyanide in effluents is 0.05 mg/L or less. Thus, the free cyanide needs to be eliminated prior to releasing the waters from cyanidation plant. Free cyanide can be removed through natural degradation (volatilization, oxidation, adsorption to other minerals, hydrolysis, biodegradation and precipitation) or by chemical processing, among which the sulfur dioxide assisted, Inco process is the most used method. In the removal process, the free cyanide is transferred to suitable OCN^- compound for disposal. Cyanide in residues and discharging solutions will disperse through different mechanisms to atmosphere. Cyanide can chemically transfer to other carbon and nitrogen species, form solid cyanometallic precipitates or adsorb to mineral surfaces. Through dispersion to atmosphere and chemical transformation cyanide is permanently eliminated. However, the cyanide precipitates can be released through dissolution and desorption in the event of changing physicochemical conditions (Johnson, 2015).

Iron

Iron is one element creating problems in hydrometallurgical processing by precipitating as slimy hydroxides, which are difficult to filtrate. Iron is usually precipitated as hematite, goethite or as various jarosite-type compounds, which can be discharged to storage ponds (Chen & Cabri, 1986). In high pressure and temperature preferable formation of iron precipitate can be achieved.

During pressure oxidation as well as cupric chloride leaching Fe can be precipitated as hematite, Fe_2O_3 (Thomas & Pearson, 2016; Miettinen *et al.*, 2013). These precipitates together with insoluble silicate minerals can be deposited in tailings heaps. In neutralization with lime iron is precipitated as $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ and $(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$.

In cyanidation under acidic conditions formation of HCN occurs. Hence, the pH of cyanidation is controlled with lime. Iron hydroxysulfates in autoclave discharge are lime consumers, which increases the potential of HCN formation (Fleuriault *et al.*, 2016). In addition, iron forms complexes with cyanide, which might lead to cyanide release in natural degradation process.

Lead

In sulfuric acid pressure oxidation the dissolved lead precipitates as lead sulfate (PbSO_4) immediately (Craig & Vinal, 1939). Lead sulfate is known to be poorly soluble in water, however, slow release of lead to environment over long period of time can be possible. Because of lead sulfate formation, presence of lead in subsequent leaching processes is unlikely. Lead does not form stable complexes with cyanide, but can be found in ionic species (Marsden & House, 2006). Removal of lead is achieved with lime precipitation from cyanide circuit. In chloride processes, lead can be precipitated with calcium carbonate in neutralization.

Sulfate

Sulfate is one of the species found in mine waters and it is particularly problematic when it is in the form of highly soluble sodium sulfate. Sulfates in water bodies can

increase salinity. The acceptable sulfate level in mine waters as per European reference is 1000 mg/L (Bowell, 2004). The acceptable sulfate level in Finnish gold mine according to environmental impact assessment (EIA) of the plant is as an average 8000 mg/L, but is aimed to be reduced to 2000 mg/L with the addition of a sulfate removal plant (Pöyry, 2016). The simulations of this study predict that the sulfate concentrations in all discharge waters are over these values [II, IV]. Thus, the waters should be treated in order to remove excess sulfate. Common sulfate removal process is precipitation as gypsum, which can be deposited in ponds.

Gaseous emissions

The main gaseous emissions predicted by the simulation and shown in GWP estimation is the direct CO₂ produced in different unit processes. Pressure oxidation contributes to the highest CO₂ emissions as an individual process. This is due to the carbonate minerals in the concentrates, such as MgCO₃ and CaCO₃, which produce CO₂ when leached, as well as the calcium carbonate used for the neutralization of effluents.

In halogen leaching, chlorine and bromine gases are produced through redox control. The production of these gases occurs *in situ* in the reactors. In addition, only required amount of the gases are produced, and thus no excess gas emission has been assumed in the simulation. Chlorine gas is very reactive and toxic to humans if exposed to the environment and inhaled (Winder, 2001).

Oxygen and air are used in many unit processes, from which the undissolved gases are let out. In pressure oxidation, oxygen is subjected to the autoclave for oxidation reactions; in cyanidation oxygen oxidizes the gold; and in cupric chloride leaching, oxygen is used to regenerate the cuprous ions back to cupric. In addition, air and oxygen is used in the cyanide detoxification processes. Almost pure oxygen was used in the simulation, thus only minor amount of nitrogen is released from the leaching unit. In addition, when working close to boiling temperatures, more water vapor could be emitted from the leaching units.

Sodium sulfite chemical is used for oxidation of CN⁻ in cyanidation or reduction of gold on silica in halogen leaching. This chemical produces SO₂ gas in excess to the processes, thus small emissions are possible. Sulfur dioxide produced in pressure oxidation can be used in gold reduction units (Lalancette *et al.*, 2015b).

In the halogen leaching and cupric chloride processes an evaporation unit is suggested for efficiently recycling the solutions in the process. The water vapor from evaporation unit is the most significant gaseous emission produced in the chloride processes. The water vapor could be condensed back to water in cooling towers and used as process water again.

5. Discussion

Simulation based LCA provides a powerful method for producing accurate environmental indicator estimations in early stages of process design. It is essential to produce early stage information for process designers, decision-makers and society. The simulation based LCA is intended to create accurate LCI data to improve the LCA of metallurgical processing. In addition, simulation enables evaluation of process performance for existing and development stage metallurgical processes. The results of this study show that HSC-Sim combined with GaBi LCA software is a suitable tool for assessing the metallurgical processes. This study has produced unbiased environmental indicator values, and evaluated the process performance of development stage cyanide-free gold leaching processes. In addition, this study presents, for the first time, evaluation of development stage gold processes and their environmental indicators.

The advantage of the methodology is that, the simulations are flexible, and can be adjusted for specific material characteristics or experimental data to validate extraction efficiencies etc. In addition, the simulations can be modified to specific conditions in the given plant, as well as to study the optimization of the process. In this work, mainly public literature was used to produce the simulations. The developed flowsheets were based on patented processes. During simulations, errors and challenges were observed. The flowsheets were modified based on the errors. For example, if the simulation was not able to reach the steady-state due to accumulation of water, modifications were made by adding unit processes such as evaporation or flows such as a solution bleed. In addition, the chemistry of the processes was modified based on errors and verified from literature, according to reported solution compositions. Scenario editor was used to evaluate different conditions in leaching systems. The selected scenarios investigated were based on available data. Simulations can be used to illustrate the aspects of full process mass balance, which are not commonly discussed in single patents or research papers. In this study, the process simulation revealed that in chloride processes the water balance is a real challenge – causing gold losses, need for excessive evaporation and bleeding solution out of process. The water balance would be manageable with exceptionally mild conditions in cupric chloride leaching, however, the material specific parameters and extraction efficiencies need to be verified in experimental work.

Currently, many LCA database creators use industry gathered data to produce average estimations of metallurgical processes. These averages are used to conduct many different LCA studies for different products that use metals. The geographical locations and country specific legislations affect the metallurgical industry. Thus, the data

gathered from all over the world to create database values can produce inaccuracy in further LCA studies using these databases. This is a problem where simulation can provide an alternative. General simulation flowsheets used for metallurgical processes can be provided by HSC-Sim, extending also to development-stage processes.

However, the simulation of development-stage processes for an unbiased part always depends on the published data. In addition, in the light of science, it can be debated that conducting LCA for incomplete processes is not possible. Nevertheless, in order to make more sustainable decisions for the future these type of methods need to be developed.

HSC-Sim has an LCA tool, which can be used to transfer the data to subsequent LCA software. In this study, the LCA software used is GaBi, but currently also openLCA can accept HSC-Sim data. Software development should focus on real time transfer of data to estimate environmental indicators. Scenario modelling can be conducted in LCA software. However, it would be beneficial if the same scenario modelling could be conducted in both HSC and LCA software at the same time. In addition, when moving towards simulation and LCA of multimetal and complex deposits, the allocation should be considered in the LCA. In processes, where multiple products are produced, the environmental impacts of the processing are necessary to divide between the products. Allocation method offers a solution to this problem. Currently, the HSC-Sim suggests only one reference product for the system, however there are usually several metals extracted from the same process.

5.1 Limitations of the research

The simulations presented in this study are solely based on literature parameter values. As stated in Chapter 2, the processing of gold ores is significantly dependent on the ore mineralogy, and the gold deposit will affect the selection of mining methods, extractive process optimization and performance.

The process simulations produced in this study describe a general and optimal processing of free-milling [I] and refractory type gold concentrates [II, IV]. However, each gold deposit should be studied experimentally in order to reveal the actual gold extraction efficiencies and mineralogy effect on unit processes. Experimental work is required to modify the simulation model, to predict the connection between solution conditions and gold extraction, which will also be individual for specific ore types. The gold speciation, liberation rate, and extraction efficiency require experimental examination for each specific material.

Furthermore, most of the published studies report development-stage leaching in laboratory scale, thus, the parameters used in the simulations are not optimized for an industrial scale process. Consequently, the mass balance can predict higher water and chemical consumptions. In addition, the chemicals are calculated as stoichiometric amounts in the simulation and the actual consumptions may vary depending on impurities etc. The actual chemistry in the processes can be much more complex. For example, in the cupric chloride process the presence of different forms of copper chloride complexes depends on the redox potential of the solution. The chemistry is simplified in the simulation, but in the real process, the presence of impurities affects the process conditions and actual dissolution reactions may vary.

Moreover, the steady state simulation does not take account the retention times and reaction times of concentrate in leaching. The gold leaching has been reported to be extremely fast in the chloride solutions, and full liberation of refractory type gold is assumed after pressure oxidation. The retention time and leaching kinetics will have an impact on the required reactor sizes. This will evidently affect the power consumption of the process, as significantly larger equipment is required for higher leaching times.

In the light of recent social and political unrest about environmental impacts of any products, processes or activities, it can be predicted that evaluation of environmental impacts should be conducted earlier. There is a need for such research that attempts to create early stage evaluations of development stage processes. This study here attempts to tackle this problem. However, the availability of data to be used in simulations has been limited. The cut-off inputs and outputs of the LCA are highlighted in Publications I, II and IV. These have been mainly related to the fact that suitable background processing has not been found from the database. In addition, the simulation models lack in accurate parameters for processing, especially regarding the chloride processes. This relates to the fact that industrial scale optimized parameter values have not been published for development stage processes. Thus, parameter estimations have been made based on values known to be used in similar unit processes. The transparency of process design is not yet at the level necessary to provide data for unbiased academic research.

The reliability and validity of the results obtained are difficult to evaluate as the methodology is not yet comprehensively standardized. This is mainly related to evaluation of data produced with HSC-Sim for LCA.

5.2 Recommendations for further work

As stated previously, the used primary raw material compositions and the simulated processes, pressure oxidation, cyanidation and halide leaching, were based on literature data. Thus, the next steps in research should be to use the simulation for existing materials. This would allow experimental validation (batch/continuous leaching, recovery of gold from solution, settling tests, filtration testing etc.) and modification of the simulations.

Furthermore, the adaption of simulation based LCA should be expanded to other technologies. There are many other cyanide-free process alternatives for replacements of cyanide. The research should start to include also other process options in addition to halide leaching alternatives. In larger scale, the simulation based LCA can be adapted to any metallurgical processing that is possible to be simulated by HSC-Sim.

In the search of sustainable respectability, LCA can be used as a tool to persuade skeptical public and more environmentally-conscious consumers, citizens and experts (Monhemius, 2006). Considering the fast development of new technologies and processes in the metallurgical industry, the early-stage assessment of environmental impacts is essential. Conducting LCA for processes not yet in commercial or operating stage, should be seen also as a marketing tool as well as a possibility to incorporate the sustainability aspect to the process design phase. Future processing that could

benefit from the use of simulation based LCA could be for example processing of multimetal deposits and secondary raw materials processing. According to recent estimations of metal markets, the demand of e.g. battery metals will increase significantly, which means that there is possibilities for new technologies. The environmental impacts of such technologies should be evaluated.

When considering the LCA part of this study, the next steps in research should be to improve the LCA results with larger databases. The LCA database used here did not include all the needed inputs of the processes, and some of the inputs were defined as cut-offs. The indicator values can be estimated more precisely, when adapting other databases. In addition, the system boundary in this study has been gate-to-gate for hydrometallurgical part of gold processing and should be in future expanded to consider mining and comminution, as well as any downstream processes for tailings and waste waters in order to research the gold extraction in cradle-to-gate approach. Extending the system boundary would make it interesting to research and compare the different extraction routes. As for tank leaching the highly energy consuming parts i.e. mining, and comminution are required and not needed in heap and in-situ leaching. The development of database directed at conduction of LCA for metallurgical processes is in need, as the early evaluation of environmental indicators should be adapted to all emerging technologies in future. However, the process selection in general will be affected by multiple different parameters, such economic performance, legislation and risk assessment of the processing, but to which simulation based LCA can contribute relevant information for environmental point of view. In addition, the evaluation of the processes should be increased in the level of sustainability assessment, taking into account also life cycle of costs (LCC) and social life cycle assessment (S-LCA).

6. Conclusions

The comparison of simulation models and environmental indicators for development stage cyanide-free hydrometallurgical processes, against those of the predominant cyanidation process, has been presented in this thesis. Future prospects of cyanide-free processes using chloride leaching media have been evaluated. This thesis evaluates the current stage, and still needed improvements, of the cyanide-free gold chloride processes to enable and support the development. Simulation based LCA has been used as an efficient tool to evaluate the process performance, to identify problems in process performance, and to estimate the indicator values based on mass balance data.

Simulation based LCA methodology does not only contribute to the evaluation of the possible flowsheet options and flowsheet development, but also creates accurate inventory data for performing LCA. In the simulations, it is possible to take into account the special conditions and sensitive adjustments of complex metallurgical processes. Simulations enable the modification of the same flowsheet to different conditions and for specific materials and their specific material characteristics. In addition, simulations can be modified according to experimental data. Thus, the LCI data provided by this method is produced precisely for the studied system and is based on hydrometallurgical expertise behind the simulations. The LCI data reported in the attached publications is valuable to researchers conducting LCA. The methodology offers essential information, as well as an understanding of the complexity of metallurgical processes, highlighting that each raw material is different. Therefore, the generalized inventory data available in commercial databases for metal production used to estimate environmental indicator values, does not take into account the uniqueness of metallurgical processes.

In this thesis, six simulation models were created using two different input materials (free-milling and refractory gold concentrate). In the preliminary study, the simulation based LCA was tested for carbon-in-pulp cyanidation process and chlorination. As chlorine gas is highly toxic, the results suggested that the technological transformation from chlorination to cyanidation was beneficial from environmental point of view [I]. However, in modern chloride processes the chlorides are introduced as salts, which mitigates the chlorine gas production and storage concerns. Thus, processes utilizing chloride salts present a competitive alternative for cyanidation. On this basis the more complicated processes were simulated, which provided an opportunity to assess more the metallurgical performance and the produced side-streams [II, IV].

Finally, the possibility of simultaneous oxidation of sulfide mineral pyrite and gold was investigated. Pyrite leaching kinetics were investigated by electrochemical method [III]. The direct cupric chloride leaching of refractory ores is possible, however, requires significantly higher leaching times, compared to direct chloride leaching of free-milling gold.

When considering the bigger picture of cyanidation vs. cyanide-free processing, this study remarks on the development points of cyanide-free chloride based processes [II, IV]. More development is needed to determine the best available technology for gold recovery from chloride solutions, as well as for optimization of water balance. These issues are still to be settled for cyanide-free alternatives, as cyanidation continues to have the benefit of stable metallurgical performance and advantage of simultaneous leaching and recovery of gold on activated carbon. In addition, due to higher recovery of gold in cyanidation also the environmental indicators show lower values. However, as more complex nature ores need to be treated, the environmental indicators should be estimated for specific cases. The value of this work is not only the LCI data created for development stage processes and the produced simulations, but also to raise awareness to the methodology that should be incorporated to any feasibility study in future.

Finally, the acceptance of any new technology requires courage and willingness to make a change. The challenge is to convince the decision-makers in the community and company level, experts, and financial partners, as well as the common public. The methodology used in this study can provide the essential information to back up the transfer to more sustainable alternatives, not only in gold industry but also in any metallurgical processing.

References

- Abe, Y., Hosaka, H., Takebayashi, K., Ishiguro, Y., Yoshimura, A., 2008. Process of Leaching gold. Patent No. US 20092041735 A1.
- Adams, M., 2016. Chloride as an alternative Lixiviant to Cyanide for Gold Ores. In: Adams, Mike D. (Ed.), *Gold Ore Processing, Project Development and Operations*. Elsevier B.V. pp. 525-531.
- Afenya, P.M., 1991. Treatment of carbonaceous refractory gold ores. *Minerals Engineering*, 4(7-11), pp.1043-1055.
- Ahtiainen, R., & Lundström M., 2019. Cyanide-free gold leaching in exceptionally mild chloride solutions. *J. Clean. Prod.*, 234, pp. 9-17. <https://doi.org/10.1016/j.jclepro.2019.06.197>.
- Althaus, H. J., & Classen, M., 2005. Life cycle inventories of metals and methodological aspects of inventorying material resources in ecoinvent (7 pp). *The International Journal of Life Cycle Assessment*, 10(1), pp. 43-49.
- de Andrade Lima, L.R.P., & Hodouin, D., 2006. Simulation study of the optimal distribution of cyanide in a gold leaching circuit. *Minerals Engineering*, 19(13), pp. 1319-1327.
- Asselin, E., & Shaw, R., 2016. Developments in arsenic management in the gold industry. In Adams, Mike D. (Ed.) *Gold Ore Processing, Project Development and Operations*. Elsevier B.V. pp. 739-751.
- Aylmore, M. G., & Muir, D.M., 2001. Thiosulfate leaching of gold—a review. *Minerals engineering*, 14(2), pp. 135-174.
- Aylmore, M.G., 2001. Treatment of a refractory gold—copper sulfide concentrate by copper ammoniacal thiosulfate leaching. *Minerals Engineering*, 14(6), pp. 615-637.
- Aylmore, M.G., 2016a. Alternative lixivants to cyanide for leaching gold ores. In: Adams, Mike D. (Ed.), *Gold Ore Processing, Project Development and Operations*. Elsevier B.V. pp. 477-484.
- Aylmore, M.G., 2016b. Thiosulfate as an alternative lixiviant to cyanide for gold ores. In: Adams, Mike D. (Ed.), *Gold Ore Processing, Project Development and Operations*. Elsevier B.V., pp. 485-523.

- Baghalha, M., 2007. Leaching of an oxide gold ore with chloride/hypochlorite solutions. *International Journal of Mineral Processing*, 82(4), pp.178-186.
- Beale, G., 2016. Water Management in Gold Ore Processing. In: Adams, Mike D. (Ed.), *Gold Ore Processing, Project Development and Operations*. Elsevier B.V., pp. 677-708.
- Bowell, R.J., 2004. A review of sulfate removal options for mine waters. In *Proceedings of Mine Water 2004 – Process, Policy and Progress*; Jarvis, A.P. Dudgeon, B. A., Younger, P. L., Eds.; Newcastle University: Newcastle, UK, pp. 75-88.
- Brierley, J.A. & Brierley, C.L., 2001. Present and future commercial applications of biohydrometallurgy. *Hydrometallurgy*, 59(2-3), pp. 233-239.
- Chen, T.T., & Cabri, L.J., 1986. Mineralogical overview of iron control in hydrometallurgical processing. *Iron Control in Hydrometallurgy*. Ellis Horwood, England, pp. 19-55.
- Cunningham, S.A., 2005. Incident, accident, catastrophe: cyanide on the Danube. *Disasters*, 29(2), pp. 99-128.
- Craig D.N., & Vinal G.W., 1939. Solubility of lead sulfate in solutions of sulfuric acid, determined by dithizone with a photronic cell. *J.Res.Natl.Bur.Stand.* 22, pp. 55-70.
- Curran, M.A., 2012. *Life cycle assessment handbook: A guide for environmentally sustainable products*. Salem, Mass.: Hoboken, N.J.: Scrivener, Wiley.
- Dai, X., Breuer, P., Hewitt, D., & Bergamin, A., 2013. Thiosulfate Process for Treating Gold Concentrates. In *World Gold 2013 Conference*, Brisbane (pp. 61-70).
- Diaz, M.A., Kelsall, G.H., & Welham, N.J., 1993. Electrowinning coupled to gold leaching by electrogenerated chlorine: I. Au (III) Au (I)/Au kinetics in aqueous Cl₂/Cl⁻ electrolytes. *J. Electroanal. Chem.*, 361(1-2), pp. 25-38.
- Dobrosz-Gómez, I., García, B.D.R., GilPavas, E., & García, M.Á.G., 2017. Kinetic study on HCN volatilization in gold leaching tailing ponds. *Minerals Engineering*, 110, pp. 185-194.
- Eksteen, J. & Taylor, A. 2019. ALTA 2019. Fit for Purpose Leaching Systems Panel Discussion Notes. In: *ALTA2019, 23.5.2019 Perth, Australia*.

- Elsner, L., 1846. Beobachtungen über das Verhalten regulinischer Metalle in einer wässrigen Lösung von Cyankalium. *Advanced Synthesis & Catalysis*, 37(1), pp.441-446.
- Ferron, C., Fleming, C., Dresinger, D., & O'Kane, T., 2003. Chloride as an alternative to cyanide for the extraction of gold – going full circle?. In: Proceedings of Hydrometallurgy, Fifth International Conference in Honor of Professor Ian Ritchie. Vol. 1. Leaching and solution purification; 2003 Aug 24–27, Vancouver. pp. 89–104.
- Finkelstein, N.P., Hoare, R.M., James, G.S. & Howat, D.D., 1966. An Aqueous Chlorination Process for the Treatment of Merrill Slimes and Gravity Concentrates from Gold Ores. Part 1: A Study of the Chemistry of the Process and a Report of Laboratory Test Work. *Journal of the Southern African Institute of Mining and Metallurgy*, 67(5), pp. 196-215.
- Fleming, C.A., 1992. Hydrometallurgy of precious metals recovery. *Hydrometallurgy*, 30, 127-162. Elsevier Science Publishers B.V., Amsterdam.
- Fleming, C.A., Dreisinger, D., & O'Kane, P. T., 2001. U.S. Patent No. 6,315,812. Washington, DC: U.S. Patent and Trademark Office.
- Fleming, C., Geldart, J., Blatter, P., Cousin, P., Robitaille, J., Young, C.A., Taylor, P.R., Anderson, C.G. & Choi, Y., 2008. Flowsheet development for Agnico Eagle's refractory gold Kittila project in Finland, In Proceedings 6th International Symposium of Hydrometallurgy 2008, Young, C.A., Taylor, P.R., Anderson, C.G., and Choi, Y., Eds., pp. 404-413.
- Fleuriault, C.M., Anderson, C. G., & Shuey, S., 2016. Iron phase control during pressure oxidation at elevated temperature. *Minerals Engineering*, 98, pp. 161-168.
- Forsström, O., 2016. Gold dissolution in chloride solution. Master's Thesis. Aalto University.
- Frankenthal, R.P. & Siconolfi, D.J., 1982. The anodic corrosion of gold in concentrated chloride solutions. *J. Electrochem. Soc.*, 129(6), pp. 1192-1196.
- Fraser, K.S., Walton, R.H. & Wells, J.A., 1991. Processing of refractory gold ores. *Minerals Engineering*, 4 (7-11), pp.1029-1041.
- Ghodrat, M., Rhamdhani, M.A., Brooks, G., Rashidi, M. & Samali, B., 2017. A thermodynamic-based life cycle assessment of precious metal recycling out of waste printed circuit board through secondary copper smelting. *Environmental Development*, 24, pp. 36-49.
- Greenwald, N. & Bateman, P., 2016. The International Cyanide Management Code: Ensuring Best Practice in the Gold Industry. In: Adams,

- Mike D. (Ed.), Gold Ore Processing, Project Development and Operations. Elsevier B.V. pp. 191-206.
- Gökelman, M., Birich, A., Stopic, S., & Friedrich, B., 2016. A review on alternative gold recovery reagents to cyanide. *Journal of Materials Science and Chemical Engineering*, 4(8), pp. 8-17.
- Haapalainen, M. & Miettinen, V., 2016. Method for gold recovery from solution. World Intellectual Property Organization. WO 2016/181039 A1.
- Haapalainen, M., 2018. Recovery of gold from solution. U.S. Patent Application, N.O. US 2018/0073103.
- Haavanlammi, L., Hyvärinen, O., Tiihonen, M. & Tontti, R., 2010. Method for recovering gold halide leaching. European Patent Office. WO 2007/093666.
- Hagelüken, C. & Meskers, C.E., 2010. Complex life cycles of precious and special metals. Linkages of Sustainability, 4. Strüngmann Forum Report. pp. 163-197.
- Hammerschmidt, J., Güntner, J., Kerstiens, B. & Charitos, A., 2016. Roasting of gold ore in the circulating fluidized-bed technology. In Adams, Mike D. (Ed.) Gold Ore Processing, Project Development and Operations. Elsevier B.V. pp. 393-409.
- Han, K.N. & Soderstrom, M., 2019. Chapter 10.14 Solvent Extraction. In: Dunne, R. C. Kawatra, S. Komar Y., Courtney A., 2019. SME Mineral Processing & Extractive Metallurgy Handbook. (pp. 1347-1358). Society for Mining, Metallurgy, and Exploration (SME). Retrieved from: <https://app.knovel.com/hotlink/pdf/id:kt011Y5K7/sme-mineral-processing/solvent-ex-references>
- Haque, N. & Norgate, T., 2014. The greenhouse gas footprint of in-situ leaching of uranium, gold and copper in Australia. *Journal of Cleaner Production*, 84, pp. 382-390.
- Haque, K.E., 1987. Gold leaching from refractory ores—literature survey. *Mineral Processing and Extractive Metallurgy Review*, 2(3), pp. 235-253.
- Harris, D.C., 1990. The mineralogy of gold and its relevance to gold recoveries. *Mineralium Deposita*, 25(1), S3-S7.
- Harris B. & White, C., 2014. Process for the recovery of gold from an ore in chloride medium with nitrogen species. Patent No. US 8894740 B2. USA. pp.11.
- Hayes, P.C., 1985. Process selection in extractive metallurgy. Hayes Publishing Co. Brisbane Australia. ISBN 0-9589197-0-4

- Henley, K. J., 1975. Gold-ore mineralogy and its relation to metallurgical treatment. *Minerals Sci. Eng.*, 7(4), pp. 284-312.
- Hewitt, D., Breuer, P. & Jeffrey, C., 2012. Cyanide detoxification of gold cyanidation tails and process streams. *Mineral Processing and Extractive Metallurgy*, 121(4), pp. 228-236.
- Hilson, G. & Monhemius, A., 2006. Alternatives to cyanide in the gold mining industry: what prospects for the future? *Journal of Cleaner Production*, 14, pp. 1158-1167.
- Hughes, H.C. & Linge, H.G., 1989. The kinetics of gold loading from gold (III) chloride solution onto fresh activated coconut carbon. *Hydrometallurgy*, 22(1-2), pp. 57-65.
- Iglesias, N. & Carranza, F., 1994. Refractory gold-bearing ores: a review of treatment methods and recent advances in biotechnological techniques. *Hydrometallurgy*, 34(3), pp. 383-395.
- ISO 14040. (2006) Environmental management, Life Cycle Assessment, Principles and framework. Finnish Standards Association SFS. pp. 49.
- ISO 14044. (2006) Environmental management, Life Cycle Assessment, Requirements and Guidelines. Finnish Standards Association SFS. pp. 96.
- Jaatinen, T., 2011. Bio-oxidation and Bioleaching of Arsenic-containing and Refractory Gold Concentrates. Master's Thesis. Tampere University of Technology. pp. 104.
- Jeffrey, M.I., Breuer, P.L. & Choo, W.L., 2001. A kinetic study that compares the leaching of gold in the cyanide, thiosulfate, and chloride systems. *Metallurgical and Materials Transactions B*, 32(6), pp.979-986.
- Johnson, C.A., 2015. The fate of cyanide in leach wastes at gold mines: An environmental perspective. *Applied Geochemistry*, 57, pp. 194-205.
- Kiipula, K., 2016. Treatment of sulfate in mine waters: Recycling perspective. Master's Thesis. Aalto University. Available: <http://urn.fi/URN:NBN:fi:aalto-201609224177>
- Kianinia, Y., Khalesi, M.R., Abdollahy, M., Hefter, G., Senanayake, G., Hnedkovsky, L., Khodadadi Darban, A. & Shahbazi, M., 2018. Predicting cyanide consumption in gold leaching: A kinetic and thermodynamic modeling approach. *Minerals*, 8(3), pp. 110.
- Klöpffer, W. & Grahl, B., 2014. Life cycle assessment: A guide to best practice. Weinheim an der Bergstrasse, Germany: Wiley-VCH.

- Konyratbekova, S.S., Baikonurova, A. & Akcil, A., 2015. Non-cyanide leaching processes in gold hydrometallurgy and iodine-iodide applications: a review. *Mineral Processing and Extractive Metallurgy Review*, 36(3), pp. 198-212.
- Kotiranta, T., Horn, S., Jansson, K. & Reuter, M.A., 2015. Towards a “minimum impact” copper concentrator: a sustainability assessment. Procemin Symposium, 15th International Minerals Processing Conference, October 21J-23, Santiago, Chile.
- Kudryk, V. & Kellogg, H.H., 1954. Mechanism and rate-controlling factors in the dissolution of gold in cyanide solution. *The Journal of the Minerals, Metals & Materials Society (TMS)*, 6(5), pp. 541-548.
- La Brooy, S.R., Linge, H.G. & Walker, G.S., 1994. Review of gold extraction from ores. *Miner. Eng.*, 7(10), pp. 1213-1241.
- Laitos, J. G., 2012a. Cyanide, mining, and the environment. *Pace Envtl. L. Rev.*, 30, i.
- Laitos, J. G., 2012b. The current status of cyanide regulations. *Engineering and Mining Journal*, 213(2), 34.
- Lalancette, J., Dubreuil, B. & Lemieux, D., 2015a. Closed loop method for gold and silver extraction by halogens. U.S. Patent No 9,206,492. pp. 7.
- Lalancette, J. Dubreuil, B. & Lemieux, D., 2015b. Method and system for gold recovery. U.S. Patent No 9,206,491. pp. 4.
- Lampinen, M., Seisko, S., Forsström, O., Laari, A., Aromaa, J., Lundström, M. & Koironen, T., 2017. Mechanism and kinetics of gold leaching by cupric chloride. *Hydrometallurgy*, 169, pp. 103-111.
- Latva-Kokko, M., Hirsi, T., Ritasalo, T., & Tiihonen, J., 2015. Improving the process performance of gold cyanide leaching reactors. In *World Gold Conference 2015–Proceedings* pp. 183-193.
- Lemieux, D., Dubreuil, B. & Lalancette J.-M., 2014. Nichromet Cyanide-free Process for Gold Extraction. 23rd World Mining Congress. 11-15th, August, Montreal, Canada.
- Leppinen, J., Hyvärinen, O., Heimala, S., Palosaari, V. & Hämäläinen, M., 2010. Method for the recovery of gold from sulphide concentrate. U.S. Patent No. 7,785,395. Washington, DC: U.S. Patent and Trademark Office.
- Levenspiel, O. 1999. *Chemical reaction engineering*, 3rd ed. John Wiley and Sons, New York, N.Y. ISBN 0-471-25424-X

- Li, J., & Miller, J.D., 2006. A review of gold leaching in acid thiourea solutions. *Mineral Processing and Extractive Metallurgy Review*, 27(3), pp. 177-214.
- Liddell, K.S., 2003. Hydrometallurgical treatment process for extraction of platinum group metals obviating the matte smelting process. U.S. Patent No. 6,579,504. Washington, DC: U.S. Patent and Trademark Office.
- Liddell, K.S., Adams, M.D., Smith, L.A., & Muller, B., 2019. Kell hydrometallurgical extraction of precious and base metals from flotation concentrates—Piloting, engineering, and implementation advances. *J.S. Afr. Inst. Min. Metall.* vol.119, 6, pp. 585-594.
- Llamas, A.A., Delgado, A.V., Capilla, A.V., Cuadra, C.T., Hultgren, M., Peltomäki, M., Roine, A., Stelter, M. & Reuter, M.A., 2019. Simulation-based exergy, thermo-economic and environmental footprint analysis of primary copper production. *Miner. Eng.*, 131, pp. 51-65.
- Lundström, M., Aromaa, J., Forsén, O., Hyvärinen & O., Barker, M. H., 2005. Leaching of chalcopyrite in cupric chloride solution. *Hydrometallurgy*, 77(1-2), pp. 89-95.
- Lundström, M., Aromaa, J. & Forsén, O., 2009a. Redox potential characteristics of cupric chloride solutions. *Hydrometallurgy*, 95(3-4), pp. 285-289.
- Lundström, M., Liipo, J., Karonen, J. & Aromaa, J., 2009b. Dissolution of six sulfide concentrates in the Hydrocopper environment. In *Proceedings of the South African Institute of Mining and Metallurgy Base Metals Conference, Kasane, Botswana.* pp. 27-31.
- Lundström, M., Ahtiainen, R. & O'Callaghan, J. 2019. Method for recovering gold. U.S. Patent Application No. 15/770,534.
- MacArthur, J.S., Forrest, R.W. & Forrest W., 1889. Process of obtaining gold and silver from ores. Letters Patent No. 403,202. Unites States Patent Office.
- Marchbank, A.G., Thomas, K.G., Dreisinger, D. & Fleming, C., 1996. Gold recovery from refractory carbonaceous ores by pressure oxidation and thiosulfate leaching. U.S. Patent No 5,536,297. pp. 17.
- Marsden. J.O. & House. I.C. 2006. *The Chemistry of Gold Extraction*. Second ed. Society for Mining, Metallurgy, and Exploration, Inc. Littleton. ISBN-13:978-0-87335-240-6.
- Mason, P.G., Wicks, F.D. & Gathje, J.C., 1985. Process for the recovery of gold from refractory ores by pressure oxidation. U.S. Patent No 4,552,589. pp. 10.
- McDonald, G.W., Saud, A., Barger, M.S., Koutsky, J.A. & Langer, S.H., 1987. The fate of gold in cupric chloride hydrometallurgy. *Hydrometallurgy*, 18(3), pp. 321-336.

- McQuiston F.W. & Shoemaker R.S., 1975. Gold and silver cyanidation plant practice. Volume 1. SME-AIME monograph Salt Lake City UT:SME-AIME
- Miettinen, V., Haapalainen, M., Ahtiainen, R. & Karonen, J., 2013. Development of gold chloride process. Proceedings of ALTA2013, Perth Australia, pp. 187-203.
- Miettinen, V., Ahtiainen, R., Valkama, K., Paatero, E., Hietala, K. & Haapalainen, M., 2016. Method of preparing a gold-containing solution and process arrangement for recovering gold and silver. U.S. Patent Application No. 14/787,404.
- Miller, J.D., Wan, R. & Díaz, X., 2016. Preg-robbling gold ores. Gold Ore Processing (Second Edition). Elsevier, pp. 885-907.
- Monhemius, J., 2006. Editorial, Section 1: life cycle and process analysis in the mining industry. Journal of Cleaner Production, 14, pp. 1040-1041.
- Moran R., 1998. Cyanide uncertainties: observations on the chemistry, toxicity, and analysis of cyanide in mining-related waters. Washington: Mineral Policy Center. MPC issue paper no. 1.
- Moyes, J. & Houllins, F., 2010. Recovering metals from sulfide materials. Patent No. US 7858056 B2. USA.
- Mudder, T.I., & Botz, M.M. 2004. Cyanide and society: a critical review. European Journal of Mineral Processing and Environmental Protection, 4(1), pp. 62-74.
- Multani, R.S., Feldmann, T., & Demopoulos, G.P. 2016. Antimony in the metallurgical industry: a review of its chemistry and environmental stabilization options. Hydrometallurgy, 164, pp. 141-153.
- Nagpal, N.K., Levy, D.A. & MacDonald, D.D., 2003. Ambient Water Quality Guidelines for Chloride: Overview Report. Prepared pursuant to Section 2(e) of the Environment Management Act, 1981. Government of British Columbia, Ministry of Environment.
- Nesbitt, C.C., Milosavljevic, E.B. & Hendrix, J.L., 1990. Determination of the mechanism of the chlorination of gold in aqueous solutions. Industrial & engineering chemistry research, 29(8), pp. 1696-1700.
- Nicol, M.J. 1976. An electrochemical and kinetic investigation of the behaviour of gold in chloride solutions, III. The gold (III)–gold (I) reaction on platinum and the disproportionation of gold (I). Nat. Inst. Metall.[Rep. S. Africa], Mineral Process Chem. Div. Rept. 1846.
- Nicol, M.J., 1980. The anodic behaviour of gold. Gold Bulletin, 13(2), pp. 46-55.

- Norgate, T. & Haque, N., 2012. Using life cycle assessment to evaluate some environmental impacts of gold production. *Journal of Cleaner Production*, 29, pp. 53-63.
- Nyberg, J., 2019. Challenges for Non-Ferrous industry - Less waste and recovering more metals. *Erzmetall*, 72(3). Presented as Plenary Lecture in European Metallurgical Conference, EMC2019 held from 23 to 26 June in Düsseldorf, Germany.
- Oraby, E.A. & Eksteen, J.J., 2014. The selective leaching of copper from a gold-copper concentrate in glycine solutions. *Hydrometallurgy*, 150, pp. 14-19.
- Oraby, E.A. & Eksteen, J.J., 2015. The leaching of gold, silver and their alloys in alkaline glycine-peroxide solutions and their adsorption on carbon. *Hydrometallurgy*, 152, pp. 199-203.
- Outotec, 2019. HSC Chemistry 9.9.2.3 <https://www.outotec.com/products/digital-solutions/hsc-chemistry/>
- Paatero, E. & Haapalainen, M. 2015. Method for recovering gold by solvent extraction. U.S. Patent No. 8,926,730. Washington, DC: U.S. Patent and Trademark Office.
- Pangum, L.S. & Browner, R.E., 1996. Pressure chloride leaching of a refractory gold ore. *Minerals Engineering*, 9(5), pp. 547-556.
- Parisien-La Salle, J.C., 2012. In-situ Adsorption of Gold (III) Chloride on Activated Carbon Under Pressure Oxidation-leaching Conditions (Doctoral dissertation, McGill University Libraries).
- Pell, R., Wall, F., Yan, X., Li, J., & Zeng, X., 2019. Mineral processing simulation based-environmental life cycle assessment for rare earth project development: A case study on the Songwe Hill project. *Journal of environmental management*, 249, 109353.
- Pöyry, 2016. Rikastamon syötemäärän sekä NP rikastushiekan varastointikapasiteetin kasvattaminen Kittilän kultakaivoksella. Agnico Eagle Finland Oy. Environmental impact assessment, EIA. Available at: https://www.ymparisto.fi/fi-FI/Asiointi_luvat_ja_ymparistovaikutusten_arviointi/Ymparistovaikutusten_arviointi/YVAhankkeet/Suurikuusikon_kaivoksen_tuotanto_ja_varastointimaaran_kasvattaminen Accessed: 29.11.2019.
- Reuter, M.A., 1998. The simulation of industrial ecosystems. *Minerals Engineering*, 11(10), pp. 891-918.
- Reuter, M.A., Van Schaik, A. & Gediga, J., 2015. Simulation-based design for resource efficiency of metal production and recycling systems: Cases-

- copper production and recycling, e-waste (LED lamps) and nickel pig iron. *Int. J. LCA*, 20(5), pp. 671-693.
- Ritcey, G.M., 1980. Crud in solvent extraction processing—a review of causes and treatment. *Hydrometallurgy*, 5(2-3), pp. 97-107.
- Ritcey, G.M., 2005. Tailings management in gold plants. *Hydrometallurgy*, 78(1-2), pp. 3-20.
- Rohner, P. & Millard, M., 2016. Treatment of Antimonial Gold Ores. In: Adams, Mike D. (Ed.), *Gold Ore Processing, Project Development and Operations*. Elsevier B.V. pp. 927-933.
- Rose, T.K., 1898. *The metallurgy of gold* (Vol. 2). C. Griffin, limited.
- Scheidema, M., Reuter, M. & Roine, A., 2016. Life cycle assessment of metallurgical processes based on physical flowsheet models. In: Kirchain, R.E., Blanpain, B., Meskers, C., Olivetti, E., Apelian, D., Howarter, J., Kvithyld, A., Mishra, B., Neelameggham, N.R., Spangenberg, J. (Eds.), *REWAS 2016: towards Materials Resource Sustainability*. Springer International Publishers, Cham, pp. 179-185.
- Schnabel, C., 1921. *Handbook of metallurgy*. 3rd ed. rev. London: Macmillan and co., limited.
- Segura-Salazar, J., Lima, F.M., & Tavares, L.M., 2019. Life Cycle Assessment in the minerals industry: Current practice, harmonization efforts, and potential improvement through the integration with process simulation. *Journal of Cleaner Production* 232, pp. 174-192.
- Seisko, S., Aromaa, J. & Lundström, M., 2019. Features affecting the cupric chloride leaching of gold. *Mineral Engineering*, 137, pp. 94-101.
- Senanayake, G., 2004. Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications. *Minerals Engineering*, 17(6), pp. 785-801.
- Sparrow, G.J. & Woodcock, J.T., 1995. Cyanide and other lixiviant leaching systems for gold with some practical applications. *Mineral Processing and Extractive Metallurgy Review*, 14(3-4), pp. 193-247.
- Sun, T.M., & Yen, W.T., 1993. Kinetics of gold chloride adsorption onto activated carbon. *Minerals engineering*, 6(1), pp. 17-29.
- Swash, P.M., & Monhemius, A.J., 1998. The Scorodite Process: A technology for the disposal of arsenic in 21st century. *Effluent treatment in the Mining Industry*. University of Concepción. p. 389.

- Syed, S., 2012. Recovery of gold from secondary sources—a review. *Hydrometallurgy*, 115, pp.30-51.
- Teir, S., Kotiranta, T., Pakarinen, J. & Mattila, H.P., 2016. Case study for production of calcium carbonate from carbon dioxide in flue gases and steelmaking slag. *Journal of CO₂ Utilization*, 14, pp.37-46.
- thinkstep, 2019. GaBi software—System and Database for Life Cycle Engineering. Copyright 1992-2016 thinkstep AG.
- Thomas, K.G. & Pearson, M.S., 2016. Pressure oxidation overview. In: Adams, Mike D. (Ed.), *Gold Ore Processing, Project Development and Operations*. (Second Edition). B.V Elsevier, pp. 341-358.
- Thomas, K.G., Pieterse, H.J., Brewe, R.E. & Fraser, K.S., 1990. Process for recovery of gold from refractory ores. U.S. Patent No 5,071,477. pp. 18.
- Tran, T., Lee, K. & Fernando, K., 2001. Halide as an alternative lixiviant for gold processing – an update. Cyanide: Social, Industrial and Economic Aspects as held at the 2001 TMS Annual Meeting. 12-15th, February, New Orleans, USA. pp. 501-508.
- Ubal dini, S., Vegliò, F., Fornari, P. & Abbruzzese, C., 2000. Process flow-sheet for gold and antimony recovery from stibnite. *Hydrometallurgy*, 57(3), pp. 187-199.
- United Nations Environmental Programme, 2000. Report: Cyanide Spill at Baia Mare Romania: UNEP/OCHA Assesment Mission, Geneva, p. 56.
- US EPA, 2019. National Recommended Water Quality Criteria. Accessed: 3.10.2019. Available: <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table>
- de Waal, S.A., 1982. A Literature Survey of the Metallurgical Aspects of Mineral in Witwatersrand ores. Mintek Report M37. Randburg. South Africa: Mintek. p. 47.
- Valtioneuvoston asetus kaatopaikoista. 202/2006. Available: <https://www.finlex.fi/fi/laki/alkup/2006/20060202#Pidp446590576>
- Wahlström, M., Laine-Ylijoki, J., Vestola, E., Vaajasaari, K., & Joutti, A., 2006. Jätteiden kaatopaikkakelpoisuuden toteaminen. Ympäristöhallinnön ohjeita 2. Ympäristöministeriö, Ympäristönsuojeluosasto. Edita Prima Oy, Helsinki. ISBN 952-11-2335-4 (PDF).
- Winder, C., 2001. The toxicology of chlorine. *Environmental research*, 85(2), pp. 105-114.

Yen, W.T., Pindred, R.A. & Lam, M.P., 1990. Hypochlorite leaching of gold ore. *Hydrometallurgy Fundamentals, Technology and Innovations*, The Society for Mining, Metallurgy and Exploration, Inc., Littleton, CO, USA, pp. 415-436.

Zhang, Y., Fang, Z. & Muhammed, M., 1997. On the solution chemistry of cyanidation of gold and silver bearing sulphide ores. A critical evaluation of thermodynamic calculations. *Hydrometallurgy*, 46(3), pp. 251-269.

Zhao, H., Chang, J., Boika, A. & Bard, A. J. 2013. Electrochemistry of High Concentration Copper Chloride Complexes. *Analytical Chemistry* 85, pp. 7696–7703.

Zhou, J. & Gu, Y., 2016. Geometallurgical Characterization and Automated Mineralogy of Gold Ores. In: Adams, Mike D. (Ed.), *Gold Ore Processing, Project Development and Operations*. Elsevier B.V. pp. 95-111.

Appendices

Appendix 1. HSC-Sim flowsheet of simulated processes; pressure oxidation, cyanidation, cyanide recovery, halogen leaching and cupric chloride leaching.

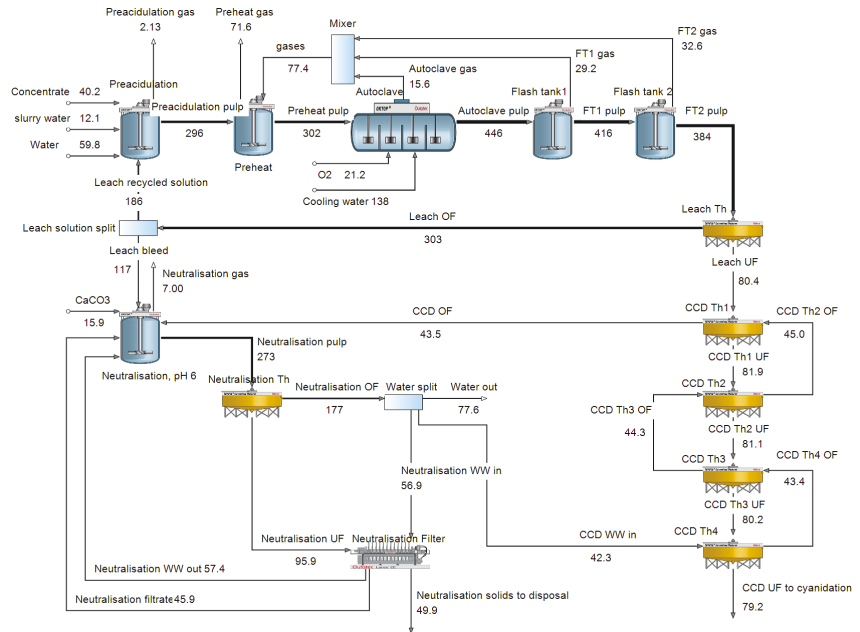


Figure 13. The HSC-Sim flowsheet of pressure oxidation, showing mass balance (t/h) for each flow. [II]

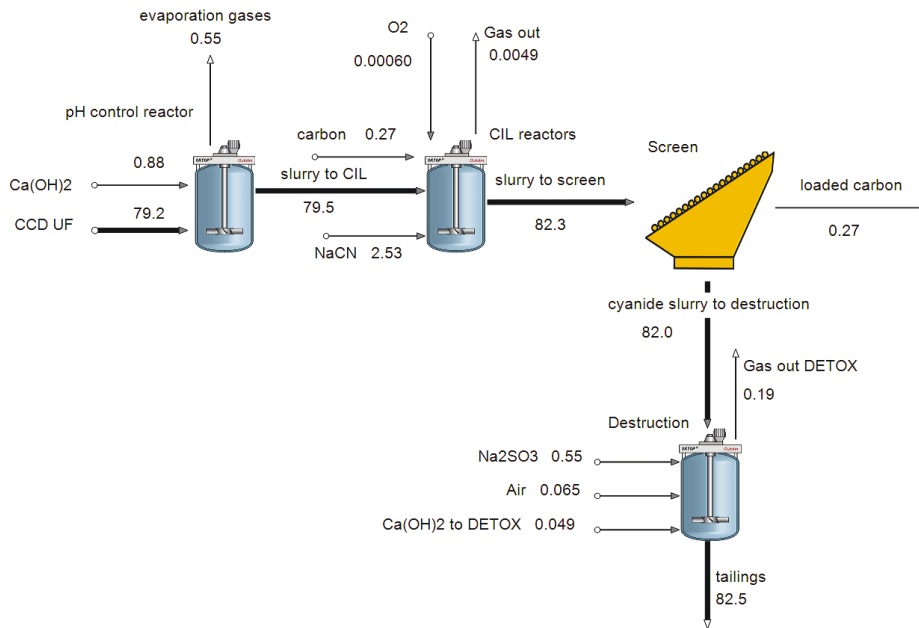


Figure 14. The cyanidation simulation flowsheet for pressure oxidized refractory gold concentrate, showing mass balance (t/h) for each flow. [II]

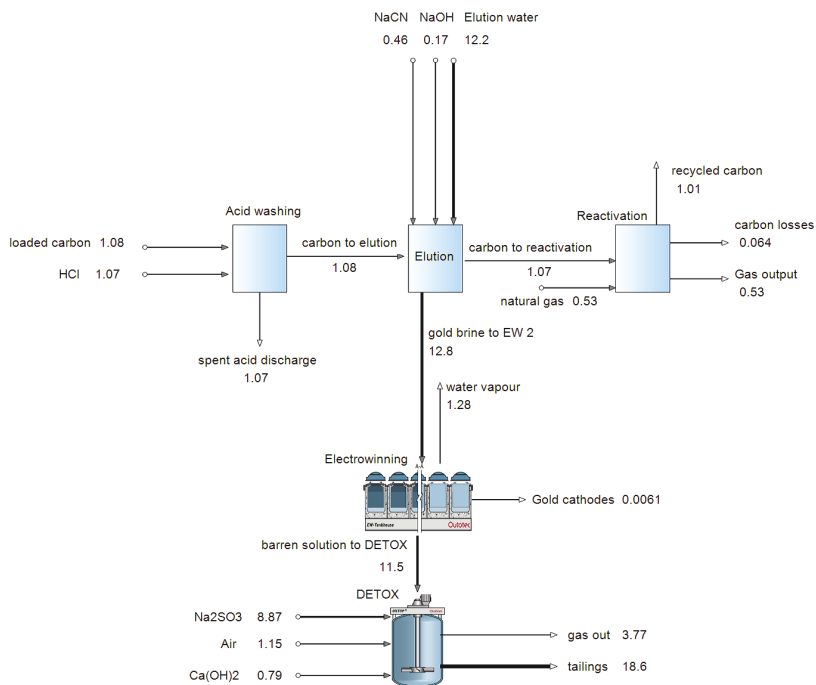


Figure 15. The flowsheet of gold recovery from activated carbon originating from cyanidation, showing mass balance (t/h) for each. [II]

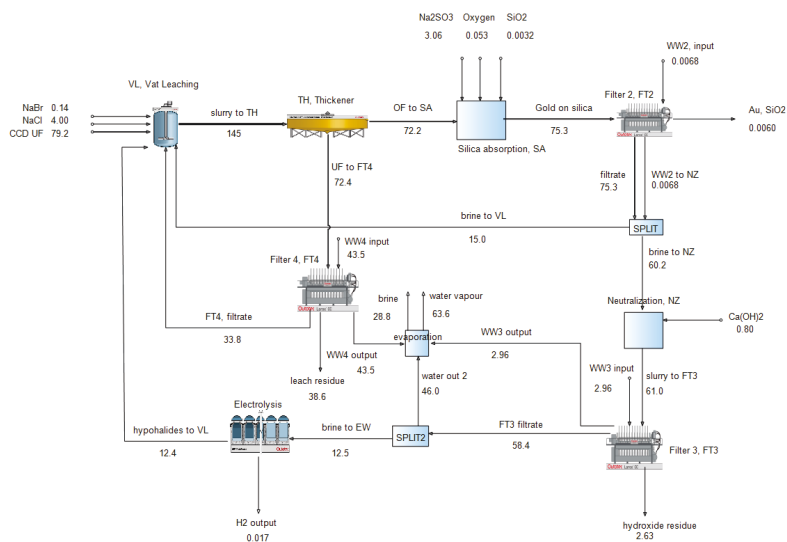


Figure 16. The flowsheet of halogen leaching simulation for pressure oxidized refractory gold concentrate, showing mass balance (t/h) for each flow. [11]



ISBN 978-952-60-3805-6 (printed)
ISBN 978-952-60-3806-3 (pdf)
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)

Aalto University
School of Chemical Engineering
Department of Chemical and Metallurgical Engineering
www.aalto.fi

**BUSINESS +
ECONOMY**

**ART +
DESIGN +
ARCHITECTURE**

**SCIENCE +
TECHNOLOGY**

CROSSOVER

**DOCTORAL
DISSERTATIONS**