

Development of chloride-based processing of free-milling and refractory gold ores and concentrates

Riina Ahtiainen



Development of chloride-based processing of free-milling and refractory gold ores and concentrates

Riina Ahtiainen

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 Aluminium of the school on 9 October 2020 at 3 pm.

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 advisor

Assistant Professor Mari Lundström, Aalto University, Finland

Preliminary examiners

Professor Michael L. Free, The University of Utah, The United States

Associate Professor James Vaughan, The University of Queensland, Australia

Opponent

Professor David Dreisinger, The University of British Columbia, Canada

Aalto University publication series

DOCTORAL DISSERTATIONS 129/2020

© 2020 Riina Ahtiainen

ISBN 978-952-64-0014-3 (printed)

ISBN 978-952-64-0015-0 (pdf)

ISSN 1799-4934 (printed)

ISSN 1799-4942 (pdf)

<http://urn.fi/URN:ISBN:978-952-64-0015-0>

Images: Vili Hyvärinen

Unigrafia Oy

Helsinki 2020

Finland



Printed matter
4041-0619

Author

Riina Ahtiainen

Name of the doctoral dissertation

Development of chloride-based processing of free-milling and refractory gold ores and concentrates

Publisher School of Chemical Engineering**Unit** Department of Chemical and Metallurgical Engineering**Series** Aalto University publication series DOCTORAL DISSERTATIONS 129/2020**Field of research** Processing of Materials**Manuscript submitted** 5 June 2020**Date of the defence** 9 October 2020**Permission for public defence granted (date)** 26 August 2020**Language** English **Monograph** **Article dissertation** **Essay dissertation****Abstract**

Cyanide leaching has dominated gold hydrometallurgical processing for over 100 years. Cyanide has many techno-economic advantages: relatively low cost, high gold extraction, and selectivity for gold. However, its toxicity and recent environmental accidents as well as the limited ability to treat complex raw materials have increased the interest towards cyanide-free gold processing. Halides are one of the most promising alternatives for cyanide, and gold chlorination was industrially used already in the 1800s for gold recovery. The advantages of chloride leaching using copper(II) or iron(III) as oxidant are fast leaching kinetics and the possibility to process more complex raw materials. In this dissertation, chloride and chloride-bromide based processing of free-milling gold ore as well as refractory and double refractory gold concentrates was investigated. The work aimed at examining leaching phenomena such as preg-robbing, as well as developing mild chloride leaching processes for free-milling ores. In addition, a direct chloride leaching route for refractory gold concentrates was studied without separate pre-oxidation.

Gold chloride-bromide leaching was found to have a relatively strong tendency for preg-robbing, with 0.1% carbon content decreasing gold extraction from 92% to 30%. Further, a 5% carbon content decreased gold extraction to below 10%. Gold recovery onto activated carbon in chloride-bromide leaching (CICl, carbon in chloride leach) was found to be an efficient method for preventing preg-robbing, evidenced by an increase in gold extraction from 0% to 80% when using CICl.

The development of milder chloride leaching showed that only minor amounts of dissolved natural oxidants, 59 mg/L of copper and 1.5 g/L of iron, allowed 87% gold extraction at a chloride concentration of 100 g/L. The redox potential was 460 – 580 mV vs. Ag/AgCl and gold extraction was supported by simultaneous CICl. At even lower chloride concentration, ($[Cl]_{aq,0} = 20$ g/L), but higher oxidant concentration ($[Cu]_{aq,0} = 18$ g/L), 72% gold extraction could be achieved. These findings suggest that gold leaching can be enabled by lower redox potentials than those suggested by the state-of-the-art literature, and even at chloride levels similar to sea water.

Another process development focused on investigating simultaneous sulfide oxidation and gold dissolution from refractory gold concentrate by aggressive chloride-bromide leaching. The results confirmed that direct chloride-bromide leaching of pyrite and arsenopyrite is possible, with high gold extraction. Gold extraction of 81% was possible with 67% sulfide oxidation from refractory concentrate, whereas 67% gold extraction was achieved with 81% sulfide oxidation from double refractory concentrate. In the future, this direct processing route may provide alternatives to the state-of-the-art pressure oxidation, roasting, and bio-oxidation processes.

Keywords gold leaching, cyanide-free, simulation, sustainability, carbon in chloride leach**ISBN (printed)** 978-952-64-0014-3**ISBN (pdf)** 978-952-64-0015-0**ISSN (printed)** 1799-4934**ISSN (pdf)** 1799-4942**Location of publisher** Helsinki**Location of printing** Helsinki **Year** 2020**Pages** 156**urn** <http://urn.fi/URN:ISBN:978-952-64-0015-0>

Tekijä

Riina Ahtiainen

Väitöskirjan nimi

Helposti käsiteltävien ja refraktoristen kultamalmin ja -rikasteiden kloridipohjaisten prosessien kehitys

Julkaisija Kemian tekniikan korkeakoulu**Yksikkö** Kemian tekniikan ja metallurgian laitos**Sarja** Aalto University publication series DOCTORAL DISSERTATIONS 129/2020**Tutkimusala** Materiaalien prosessointi**Käsikirjoituksen pvm** 05.06.2020**Väitöspäivä** 09.10.2020**Väittelyluvan myöntämispäivä** 26.08.2020**Kieli** Englanti **Monografia** **Artikkeliväitöskirja** **Esseeväitöskirja****Tiivistelmä**

Syanidiliuotus on dominoinut kullan hydrometallurgista prosessointia yli 100 vuotta. Syanidilla on useita teknistaloudellisia hyötyjä; se on suhteellisen halpa kemikaali ja mahdollistaa korkean kullan saannon sekä selektiivisyyden liuotuksessa. Syanidikemikaalin myrkyllisyys, sen aiheuttamat ympäristövahingot ja rajalliset mahdollisuudet kompleksisten raaka-aineiden käsittelyssä ovat lisänneet kiinnostusta syanidivapaita kultaprosesseja kohtaan. Halidiliuotus on yksi lupaavimmista vaihtoehdoista syanidiprosessille, käytettiin klooria jo 1800-luvulla kullan talteenotossa teollisessa mittakaavassa. Kloridiliuotuksessa liuennneiden kupari(II)- tai rauta(III)kloridien käyttö hapettimena mahdollistaa nopean liuotuskinetiikan lisäksi kompleksisten raaka-aineiden käsittelyn. Tässä väitöskirjatutkimuksessa tutkittiin vapaata kultaa sisältävän helposti käsiteltävän kultamalmin kloridipohjaista liuotusta. Lisäksi työssä tutkittiin kloridibromidipohjaista liuotusta kahdelle erityyppiselle refraktoriselle kultarikasteelle. Työn tarkoituksena oli tutkia liuotusilmioita, kuten kullan takaisinpelkistymistä lähtömateriaaliin sekä kehittää laimea kloridiliuotusprosessi helposti käsiteltävälle kultamalmin. Lisäksi työssä tutkittiin suoraliuotusta refraktorisille kultarikasteille ilman erillistä esihapetusta.

Kullalla havaittiin olevan melko voimakas taipumus takaisinpelkistymiseen kloridibromidiliuotuksessa. 0,1%:n hiilipitoisuus laski kullan saannon 92%:sta 30%:iin ja edelleen 5%:n hiilipitoisuus alle 10%:iin. Kloridibromidiliuotuksessa kullan talteenoton aktiivihieleen (CICL) havaittiin olevan tehokas menetelmä kullan takaisinpelkistymisen vähentämiseksi, ja näin kullan saanto pystyttiin nostamaan 0%:sta 80%:iin.

Laimean kloridiliuotuksen kehitystyö osoitti, että pieni määrä kultaraaka-aineesta liuennutta hapetinta, kuparia 59 mg/L ja rautaa 1,5 g/L, mahdollisti 87%:n kullan saannon 100 g/L:n kloridipitoisuudella, kun kulta samanaikaista otettiin talteen aktiivihieleen. Redox-potentiaali oli tuolloin 460 – 580 mV vs. Ag/AgCl. Jopa alhaisemmalla kloridipitoisuudella ($[Cl]_{aq,o} = 20$ g/L), mutta korkeammalla hapettimen pitoisuudella ($[Cu]_{aq,o} = 18$ g/L), saavutettiin 72%:n kullan saanto. Tutkimuksessa nähtiin, että kullan liuotus on mahdollista alhaisemmalla redox-potentiaalilla kuin kirjallisuudessa on esitetty, jopa merivettä vastaavalla kloridipitoisuudella.

Lisäksi väitöskirjatutkimus kohdistui refraktoristen kultarikasteiden suoraliuotukseen eli samanaikaiseen sulfidimineraalien hapetukseen ja kullan liuotukseen. Tulokset vahvistivat, että pyriitin ja arsenopyriitin suoraliuotus on mahdollista aggressiivisella kloridibromiliuotuksella. Refraktorisesta rikasteesta saatiin 81% kullan saanto, kun 67% sulfideista hapetettiin. Toisesta hiilipitoisesta refraktorisesta rikasteesta saatiin kullasta liuotettua 67%, kun 81% sulfideista hapetettiin. Tulevaisuudessa tämä refraktoristen kultarikasteiden suoraliuotus voi tarjota vaihtoehdon käytössä oleville paineliuotus-, pasutus- ja biohapetusprosesseille.

Avainsanat kulan liuotus, syanidivapaa, mallintaminen, kestävyys, hiili kloridiliuotuksessa**ISBN (painettu)** 978-952-64-0014-3**ISBN (pdf)** 978-952-64-0015-0**ISSN (painettu)** 1799-4934**ISSN (pdf)** 1799-4942**Julkaisupaikka** Helsinki**Painopaikka** Helsinki**Vuosi** 2020**Sivumäärä** 156**urn** <http://urn.fi/URN:ISBN:978-952-64-0015-0>

Acknowledgements

This doctoral thesis was carried out during the years 2015-2020, supported by a collaboration between Aalto University, Department of Chemical and Metallurgical Engineering, research group of Hydrometallurgy and Corrosion, Espoo, Finland, and Outotec (Finland) Oy, Outotec Research Center (ORC) Pori, Finland.

First of all, I would like to express gratitude to Professor Mari Lundström for persuading me to start doctoral studies, as well as for her continuous support and academic advice throughout my doctoral studies. Mari has believed in me and encouraged me through the whole process, and, in addition, she introduced me to the academic world. Thank you, Mari, so much for this memorable trip. Next, I would like to thank my co-author Jussi Liipo for his professional mineralogical analysis as well as all his support during the review processes of the thesis publications. I would like to present my special thanks to Janne Karonen, who has made it possible to complete my doctoral studies with his continuous support. Further, I wish to thank my old/present colleagues: John O'Callaghan, Ville Miettinen, Tero Kravtsov, Tuukka Kotiranta, and Jari Tiihonen for guidance on the topics of gold chloride-bromide leaching, mineralogy, modeling, and gold cyanide leaching.

In addition, I want to thank all my colleagues and friends at ORC. All of you have helped and supported me so many times during my journey with this thesis work. Specifically, I wish to thank: Annukka Mäkinen, Heini Elomaa, Marjaana Honkanen, Vili Hyvärinen, Suvi Lehto, Saana Pulkkinen, and Piia Viitikko. I would also like to thank Sipi Seisko from Aalto. My sincere thanks also go to all my other friends from Lappeenranta University of Technology (LUT) and Tuula Salminen.

Long time ago I got a phone call from Mari saying, "You will become a doctor!" I had no other options than apply to the doctoral school to Aalto. And now, finally, I have done it! Last but not least, I would like to thank my parents Antti and Raija and sisters Sanna, Jaana, Paulina, and Elena, since without them, I would not have survived through the thesis process!

Pori, 15 April 2020
Riina Ahtiainen

Contents

Acknowledgements	I
List of abbreviations and symbols.....	V
List of Publications.....	VII
Author's contribution.....	VIII
1. Introduction.....	1
1.1 Background	1
1.2 Objective of this thesis.....	4
1.3 New scientific contribution.....	5
1.4 Structure of this thesis	8
2. Theoretical background	9
2.1 Classification of gold ores	9
2.1.1 Free-milling ores	10
2.1.2 Complex ores	11
2.1.3 Refractory ores	12
2.2 Pre-treatment of refractory gold ores.....	12
2.2.1 Fine grinding	12
2.2.2 Roasting	13
2.2.3 Bio-oxidation	13
2.2.4 Pressure oxidation (POX).....	15
2.2.5 Alternative oxidation methods	16
2.3 Prevention of preg-robbing phenomenon	17
2.4 Gold leaching	19
2.4.1 Cyanide leaching	20
2.4.2 Thiosulfate leaching.....	22
2.4.3 Thiourea leaching.....	22
2.4.4 Glycine leaching	23
2.4.5 Chloride leaching.....	24
2.5 Process simulation and environmental analysis	27

3.	Experimental method	29
3.1	Batch leaching experiments.....	29
3.1.1	Leaching set-up	32
3.1.2	Analysis of solution and solid samples	33
3.1.3	Calculation of extraction	34
3.2	Simulation.....	35
3.2.1	Parameters in chloride process simulations	36
3.2.2	Parameters in cyanide process simulation.....	41
4.	Results.....	43
4.1	Preg-robbing phenomena in chloride-bromide leaching	43
4.1.1	Prevention of preg-robbing in chloride leaching.....	44
4.1.2	Gold chloride complex in chloride solution	45
4.2	Free-milling ore.....	47
4.3	Comparison of process models for free-milling gold ore	51
4.3.1	Gold leaching and recovery	52
4.3.2	Water balance.....	53
4.3.3	Bleed treatment.....	54
4.3.4	Consumptions of chemicals and auxiliaries.....	55
4.3.5	Products and emissions	57
4.3.6	Life cycle inventory, LCI.....	59
4.4	Refractory and double refractory concentrates.....	62
5.	Discussion	67
5.1	Leaching of free-milling gold ore	67
5.2	Holistic processing of free-milling ore in chloride media	70
5.3	Leaching of refractory gold concentrates	72
5.4	Recommendations for future work.....	72
6.	Conclusions.....	75
	References	77

List of abbreviations and symbols

Abbreviations

Act. C	activated carbon
bv	bed volume
CAPEX	capital expenditure
CICl	carbon in chloride leach
CIL	carbon in leach
CIP	carbon in pulp
DR	double refractory gold concentrate
EDRR	electrodeposition-redox replacement
FA	fire assay method
FAAS	flame emission spectrometry
FM	free-milling gold ore
GFAAS	graphite furnace atomic absorption spectrometry
GLS	gas liquid solid
HSC-Sim	HSC Sim, HSC Chemistry software
IC	ion chromatography
ICP-MS	inductive coupled plasma mass spectrometry
ICP-OES	inductive coupled plasma optical emission spectrometry
Inco	cyanide destruction process
LCA	life cycle assessment
LCI	life cycle inventory analysis
OPEX	operating expense
PGM	platinum group metals
POX	pressure oxidation
R	refractory gold concentrate
RIL	resin in leach
RIP	resin in pulp
RV-2	para nitro benzol azo salicylic acid
S/L	solid concentration
SCE	saturated calomel electrode
SHE	standard hydrogen electrode
SMBS	sodium metabisulfite
t	metric tonne (1 000 kg)
TSF	tailings storage facilities
WAD	weak acid dissociable cyanide
Zedra	carbon elution process for cyanide media loaded activated carbon

Subscriptions

o	initial
aq	aqueous solution
C	activated carbon
final	final solution
i	moment of time
loaded	loaded activated carbon
res	leach residue
s	solid
sample	solid or liquid sample

Symbols

β_2	stability constant
β_4	stability constant
AC_{Au}	accountability of gold, %
c_{aq}	concentration in solution, g/L
c_C	content in activated carbon, g/t
c_s	content in solid, g/t
E_{Au}	gold extraction, %
m	mass, g
$R_{aq,Au}$	gold recovery to solution, %
R_{Au}	gold recovery over the process, %
$R_{C,Au}$	gold recovery onto activated carbon, %
V	volume, L
T	temperature, °C
t	time, h

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. **Ahtiainen, Riina**; Lundström, Mari. 2016. Preg-robbing of gold in chloride-bromide solution. *Physicochemical Problems of Mineral Processing*, volume 52, pages 244-251. ISSN: 2084 – 4735 (online). DOI: 10.5277/ppmp160121.
- II. **Ahtiainen, Riina**; Lundström, Mari; Liipo, Jussi. 2018. Preg-robbing verification and prevention in gold chloride-bromide leaching. *Minerals Engineering*, volume 128, pages 153 – 159. DOI: 10.1016/j.mineng.2018.08.037.
- III. **Ahtiainen, Riina**; Lundström, Mari. 2019. Cyanide-free gold leaching in exceptionally mild chloride solutions. *Journal of Cleaner Production*, volume 234, pages 9 – 17. DOI: 10.1016/j.jclepro.2019.06.197.
- IV. **Ahtiainen, Riina**; Liipo, Jussi; Lundström, Mari. 2020. Simultaneous sulfide oxidation and gold dissolution by cyanide-free leaching from refractory and double refractory gold concentrates. Submitted to *Minerals Engineering*, 6/2020.

Author's contribution

Publication I: “Preg-robbing of gold in chloride-bromide solution”

Conceptualization and methodology were by RA and ML, and validation and analysis of results by RA. The original draft was written by RA and reviewed and edited by ML.

Publication II: “Preg-robbing verification and prevention in gold chloride-bromide leaching”

JL conducted the mineralogical analysis. Conceptualization and methodology were by RA and ML, and validation and analysis of results by RA. The original draft was written by RA and reviewed and edited by JL and ML.

Publication III: “Cyanide-free gold leaching in exceptionally mild chloride solutions”

Conceptualization and methodology were by RA and ML, and validation and analysis of results by RA. The original draft was written by RA and reviewed and edited by ML.

Publication IV: “Simultaneous sulfide oxidation and gold dissolution by cyanide-free leaching from refractory and double refractory gold concentrates”

JL conducted the mineralogical analysis. Conceptualization and methodology were by RA and ML, and validation and analysis of results by RA. The original draft was written by RA and reviewed and edited by JL and ML.

1. Introduction

Gold has been known since 3600 BCE in Egypt and it might have been the first metal observed and collected because it occurs in its native state (Rose, 1898; Marsden and House, 2006). The name “gold” originates from the historical English word “geolo” that means yellow (Macdonald, 2007). On the other hand, the word “gold” can be connected to the Sanskrit word “jvalita,” which may be derived from the verb “jval,” to shine (Rose, 1898). The chemical symbol of gold, Au, comes from the Latin name for gold, “Aurum” (glowing dawn) (Macdonald, 2007). From early times gold has been used mostly in decoration and jewelry (Rose, 1898; Marsden and House, 2006). The first gold boom town was Coptos (present Quft) on the eastern side of the Nile in Egypt before 2100 BCE (Habashi, 2005). Since then, many methods have been developed for gold recovery including gravity separation, amalgamation, chlorination, and cyanidation. The innovation of cyanidation in the 19th century moved gold hydrometallurgy into the next century, and has the raised techno-economic feasibility of gold processing, but also increased the level of environmental concern. (Marsden and House, 2006)

1.1 Background

Gold ores can be classified as free-milling, complex, and refractory. Free-milling ores can be classified as raw materials that allow higher than 90% gold extraction with 20 – 30 h of cyanide leaching (with raw material particle size $d_{80} < 75 \mu\text{m}$). In complex ores, cyanide and/or oxygen consumption is high due to side reactions. One class of complex ores is preg-robbing ores, which are known to cause gold adsorption/precipitation back to the ore, i.e., leach residue. (La Brooy *et al.*, 1994) Preg-robbing compounds are most commonly carbonaceous materials such as amorphous carbon, but also chloride, layered silicate, copper minerals, clays, and some sulfide minerals can be defined as preg-robbing (Adams and Burger, 1998; Miller *et al.*, 2005). Traditionally, the preg-robbing phenomenon has been prevented by using a competitive adsorbent (carbon in leach (CIL), resin in leach (RIL)), blinding/blanking with surfactants and oils, or by roasting, chlorination, nitric acid treatment, microbial deactivation, or thiosulfate leaching (Miller *et al.*, 2005).

Refractory gold ores can be classified on the basis of gold extraction: highly refractory, moderate refractory, or mildly refractory. In refractory ores, gold is

locked within a sulfide matrix. Gold can be locked in the host material in different ways: physically, chemically as gold alloys/compounds, gold substitution in the sulfide lattice, or gold surface passivation due to the formation of a chemical layer. (La Brooy *et al.*, 1994) Gold can be liberated by physical (e.g., fine grinding), chemical (e.g., pressure oxidation and chlorine leaching), thermal (e.g., roasting and pyrolysis), or biological pre-treatment (La Brooy *et al.*, 1994; Marsden and House, 2006).

For over 100 years cyanide has been the prominent leaching reagent at gold mines (Hilson and Monhemius, 2006). Cyanide has many advantages: its relatively low cost, effectiveness for gold dissolution, and selectivity for gold over other metals (Marsden and House, 2006). Over the years, the process development of cyanidation (e.g., heap leaching, refractory gold pre-treatment methods, cyanidation under high oxygen over pressure, and CIL) has increased the efficiency of gold cyanide leaching (Habashi, 2005). Approximately 20% of global cyanide production is used for sodium cyanide production. In turn, 90% of sodium cyanide production (18% of total cyanide production) is used in mining, mostly for gold recovery. The rest (>1.4 million t) is used annually in the production of organic chemicals (e.g., nitrile, nylon, and acryl plastics), electroplating, metal processing, steel hardening, photographic applications, food, agriculture, paints, synthetic rubber production, road salt, and in pharmaceutical applications. (Logsdon *et al.*, 1999; Kuyucak and Akcil, 2013)

Typically, gold cyanide leaching operates with relatively dilute cyanide concentrations (0.1 – 0.5 g/L) (Logsdon *et al.*, 1999). However, environmental accidents have deteriorated the reputation of cyanide, e.g., due to the accidents in 1992 at Galactic Resources Ltd., Colorado, USA, and in 1998 at Kumtor Mine, Kyrgyzstan. Usually the reason for cyanide leaks from the process into nature are tears and/or punctures in protective heap leach liners or spills from an overflowing solution pond or tailings storage area. (Hilson and Monhemius, 2006) Failures in process operation may cause the formation of hydrogen cyanide gas, which is immediately lethal at exposures of 300 mg/m³ (Simeonova and Fishbein, 2004). Hydrogen cyanide and liberated free cyanide ions from other cyano-compounds are highly toxic to almost all forms of fauna (Souren, 2000). The main weak acid dissociable (WAD) cyanide complexes are stable in the tailings storage facility (TSF) environment. The WAD complexes can release cyanide ions into solution under varying environmental conditions. Consequently, it is justified to regulate the usage and release of free, WAD, and other forms of cyanide. (Donato *et al.*, 2007)

Various actions have been conducted to prevent hazardous exposure of nature to cyanide. For example, wildlife deaths can be reduced by careful planning of the location of cyanide-bearing ponds, locating them close to the production equipment rather than the native vegetation. Additionally, seasons affect wildlife deaths in hot tropical climates. During the dry season, wildlife might need to rely on the waste in process ponds due to lack of fresh water, compared to the wet season when more fresh water is available. (Donato *et al.*, 2017) Some animals, like bats, are also known to naturally avoid saline water bodies and

favor fresh water bodies, therefore separate fresh water ponds have been installed at mine sites (Griffiths *et al.*, 2014).

Because cyanide is clearly an element that is toxic and poses a risk, the interest in cyanide-free leaching reagents has increased (Marsden and House, 2006; Laitos, 2013). Cyanide-free leach reagents should be low cost and/or recyclable, selective for gold, non-toxic, and compatible with recovery process in order to compete with cyanide. In addition, cyanide-free leach reagents may have potential advantages such as faster gold leaching kinetics, operation in acidic media (more suitable for refractory ore treatment), or high selectivity for gold and silver. (Hilson and Monhemius, 2006; Marsden and House, 2006)

Potential alternatives that have been investigated for cyanide leaching are e.g., thiourea leaching, thiocyanide, thiosulfate, ammonia, and halides (bromine/bromide, iodine/iodide and chlorine/chloride) (Marsden and House, 2006; Hilson and Monhemius, 2006). Chlorination was in commercial use in the 1800s; however, currently there are no commercially operating chloride-based leaching processes for primary ores or concentrates (Hilson and Monhemius, 2006). Several such processes have been tested and piloted for gold chloride leaching, e.g., Platsol™ (Fleming, 2002; Dreisinger *et al.*, 2005), the Intec process (Intec Ltd., 2009), Nippon N-Chlo (Yoshimura and Abe, 2017), Dundee (Lalancette *et al.*, 2015), the Neomet gold process (Harris and White, 2011), and Outotec's gold chloride process (Miettinen *et al.*, 2014; Lundström *et al.*, 2016), but none has reached industrial scale yet.

Some details of different developmental-stage chloride leaching processes for gold are described below. The Platsol™ process operates at over 200 °C temperature and over 600 kPa pressure (Fleming, 2002; Ferron *et al.*, 2003). Also, the Neomet gold process operates at increased pressure (170 – 529 kPa) and uses nitric acid as an oxidant with copper(II), iron(III), and oxygen gas (Harris and White, 2011). The Intec process operates at atmospheric pressure. It uses a relatively aggressive solution, i.e., high chloride (~200 g/L) and bromide (~25 g/L) concentrations (Intec Ltd., 2009), to support gold leaching. The Outotec's gold chloride process operates at approximately the same chloride concentrations but with a larger variation in bromide concentration (0 – 100 g/L) (Miettinen *et al.*, 2014; Lundström *et al.*, 2016). In the N-Chlo process, >100 g/L bromide concentration is used with a 1:3 bromide to chloride ratio (Yoshimura and Abe, 2017). The Dundee Sustainable Technologies process is known to use hypohalides, which react with hydrochloric acid forming chlorine and bromine. Chlorine is used as an oxidant with a catalytic amount of bromine. (Dundee Sustainable Technologies, 2014) Both chlorine and bromine are also used as a ligand for complexation (Lalancette *et al.*, 2015). It is evident that all developmental-stage processes operate under aggressive conditions, either chemical- or pressure wise, to ensure gold extraction. This causes challenges with highly corrosive process conditions, increasing the cost not only of construction materials but also of chemicals. Also, the lack of an industrially proven gold recovery method (cf. cyanide processes) and the tendency for pre-robbing along with relatively unstable gold chloride complexation may

challenge the feasibility of the process. (Aylmore, 2005; Marsden and House, 2006)

Comparing the environmental load of the state-of-the-art and developmental-stage processes is a challenging task. Process simulation is a tool that can predict the inputs and outputs of an investigated process (i.e., mass and energy balance). Further, it can be used to feed information for life cycle assessment (LCA) already in an early stage of project development and thus provide support in the evaluation of environmental feasibility. (Reuter, 1998; Pell *et al.*, 2019) Along with novel cyanide-free gold process development, it is essential, although this is not widely applied in scientific literature, to build a life cycle inventory (LCI) throughout the experimental research, even early in the development phase.

1.2 Objective of this thesis

The main objective of this thesis is to investigate gold leaching behavior, limitations, and opportunities, specifically in copper(II) and iron(III) chloride leaching systems. The work investigates three different types of raw materials: free-milling gold ore, as well as refractory and double refractory gold concentrate.

The specific objectives of this thesis are:

1. to investigate the preg-robbing phenomenon in chloride-bromide leaching, with possibilities for preventing preg-robbing
2. to leach gold from free-milling gold ore in mild chloride leaching conditions, and to determine the effects of leaching conditions on process mass and energy balance
3. to leach gold directly from refractory and double refractory gold concentrates, with simultaneous sulfide oxidation in chloride-bromide media.

The objectives with their correlation to the thesis publications (I – IV) are presented in Figure 1.

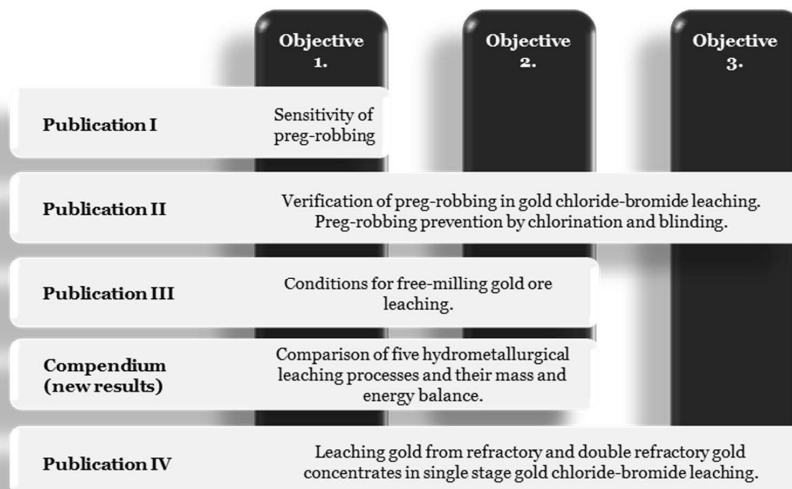


Figure 1. Relation between objectives, Publications I – IV, and new results in the compendium section.

1.3 New scientific contribution

The new scientific contribution of the thesis is based on experimental work (Publications I-IV) as well as process simulation (new results in the compendium section). All the leaching experiments of the thesis were carried out as batch leaching tests. Preg-robbing research was conducted using chloride-bromide media. The chloride leaching of free-milling gold ore was investigated in a variety of chloride leaching conditions, by changing parameters such as the chloride concentration, initial copper(II)/iron(III) concentration (oxidant), solid concentration, temperature, pH/acid concentration, and carbon-in-chloride-leach (CICl). Followed by the experimental work, four different chloride process models as well as the cyanide process were simulated for free-milling raw material (unpublished results of this thesis). The simulated processes were: *high copper* ($[\text{Cl}]_{\text{aq}} = 225 \text{ g/L}$, $[\text{Cu}]_{\text{aq}} = 100 \text{ g/L}$), *low copper* ($[\text{Cl}]_{\text{aq}} = 100 \text{ g/L}$, $[\text{Cu}]_{\text{aq}} = 5 \text{ g/L}$), *low iron* ($[\text{Cl}]_{\text{aq}} = 100 \text{ g/L}$, $[\text{Fe}]_{\text{aq}} = 5 \text{ g/L}$), *sea water* ($[\text{Cl}]_{\text{aq}} = \sim 19 \text{ g/L}$, $[\text{Cu}]_{\text{aq}} = 18 \text{ g/L}$), and *cyanide* ($[\text{NaCN}]_{\text{aq}} = 3 \text{ g/L}$) leaching processes. Additionally, simultaneous sulfide oxidation and gold dissolution was investigated with refractory and double-refractory gold concentrates.

Based on the experimental and simulation work carried out, the following findings are believed to be original and relate to objective 1 (findings 1 – 5), objective 2 (findings 6 – 10), and objective 3 (findings 11 – 13):

- 1) The tendency towards preg-robbing in chloride-bromide media is very strong. Addition of as little as 0.01% activated carbon powder into non-preg-robbing ore can decrease the gold extraction from 92% to 70%, and furthermore, 5% carbon decreases gold recovery to almost zero. (Publication I)

- 2) The graphite carbon naturally present in the raw material shows similar preg-robbing behavior as commercially available activated carbon. An experimentally based equation - derived from the addition of activated carbon - predicted 91.4% gold loss with raw material having 3.3% carbon content. With preg-robbing concentrate (3.3% carbon content), gold extraction as low as 2% was evident. (Publication II)
- 3) Chlorination is a known process, used as pre-treatment to prevent preg-robbing in cyanide leaching process. In the current thesis chlorination was investigated as pre-treatment prior to chloride-bromide leaching. It was shown that gold extraction could be increased and preg-robbing prevented by chlorination (Cl_2) pre-treatment also before gold chloride-bromide leaching. Gold extraction was then increased from 2% to 45%. (Publication II)
- 4) Activated carbon addition (CICl) was shown to prevent preg-robbing in chloride and chloride-bromide media. Gold extraction was increased from 0% to 80% by using activated carbon recovery for pre-oxidized double refractory concentrate. (Publication IV)
- 5) In mild chloride leaching (100 g/L of chloride), increased gold extraction can be achieved by simultaneous recovery on carbon (CICl). Gold extraction increased from 78% to 94% (copper(II), 5 g/L, as oxidant) and from 41% to 85% (iron(III), 5 g/L, as oxidant). In the absence of carbon, the gold chloride complex did not stay equally stable in solution compared to a higher (e.g., 150 g/L) chloride concentration. (Publication III)
- 6) Generally, it is known that chloride leaching can have notable faster kinetics vs. cyanidation. In the current thesis, the maximum gold concentration was reached at 5 hours in chloride-bromide leaching, whereas it took 24 hours in cyanide leaching. However, approximately the same final gold extraction (>90%) was reached in chloride-bromide and cyanide media. (Publication I)
- 7) Gold leaching out of the raw material was evident even at redox potentials as low as 520 mV (vs. Ag/AgCl, pH 2.5 – 3.0) in chloride media. In addition, gold dissolution could be conducted without any initial addition of copper(II) or iron(III) when the oxidant originated in-situ (copper 0.02% and iron 0.8%, from the ore). 87% gold extraction could be reached with a chloride concentration as low as 100 g/L. (Publication III)
- 8) Gold chloride leaching was shown to be possible at very mild chloride concentrations; similar to the level of sea water (20 g/L) or even lower with 10 g/L when using CICl mode (i.e., providing simultaneous gold recovery onto activated carbon in chloride leaching). The gold extraction achieved with sea water chloride concentration was 72% and 64% with a chloride concentration of 10 g/L. (Publication III)

- 9) Process simulation suggests that the management of the water balance is challenging in chloride processes. Evaporation is needed, but it is also a high cost option for reagent circulation. Need of evaporation was 234 t/kg_{Au} when gold leaching solution contained 100 g/L copper and 225 g/L chloride, and decreased to 168 t/kg_{Au} when copper concentration decreased to 5 g/L and chloride 100 g/L. (New result in the compendium section)
- 10) Process simulation showed that milder leaching conditions ($[Cl]_{aq} = 100$ g/L and $[Cu]_{aq} = 5$ g/L or $[Fe]_{aq} = 5$ g/L) combined with an evaporation unit process in the holistic flow sheet can decrease the chemical consumption needed in gold chloride leaching. (New result in the compendium section)
- 11) The gold extraction was found to be almost linearly dependent on sulfide oxidation from the investigated refractory gold concentrate (gold is mainly in arsenopyrite and pyrite): 97% sulfide oxidation resulted in 99% gold extraction, 67% sulfide oxidation resulted in 81% gold extraction, and 46% sulfide oxidation resulted in 67% gold extraction. However, the same was not evident for the double refractory gold concentrate (gold is mainly in arsenopyrite and pyrite and concentrate contains graphitic carbon that cause preg-robbing) when ClCl was used for gold recovery: over 99% sulfide oxidation resulted in 80% gold extraction, and 81% sulfide oxidation resulted in 67% gold extraction. It seems that the nature of the pyrite/arsenopyrite refractoriness has a strong effect on the required degree of sulfide oxidation. (Publication IV)
- 12) Gold extraction and recovery from refractory and double refractory materials is possible in a single process stage. The sulfide was oxidized, gold was liberated, dissolved, and recovered onto activated carbon from refractory gold concentrates in chloride-bromide leaching, e.g., 67% gold extraction could be achieved with 81% sulfide oxidation from double refractory gold concentrate. (Publication IV) There are indications of simultaneous oxidation of refractory minerals with in-situ gold recovery in the open literature. However, to the best of the author's knowledge there are previously no systematic studies of simultaneous oxidation of double refractory ore with in-situ gold recovery in chloride-based systems.
- 13) Lead(II) nitrate is used as additive in gold cyanide leaching to increase gold extraction. In the current thesis lead(II) nitrate addition was investigated in chloride-bromide media and it was shown that gold extraction could be increased with the addition of lead(II) nitrate from 67% to 88% using double refractory concentrate direct chloride-bromide leaching when gold was recovered by ClCl. (Publication IV)

1.4 Structure of this thesis

This thesis focuses on cyanide-free gold chloride and chloride-bromide leaching. Batch tests were conducted for free-milling ore, refractory concentrate, and double refractory gold concentrate. This thesis contains three published peer-reviewed scientific publications as well as one submitted manuscript (Publications I – IV), in addition to the compendium section. The publications are attached in the Appendixes.

Gold chloride/chlorine leaching has a long history. Therefore, the history of gold hydrometallurgy is briefly presented from its early days to the present day in the Theoretical background (Chapter 2). Chapter 2 also introduces one classification method for gold ores and concentrates. Also, the commonly used methods for sulfide oxidation of refractory ores/concentrates, e.g., roasting, pressure oxidation, and biological oxidation and presents the phenomenon of preg-robbing are presented. Due to the bad reputation that cyanide has, alternative cyanide-free lixivants have also been summarized such as thiosulfate, thiourea, glycine, and chloride.

The Experimental methods (Chapter 3) introduces the batch leaching set-up, and the parameters and analysis methods used. Additionally, the theory behind the process simulation is presented.

The Results (Chapter 4) presents the main results of the thesis: preg-robbing behavior and its prevention in chloride-bromide leaching (Publications I and II), the leaching of free-milling gold ore in exceptionally mild chloride leaching conditions (Publication III), the comparison of chloride leaching processes and the cyanide leaching process for free-milling gold ore (new results of the compendium), and refractory sulfide mineral oxidation with simultaneous gold leaching in chloride-bromide media (Publication IV).

The Discussion (Chapter 5) includes the main findings of the thesis. Recommendations for future research are also presented. Chapter 6 presents the conclusions.

2. Theoretical background

Many methods have been used for the recovery of gold, e.g., gravity separation, amalgamation, chlorination, and cyanidation. The earliest gold recovery method was gravity separation or manual sorting (e.g., panning). (Marsden and House, 2006) The amalgamation of gold was published in Biringuccio's book (*De la Pirotechnia*) as early as 1540 (Rose, 1898). Today, the amalgamation process is illegal in many countries due to the toxicity of mercury (Habashi, 2005). Chlorine gas was discovered in 1774 (Marsden and House, 2006) and the Plattner process utilizing chlorine for gold oxidation and complexation was introduced in 1848. In this process, gold leaching was conducted in a wooden vat, and gold was recovered from the solution using iron(II) sulfate. In the Mears process (developed 1877), the vat was replaced with a rotating barrel. The barrel needed to be airtight due to the chlorine gas and needed an air feed to increase pressure. The Thies process was further modified from the Mears process. In the Thies process, chloride was produced in-situ from bleaching powder and sulfuric acid in a barrel. (Rose, 1898) The cyanide leaching process was invented in the late 19th century by several researchers around the world. Nowadays, the cyanide process is based on the patents of MacArthur and the Forrest brothers in 1887–1888. With the improved technical feasibility of using cyanide rather than chlorine gas, gold hydrometallurgy moved into the 20th century along with cyanidation. (Marsden and House, 2006)

2.1 Classification of gold ores

Gold ores can be classified into three groups: free-milling, complex, and refractory. Free-milling ores give high gold extraction (>90%) with 20–30 h (d₈₀ <75 μm) of cyanide leaching. It is not economical to recover gold from complex ores by simple cyanidation. In these materials, cyanide or oxygen consumption is too high or alternatively preg-robbing decreases or even prevents gold recovery. In refractory ores, gold is often locked within a sulfide matrix, which needs to be oxidized to liberate the gold. These refractory gold ores can be classified based on the gold extraction in direct cyanide leaching. Gold extraction of less than 50% correspond to highly refractory raw material, whereas 50–80% gold extraction corresponds to moderate refractory, and 80–90% gold extraction to mildly refractory. Raw materials allowing

90–100% gold extraction in direct cyanide leaching are known as non-refractory, i.e., free-milling ores. (La Brooy *et al.*, 1994)

2.1.1 Free-milling ores

Crushing and grinding are the only pre-treatments conducted for free-milling gold ores to liberate gold from gangue minerals prior to hydrometallurgical gold extraction. The fineness of grinding for cyanide leaching is ore dependent and affects the gold exposure to leaching and the consequent gold extraction level. (La Brooy *et al.*, 1994) Free-milling ores can be classified as: placer, palaeoplacers, quartz vein, oxide, and sulfide ores (La Brooy *et al.*, 1994; Marsden and House, 2006).

Placer ores are special cases of free-milling ores, where no pre-treatment is needed, not even crushing and/or grinding. Gold can be recovered directly from such raw deposits by physical methods, e.g., sluices, onto blankets or centrifugal concentrators e.g., the Knelson, and the Falcon. (La Brooy *et al.*, 1994; Cole *et al.*, 2012) Placer deposits are formed away from a primary deposit by weathering and hydraulic transportation of gold particles. Placer ores can in turn be classified into eluvial, colluvial, fluvial, and marine placer ores. (Marsden and House, 2006)

In palaeoplacers, gold is unliberated, typically with quartz, in a matrix of pyrite, fine quartz, micaceous materials, and small quantities of heavy resistant minerals, e.g., magnetite, uraninite, platinum group metals (PGM), and titanium minerals. Many of this type of quartz rich ores are very hard and require therefore intensive grinding to expose gold for hydrometallurgical extraction. (Marsden and House, 2006)

In oxide ores, gold often occurs with iron oxides (e.g., hematite, magnetite, goethite, or limonite) or with manganese oxides/hydroxides. The oxide ores may also contain some clay (e.g., pyrophyllite, talc, kaolinite, and montmorillonite) and clay-forming minerals, which can have a negative impact on the process by decreasing permeability (in heap or dump leaching) and increasing slurry viscosity and/or blinding of activated carbon, challenging the gold recovery (in reactor leaching). Carbonate minerals (e.g., calcite, dolomite, and siderite) are also common in oxide ores. In addition, oxide ores may contain various copper oxide minerals, which dissolve in alkaline cyanide leaching conditions and interfere with gold leaching and recovery processes, e.g., by increasing cyanide consumption. (Marsden and House, 2006)

Some sulfide ores (e.g., pyrrhotite, marcasite, covellite, digenite, chalcocite, arsenic, antimony, and zinc sulfides) can also be classified as free-milling ores, as the gold content is typically higher in sulfide ores than in oxide ores. Sulfide ores can also contain some refractory compounds. This kind of raw material may benefit from grinding to a finer particle size compared to oxide and palaeoplacers in order to liberate the gold from refractory compounds. One processing challenge with sulfide ores is that they increase the cyanide and/or oxygen consumption in cyanide leaching and may in some cases even require oxygen or hydrogen peroxide to be used, instead of the usual compressed air alone. (La Brooy *et al.*, 1994)

2.1.2 Complex ores

Complex ores can be divided into cyanide-consuming, oxygen-consuming, and preg-robbing gold ores. Complex ores usually contain a range of sulfide minerals (e.g., pyrrhotite, marcasite, covellite, digenite, chalcocite, arsenic and antimony sulfides, and zinc sulfide). The side reactions of these minerals can increase the cyanide consumption. A copper sulfide content >1% can already challenge the economics of the process due to an increase in cyanide consumption, whereas pyrrhotite oxidation to iron(III) and thiocyanate is known to increase both oxidant and cyanide consumption. The presence of reactive sulfides has been decreased by different methods, such as flotation or chemical pre-treatment. (La Brooy *et al.*, 1994) Also, high silver content (>10 g/t) and/or gold in the electrum can increase cyanide consumption, whereas the presence of sulfide ions may result in the formation of a passivation silver sulfide layer on electrum, preventing the access of cyanide solution to the gold surface (Marsden and House, 2006).

In addition, preg-robbing ores are classified as complex ores (La Brooy *et al.*, 1994). In preg-robbing ores, gold is exposed to leaching, although some compounds present in the ore mineralogy can adsorb the dissolved gold back to the raw material after leaching. This phenomenon reduces or even prevents gold extraction. (Marsden and House, 2006) Preg-robbing behavior is most often associated with the carbonaceous materials present in the ore, such as hydrocarbon, humic acid, native carbon (Marsden and House, 2006), amorphous carbon (free reactive carbon without a crystalline structure), and graphitic carbon (Mohammadnejad *et al.*, 2013). The presence of carbonaceous material or a total carbon analysis of the raw material is not necessarily directly proportional to an increase in gold losses. Native carbon and amorphous carbon have been found to cause strong preg-robbing. However, it has been suggested that graphitic carbon for instance has a lower preg-robbing activity. (Mohammadnejad *et al.*, 2013) Typically, hydrocarbons have only a minor effect on preg-robbing (Sibrell *et al.*, 1990). In addition to carbonaceous materials, sulfidic minerals such as chalcopyrite, zinc sulfide, lead sulfide, arsenopyrite, and pyrite can also cause preg-robbing. This occurs typically if the solution redox potential is not high, i.e., a non-oxidative environment at lower redox potentials. (Mikhlin and Romanchenko, 2007) Also, goethite and alumina can adsorb gold on the mineral surface (Goodall *et al.*, 2005). Some silicates (e.g., quartz, feldspar, kaolinite, pyrophyllite, and mechanically activated silica) can also cause preg-robbing in chloride solutions (Mohammadnejad *et al.*, 2013) and this tendency has even been utilized for gold recovery (Dundee Sustainable Technologies, 2014). The preg-robbing behavior related to non-carbonaceous materials is more dependent on the solution properties and redox potential, whereas carbonaceous materials can cause high preg-robbing even in highly oxidizing solutions (Marsden and House, 2006).

2.1.3 Refractory ores

Refractory ores are ores where gold cannot be accessed by direct cyanide leaching. In minerals, gold can be locked physically (in e.g., sulfides, oxides, and silicates), chemically as gold alloys (e.g., electrum, gold tellurides, aurostibite, or maldonite), gold substitution in the sulfide lattice (e.g., “solid solution” gold in arsenopyrite), and gold surface passivation due to the formation of a chemical layer. (La Brooy *et al.*, 1994)

Arsenopyrite, pyrite, and chalcopyrite are known to be the most common gold-locking sulfide minerals (La Brooy *et al.*, 1994). Refractory minerals can also be classified based on the dominating base metal in sulfide minerals, i.e., iron-based (pyrite and pyrrhotite), arsenic-based (arsenopyrite, realgar, and orpiment) and copper-based (chalcopyrite and bornite) minerals. The gold content in sulfide minerals is heavily dependent on the ore type. (Fraser *et al.*, 1991) The gold content can be as high as 15 200 g/t in arsenopyrite, 132 g/t in pyrite, 72 g/t in tetrahedrite, and 7.7 g/t in chalcopyrite. However, it needs to be noted that these minerals do not necessarily contain gold, and the content can also be zero or very low. (Marsden and House, 2006) Gold is more often associated with arsenopyrite than pyrite in ore containing arsenopyrite and pyrite (Fraser *et al.*, 1991) due to better matching atomic spacing, crystal chemistry, and a similar formation temperature to gold (Marsden and House, 2006).

2.2 Pre-treatment of refractory gold ores

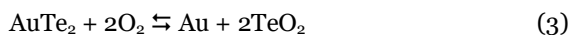
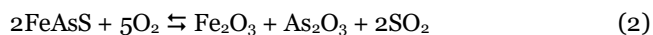
Gold can be liberated from refractory ores by physical (e.g., fine grinding), thermal, biological, or chemical (e.g., pressure oxidation (POX), nitric acid oxidation, and chlorine oxidation) pre-treatment (La Brooy *et al.*, 1994). Industrially applied methods for sulfide oxidation are roasting, bio-oxidation, and pressure oxidation (Marsden and House, 2006).

2.2.1 Fine grinding

Fine grinding (100% <38 µm) or ultrafine grinding (1 – 20 µm) is suitable for liberating fine gold from arsenopyrite and pyrite refractory ores, especially for moderate and mildly refractory gold ores (Corrans and Angove, 1991; La Brooy *et al.*, 1994). Grinding can also be used after oxidation (e.g., roasting, pressure oxidation, bio-oxidation) to remove a core surface from the top of a gold particle (Corrans and Angove, 1991; Miller and Brown, 2005). Optimization of grinding parameters in fine and ultrafine grinding is important because gold liberation is not only dependent on particle size distribution, but also because the intensity of grinding highly affects the energy consumption (Mariano and Evans, 2018; Wikedzi *et al.*, 2018).

2.2.2 Roasting

Roasting covers thermal pre-treatment methods that have been used to break down sulfides and to liberate gold. In roasting, sulfide minerals are converted to oxides in the presence of oxygen; roasting has been in industrial operation for over 80 years. (La Brooy *et al.*, 1994; Nan *et al.*, 2014) In the roasting process (typically at $T = 650 - 700$ °C), pyrite is oxidized to hematite and sulfur dioxide, Eq. (1), and arsenopyrite to hematite, arsenic trioxide, and sulfur dioxide, Eq. (2). Also, gold tellurides can be decomposed in roasting to gold and telluride dioxide, Eq. (3). (La Brooy *et al.*, 1994; Marsden and House, 2006)



The kinetics of pyrite and arsenopyrite oxidation is low at lower temperatures (400 – 450 °C), whereas at high temperatures (700 – 750 °C) the porous structure of the calcine might collapse and cover the gold surface with iron oxide, causing sintering. Local hot spots due to high local sulfur content, poor temperature control, or too long roasting time (over-roasting) can also result in the sintering effect. High sulfur content in the raw material corresponds to high sulfur dioxide formation, which can be converted by catalytic conversion to sulfur trioxide, and further adsorbed into sulfuric acid, forming oleum ($\text{H}_2\text{S}_2\text{O}_7$), Eq. (4). Dilution of oleum produces commercial grade sulfuric acid. (Marsden and House, 2006)

2.2.3 Bio-oxidation

Bio-oxidation has been used industrially in sulfide mineral oxidation since 1986 (Miller and Brown, 2005). Bio-oxidation is commonly conducted in aerated slurries at ambient temperature and pressure in acidic solution (pH 1 – 1.8). The bacteria used depend on the operation temperature: at 35 – 45 °C for example *Thiobacillus thio-oxidans* and *Thiobacillus ferro-oxidans*, at 45 – 65 °C for example *Sulfobacillus acidophilus*, and at 65 – 80 °C *Sulfolobus*, for example. (Marsden and House, 2006) Bio-oxidation of pyrite can be carried out by contact leaching, non-contact leaching, or cooperative leaching, Figure 2 (Rawlings *et al.*, 1999).

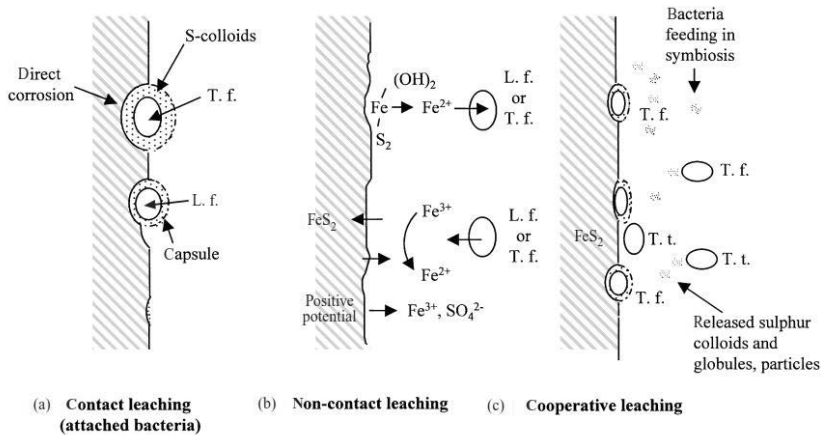
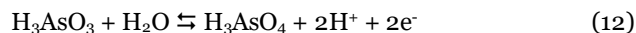
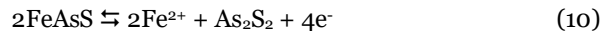
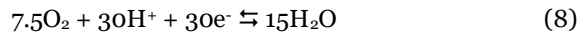
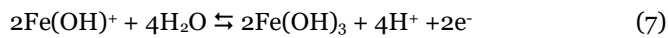
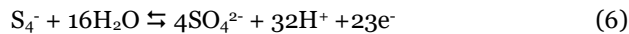
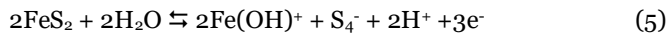


Figure 2. Direct and indirect interaction of bacteria with pyrite a) contact leaching *Thiobacillus ferro-oxidans* (T.f.) or *Leptospirillum ferro-oxidans* (L.f.), b) non-contact leaching, and c) cooperative leaching in which soluble energy carriers (Fe^{2+} and SO_4^{2-}) are generated by T.f. for use by bacteria in solution such as *Thiobacillus thiooxidans* (T.t) (Rawlings *et al.*, 1999).

It has been presented that pyrite (Eq. (5)) can be oxidized by iron(III) ions. The S_4^- species (Eq. (6)) and iron(II) ions (Eq. (7)) formed can be oxidized by bacteria, whereas the reduction reaction at the bacteria could be described by Eq. (8). The total chemical reaction is presented in Eq. (9). (Blight *et al.*, 2000) It is suggested that arsenopyrite oxidizes in two stages: arsenic(II) sulfide covers the arsenopyrite surface (Eq. (10)) in the first stage and arsenic(II) sulfide oxidizes to arsenic(III) acid by Eq. (11) and later to arsenic(IV) acid (Eq. (12)) in the second stage in the presence of Eq. (7). (Jiang *et al.*, 2008)



The disadvantages of bio-oxidation that have been mentioned are the slow reaction rate, bacteria selectivity for temperature, low operational pH and therefore higher tendency for corrosion of process equipment, possibility of carbon deactivation in CIP due to fouling, accumulation of organic residue from

the bacterial reactions, and possible foaming (La Brooy *et al.*, 1994). During bio-oxidation, base metals (copper and zinc sulfides) can also be dissolved simultaneously, enhanced by the bacterial oxidation of iron(II) to iron(III) (Marchevsky *et al.*, 2017).

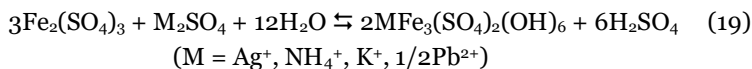
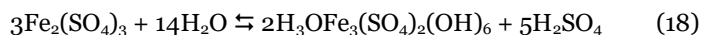
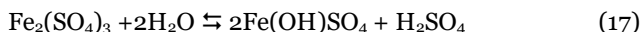
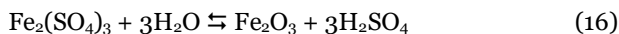
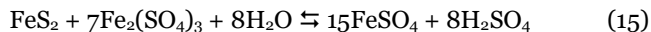
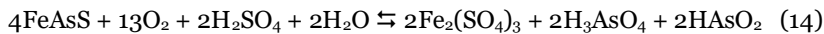
Bio-oxidation can also result in increased cyanide consumption during the subsequent gold leaching, due to the high iron content in the jarosite formed at higher redox potentials, leading to iron dissolution and iron(III) cyanide complex formation (Ciftci and Akcil, 2010). It has been presented that three types of jarosite can be formed in bio-oxidation. Jarosite can form pseudomorphs (i.e., original mineral is replaced with another while the original appearance and dimensions remain), but also precipitate directly in the solution or alternatively as a thin film on the pyrite grains. (Henao and Godoy, 2010) Consequently, this thin film around the grains can passivate the pyrite (Márquez *et al.*, 2006). These kinds of films have not been reported on pyrite after alternative chemical oxidation routes (Holmes *et al.*, 1999). The development of biological agents in the mining industry is an ongoing trend and it is likely that the interest in biotechnologies will grow in the future (Zammit *et al.*, 2012).

2.2.4 Pressure oxidation (POX)

Compared to bio-oxidation, pressure oxidation (POX) is a more aggressive ($T = 170 - 225\text{ }^{\circ}\text{C}$) and substantially faster (1–3 h) hydrometallurgical oxidation method for refractory raw materials. The pressure oxidation process can be carried out in alkaline or acidic conditions. The primary oxidant in the POX process is considered being dissolved oxygen, Eqs. (13) – (14), (Marsden and House, 2006) whereas oxygen may also oxidize iron(II), and consequently dissolved iron(III) can also oxidize sulfidic minerals, e.g., total reaction of pyrite Eq. (15). It is presented that sulfide oxidize to thiosulfate and further to sulfate by iron(III). (Garrels and Thompson, 1960; Moses *et al.*, 1987; Rimstidt and Vaughan, 2003) In order to prevent elemental sulfur formation, temperatures higher than $160\text{ }^{\circ}\text{C}$ are typically used, leading to sulfate formation, Eq. (13). Moreover, an operating temperature as high as $230\text{ }^{\circ}\text{C}$ has been used. (La Brooy *et al.*, 1994; Zaytsev *et al.*, 2013) The oxidation of arsenopyrite and pyrite is improved by higher oxygen partial pressure and temperature, as these are linked to the amount of dissolved oxygen in solution, and thus to the amount of oxidant available for reactions (Rusanen *et al.*, 2013). Also, the finer particle size increases the reactive surface area of sulfides for oxidation (Zaytsev *et al.*, 2013).

In the autoclave, pyrite and arsenopyrite dissolve forming iron(III) sulfate, which is transformed by hydrolysis into solid form such as hematite, Eq. (16), basic iron(III) sulfate, Eq. (17), jarosite, Eqs. (18) and (19), and ferric arsenate, Eq. (20). Basic iron sulfates form under acidic conditions ($\text{pH} < 2$) and at high temperature ($> 140\text{ }^{\circ}\text{C}$), Eq. (17). The hot cure process ($\text{pH} < 1$ and temperature $< 140\text{ }^{\circ}\text{C}$) is used after pressure oxidation to break down the basic iron sulfate formed in the autoclave in a controlled manner. (Fleming, 2010) As reactions Eq. (13) and Eq. (14) are known to be exothermic, concentrates with over 4% sulfide content do not require additional heating and are generally more

suitable raw materials for pressure oxidation compared to gold ores and concentrates with lower sulfide content (Marsden and House, 2006).



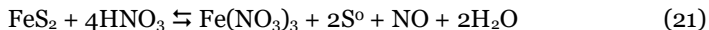
The presence of chloride ions and organic carbon cause gold losses in pressure oxidation. Gold may dissolve in the presence of chloride ions, forming gold chloride complexes, which then reduce onto on the organic carbon surface already during POX treatment (preg-robbing). The reduced gold does not dissolve during cyanidation but causes gold losses in the process leach residue. (Zaytsev *et al.*, 2013)

Alkaline pressure oxidation operates at similar temperatures, pressure, and oxygenation to acidic pressure oxidation, but under neutral or slightly alkaline conditions. The process is applicable for the treatment of refractory raw materials that contain high amounts of carbonates (>10% CO₃²⁻) and have a low sulfur content (<2%). The process favors low levels of sulfuric acid formation (low sulfur content) and the high neutralization capacity (high carbonate content) of the raw material, decreasing chemical consumption. (La Brooy *et al.*, 1994; Marsden and House, 2006)

2.2.5 Alternative oxidation methods

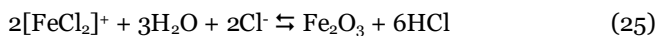
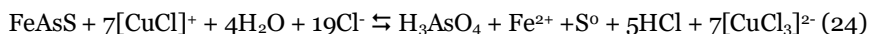
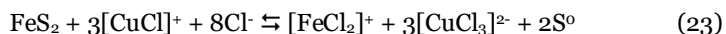
Direct chemical oxidation of refractory gold ore and concentrate can also be carried out in alkaline conditions (Nan *et al.*, 2014), in nitric acid, sulfuric acid, or chloride solution (La Brooy *et al.*, 1994). Use of nitric acid as an oxidant for refractory (pyrite and arsenopyrite) ores and concentrates has been investigated since the 1980s, and it has been suggested that it provides the fastest sulfide oxidation kinetics in atmospheric pressure compared to other chemical oxidation methods (Marsden and House, 2006). In nitric acid solution, pyrite is oxidized to iron(III) and elemental sulfur, Eq. (21), and then consequently to sulfuric acid and nitric oxide, Eq. (22) (Kadioğlu *et al.*, 1995). Several nitric acid

oxidation processes have been patented and developed, e.g., the Nitrox, Arseno, NSC, Redox, and HMC processes. Nitric acid oxidation has been used at least in Idaho, United States. (La Brooy *et al.*, 1994; Marsden and House, 2006)



Chlorine gas is a strong oxidizer and thus it has been used in historical gold leaching processes for gold dissolution. However, chlorine and/or chloride-based systems can also be used for the oxidation of refractory sulfide minerals. (Marsden and House, 2006) Pyrite leaching has been investigated with the electrochemical generation of hypochlorite from sodium chloride solution (Arslan and Duby, 1997), with chloride-hypochlorite (Li *et al.*, 2015), with chloride dioxide (Dong *et al.*, 2019), and with chloride solutions having an additional oxidant such as copper(II) present (Nicol *et al.*, 2018; Elomaa *et al.*, 2018).

A copper(II) chloride complex as well as an iron(III) chloride complex are able to provide high oxidative power in chloride solutions (Muir, 2002). Therefore, direct atmospheric leaching of pyrite and arsenopyrite can also be conducted in chloride solutions, Eqs. (23) – (24) (Leppinen *et al.*, 2010; Elomaa *et al.*, 2018). With a suitable pH adjustment, iron can be precipitated as hematite in atmospheric pressure, Eq. (25), (Riveros and Dutrizac, 1997; Leppinen *et al.*, 2010; Miettinen *et al.*, 2013;) or as jarosite (Cohen *et al.*, 2005). Arsenic precipitates as ferric arsenate, Eq. (26) (Leppinen *et al.*, 2010).



The current thesis investigated further the direct leaching of refractory gold concentrate in chloride-bromide leaching, requiring long leaching times ($t = 60$ h) for high sulfide oxidation (67%).

2.3 Prevention of preg-robbing phenomenon

Several methods such as roasting (Miller *et al.*, 2005), biodegradation (Ofori-Sarpong and Osseo-Asare, 2013), chlorination (Cl_2 pre-treatment), long-term oxidation (Sibrell *et al.*, 1990; Marsden and House, 2006), and blinding (Zhou *et al.*, 2013) have been used or investigated to prevent preg-robbing during gold leaching in different lixiviants. Industrially, graphitic carbon pre-flotation has also been applied to decrease the presence of preg-robbing substances in the

raw material, e.g., at the Agnico-Eagle Mines, Kittilä Mine (Doucet *et al.*, 2010). Depending on the ore characteristics, gold leaching in a non-cyanide environment, e.g., ammoniacal thiosulfate solution, has been suggested to increase gold recovery from carbonaceous ore. Roasting has been used traditionally for sulfide oxidation, and also for the oxidation of carbonaceous material, Eq. (27), prior to leaching. The graphitic carbon can also be oxidized by roasting. Roasting temperatures of less than 600 °C are common in the oxidizing of carbonaceous material. (Miller *et al.*, 2005; Thomas and Cole, 2005) Sulfide mineral oxidation by roasting is presented in more detail in section 2.2.2.

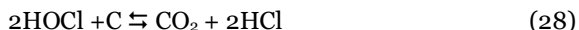


Pre-treatment with the fungus *Phanerochaete chrysosporium* has also been investigated as an alternative to reduce preg-robbing activity. It has been suggested that fungus pre-treatment may impact carbon activity in three different ways: first, by carbon loss and carbon surface oxidation (Ofori-Sarpong *et al.*, 2013) when the continuous graphite carbon structure is disrupted by fungal degradation (Liu *et al.*, 2016). Second, the surface area of the carbon is reduced by plugging pores with fungal mycelia and microbial-produced slime. Third, fungal activity enlarges the micropores that preg-robbing prefers. (Ofori-Sarpong *et al.*, 2013) It has been shown that gold adsorption to carbonaceous material could be reduced by 70 – 97% in cyanide solution with *P. chrysosporium* pre-treatment (Ofori-Sarpong and Osseo-Asare, 2013) by oxidation of 34% of the elemental carbon (Liu *et al.*, 2016). Also, it has been stated that *Thiobacillus ferro-oxidans*, *Thiobacillus thio-oxidans*, and *Leptospirillum ferro-oxidans* reduce the preg-robbing of carbonaceous matter due to electrostatic repulsion with organic matter or by blocking the active sites of the carbonaceous material (Yang *et al.*, 2013).

Many blinding agents such as light petroleum oils, anionic and non-ionic surfactants, and cationic surfactants (e.g., kerosene, fuel oil, and RV-2 (para nitro benzol azo salicylic acid)) have been tested and used to prevent preg-robbing to some extent in conventional cyanide leaching processes. Blinding chemicals can block the active sites of carbon, thus preventing preg-robbing. (Afenya, 1991) Often, a high concentration of the blinding chemical (~1%) is required to affect the preg-robbing activity of natural carbon (Adams and Burger, 1998).

Chlorination (Cl₂ pre-treatment) was used for preg-robbing prevention industrially in the 1970s and 1980s in gold cyanide leaching plants (Sibrell *et al.*, 1990). The mechanism of preg-robbing prevention with chlorination is not known in detail. Direct oxidation is theoretically possible, Eq. (28). However, it has been suggested that the mechanism of chlorination pre-treatment is the modification of the active sites of carbon rather than carbon oxidation. Chlorohydrocarbon or the carbonyl structures of carboxyl groups (COOH) are formed, and passivate and block the active sites of carbon. (Marsden and House, 2006). It has been suggested that, during chlorination, the surface of

carbonaceous material ionizes and obtains a negative charge, thus the negatively charged gold cyanide complex repels the negative carbonaceous material (Sibrell *et al.*, 1990). Chlorination pre-treatment was practiced industrially at least at Newmont Carlin, Nevada in the 1970s and at Jerritt Canyon, Nevada in the 1980s, for sulfide-carbon-rich and carbon-rich ores, respectively. These plants were reported to have run down due to lack of carbonaceous oxide ore and the price of chlorine gas. (Miller *et al.*, 2005; Marsden and House, 2006)



Maybe the most common method to prevent preg-robbing is to provide a competitive adsorbent during leaching. In the cyanide industry, typically activated carbon (CIL) or resin (RIL) is used. (Miller *et al.*, 2005) Carbons used in gold recovery are typically prepared from coconut shells by activation treatment. In the first stage of the activation process, material is heated to 500 °C in the presence of a dehydrating agent to remove most of the impurities (e.g., carbon monoxide, carbon dioxide, and acetic acid). In the second stage, the carbonized material is heated to 700 – 1000 °C in an oxidizing atmosphere of steam, carbon dioxide, and/or oxygen to burn off the tar-like residue and to develop an internal porous structure. The activation of carbon is catalyzed by iron and copper oxides and carbonates of the alkali metals. (Marsden and House, 2006) This kind of activated carbon, with a particle size larger than that of the gold ore, can provide an attractive adsorption site for gold instead of the natural carbon present in the ore. The separation of activated carbons from the gold leaching slurry can then be conducted based on particle size. A similar principle is used when applying ion-exchange resins in leaching. (Miller *et al.*, 2005) Strong and weak base resins are used in resin in leach. Strong base resins have a high loading capacity and fast loading rate, but they have poor selectivity and are difficult to elute. Weak base resins have been suggested as more selective, and elution is much easier, but the loading capacity (25 – 50% lower) is lower and the loading rate slower. (Marsden and House, 2006)

2.4 Gold leaching

As gold is a very noble metal, it requires a complexant in addition to an oxidant to allow dissolution into the solution. Gold can dissolve in gold(I) or gold(III) form, and only a relatively low number of ligands are able to form a sufficiently stable complex with gold, Table 1. Industrially, cyanide is the most widely used ligand in gold leaching, supported by the fact that the gold cyanide complex is very stable in solution. In order to challenge cyanide, the new cyanide-free leach reagents should be low cost and/or recyclable, selective for gold, non-toxic, and compatible with the gold recovery processes. Currently, the most promising alternatives for cyanide are thiosulfate, thiourea, glycine, and chloride. (Aylmore, 2005; Hilson and Monhemius, 2006) Industrially, thiosulfate is the

only cyanide-free complexation agent used for primary raw materials, and is used at Barrick's Goldstrike plant in Nevada (Barric, 2016).

Table 1. Stability constants for most commonly studied gold complexes at 25 °C (Aylmore, 2005).

Ligand	Au(I) or Au(III) complex	log β_2 or β_4
CN ⁻	Au(CN) ₂ ⁻	38.3
S ₂ O ₃ ²⁻	Au(S ₂ O ₃) ₂ ³⁻	28.7
CS(NH ₂) ₂	Au(NH ₂ CSNH ₂) ₂ ⁺	23.3
Cl ⁻	AuCl ₂ ⁻	9.1
	AuCl ₄ ⁻	25.3
Br ⁻	AuBr ₂ ⁻	12
	AuBr ₄ ⁻	32.8
I ⁻	AuI ₂ ⁻	18.6
	AuI ₄ ⁻	47.7
HS ⁻	Au(HS) ₂ ⁻	29.9
NH ₃	Au(NH ₃) ₂ ⁺	26.5
Glycinate	Au(NH ₂ CH ₂ COO) ₂ ⁻	18
SCN ⁻	Au(SCN) ₂ ⁻	17.1
	Au(SCN) ₄ ⁻	43.9
SO ₃ ²⁻	Au(SO ₃) ₂ ³⁻	15.4

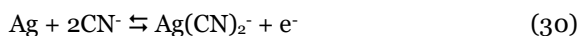
2.4.1 Cyanide leaching

The triumphant march of the cyanide leaching process started from the low-grade deep Witwatersrand ore, where gold occurred in fine particles. Using the cyanide leaching process, the gold extraction was increased from 55 – 65% (by amalgamation and chlorination) to 90%. (Habashi, 2005; Marsden and House, 2006) Later, cyanide leaching and ancillary processes were developed, e.g., cyanide heap leaching, CIP, CIL, RIP (resin in pulp), and RIL processes. The Elsner equation (Eq. (29)) is considered as the basis for the state-of-the-art understanding of gold leaching, with oxygen acting as the oxidant for gold dissolution, whereas cyanide complexes the dissolved gold and keeps it stable in solution. (Marsden and House, 2006) Iron(III) cyanide has been suggested to be a more efficient oxidant than air to dissolve gold and silver sulfide in cyanide leaching (Xie and Dreisinger, 2009).



Cyanide leaching is usually carried out at ambient temperature due to the cost associated with increased temperatures. However, higher temperatures (50 – 65 °C) have been used with high grade gold concentrates such as gravity concentrates. The typical pH used in cyanidation is >9.4 to prevent cyanide loss by hydrolysis, and also to avoid the formation of toxic hydrogen cyanide gas. The cyanide and oxygen concentrations, temperature, pH, exposed surface area of gold, degree of agitation, gold purity, and the presence of other ions have an effect on the cyanide leaching kinetics. In addition to gold dissolution (Eq. (29)), cyanide and oxygen react with the other minerals and dissolved species present

in the system, and therefore the consumption of these chemicals depends on the side reactions as well. For example, silver is known to form a cyanide complex by the reaction shown in Eq. (30). Most copper minerals (such as bornite, covellite, and copper oxides and carbonates) dissolve, copper being highly soluble in cyanide solution as copper(I) cyanide complexes. Chalcopyrite is the least soluble copper sulfide mineral in cyanide solution. (Marsden and House, 2006) Copper can be dissolved from copper-rich gold concentrate by ammoniacal (0 – 34 g/L) cyanide leaching with lower cyanide consumption (90% lower than without ammoniacal addition) (Bas *et al.*, 2015). Also, the addition of glycine (0.25 – 1 g/L) can affect the gold dissolution kinetics of copper-bearing gold ores (Oraby and Eksteen, 2015a). Hematite, magnetite, goethite, siderite, and iron silicates are insoluble in alkaline cyanide solutions, but for example pyrrhotite reacts with cyanide according to Eq. (31). Elemental sulfur (which may be formed during oxidative pre-treatment or sulfide dissolution in dilute cyanide solution) reacts with cyanide solution, forming thiocyanate, Eq. (32). (Marsden and House, 2006; Rabieh *et al.*, 2017)

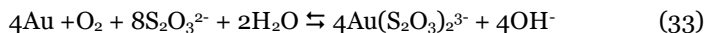


Usually gold extraction increases when the particle size decreases (due to gold liberation); however, at the same time more surface area is exposed for cyanide-consuming side reactions. Therefore, the optimal particle size may require a compromise between gold extraction and cyanide consumption. A typical particle size (d80) in cyanide leaching is 45 – 150 μm . Cyanide leaching is often a mass transport-controlled reaction; therefore the reaction rate depends on the thickness of the diffusion layer and the mixing characteristics of the bulk solution. (Marsden and House, 2006)

Gold recovery to activated carbon is widely used in cyanide leaching (Marsden and House, 2006), either during leaching (CIL) or after leaching (CIP). The gold cyanide complex ($[\text{Au}(\text{CN})_2]^-$) is physically adsorbed into activated carbon. Gold loading from synthetic solution to activated carbon can be described by the empirical Freundlich equation, which relates the amount of gold adsorbed to the concentration of gold remaining in solution at equilibrium. (McDougall and Hancock, 1981) In gold cyanide processes, a typical gold loading of 5 000 – 7 000 $\text{g}_{\text{gold}}/\text{t}_{\text{carbon}}$ is achieved, before the carbon is subjected to washing and elution, and the eluted gold to electrowinning and casting into doré gold bars (Fleming *et al.*, 2011). As an alternative to carbon adsorption, gold can also be recovered by direct cementation, i.e., by applying sacrificial metal such as iron or zinc to reduce gold to the metallic form (Angelov and Groudev, 2002).

2.4.2 Thiosulfate leaching

Similar to cyanide leaching, gold is oxidized by oxygen (and/or copper(II)) in thiosulfate leaching, Eq. (33) (Marsden and House, 2006). Thiosulfate ($S_2O_3^{2-}$) is an alternative gold leaching media, and was used as long ago as the early 1900s (Aylmore and Muir, 2001). Thiosulfate leaching is carried out in alkaline conditions due to the decomposition of thiosulfate by acid. The process operates at $pH > 8.5$. In thiosulfate leaching, the parameters dominating the leaching kinetics are the thiosulfate concentration (typically 11 – 22 g/L), dissolved oxygen, temperature (typically 40 – 60 °C), solid concentration (typically 10–40%), and copper concentration (typically 0.5 – 1 g/L) (Hilson and Monhemius, 2006; Ha *et al.*, 2014).



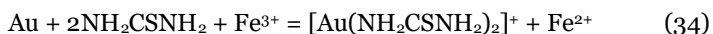
The consumption of thiosulfate is one issue in thiosulfate leaching, as dissolved oxidizing reagents such as copper(II) or iron(III) can oxidize thiosulfate as well. Therefore, an oxidant stabilizer (e.g., ammonia or an open chain polyamide ligand for copper and oxalate for iron) is often used to decrease this oxidation. The slow gold dissolution kinetics and complex chemistry in copper-thiosulfate systems have been mentioned as the drawbacks of thiosulfate leaching. (Muir and Aylmore, 2005; Hilson and Monhemius, 2006)

Gold recovery in thiosulfate solutions can be conducted by reduction with metallic copper, iron, zinc or aluminum or soluble sulfides, or solvent extraction (alkyl phosphorus ester and primary, secondary, and tertiary amines). However, gold recovery from resin or activated carbon is not easy. It has been suggested that the high negative charge of the complex, the steric limitations of the molecular structure, or specific interactions of the ligand group with carbon active sites may be reasons for the low gold loading on activated carbon. Typically, thiosulfate leaching has been proposed for complex ores and concentrates with high cyanide-consuming copper content, as the dissolved copper in thiosulfate solution can even be beneficial to increase gold dissolution kinetics. (Aylmore and Muir, 2001; Xu *et al.*, 2017) Gold thiosulfate complexes are not highly preg-robbing due to their very weak affinity to carbonaceous substances, i.e., one advantage of thiosulfate leaching that has been suggested is its suitability to treat carbonaceous preg-robbing ores (e.g., Goldstrike) (Schmitz *et al.*, 2001; Xu *et al.*, 2017).

2.4.3 Thiourea leaching

The earliest patent of gold thiourea (NH_2CSNH_2) leaching is from 1906 by Moir. Canmet and Mintek investigated gold thiourea extraction in underground and in-stope applications (gold recovery from footwalls, hanging walls, sidewalls, and the support packs of the stope by spraying lixiviant to leach fine gold from cracks and crevices). Newmont Mining and Barrick Gold have also investigated possibilities for the use of thiourea leaching for pre-treated refractory ores. Thiourea leaching is carried out in acidic solution in the

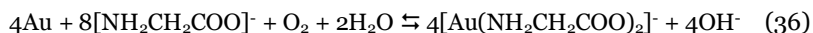
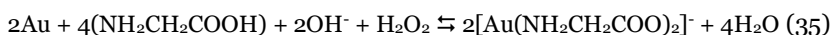
presence of an oxidant e.g., iron(III) ion, hydrogen peroxide, manganese dioxide, monoperoxysulfate, or ozone. Dissolved gold forms a cationic complex with thiourea according to Eq. (34). (Ubalini *et al.*, 1998; Aylmore, 2005; Hilson and Monhemius, 2006)



One challenge related to thiourea leaching is its rapid decomposition in typical leaching conditions (pH = 1 – 3, $[\text{Fe}]_{\text{aq}} = 5 \text{ g/L}$, $[\text{NH}_2\text{CSNH}_2]_{\text{aq}} = 10 \text{ g/L}$) (Hilson and Monhemius, 2006). Thiourea is oxidized during leaching by the oxidant (e.g., iron(III)) and in acidic conditions forms formamidine disulfide. An increase of pH and temperature can decrease this decomposition reaction. (Örgül and Atalay, 2002) In addition, thiourea is suspected to be carcinogenic (Marsden and House, 2006). In any case, thiourea has a lower toxicity and higher gold dissolution rate than cyanide (Hilson and Monhemius, 2006). The most successful gold leaching applications with thiourea have been for high cyanide-consuming ores such as antimony or sulfidic ores after bacterial or pressure oxidation. One small-scale industrial application of gold thiourea leaching was demonstrated at the New England Antimony Mines in Australia in 1982 for gold-antimony concentrate. (Aylmore, 2005; Hilson and Monhemius, 2006) Gold recovery from thiourea solution using activated carbon has been suggested to be effective. Gold can then be further recovered from activated carbon by elution with hydroalcoholic solution, and subsequently the gold can be reduced to elemental form by electrowinning. (Ubalini *et al.*, 1998).

2.4.4 Glycine leaching

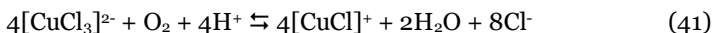
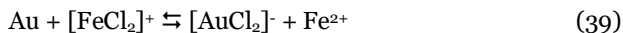
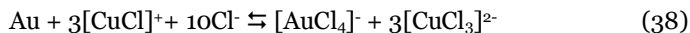
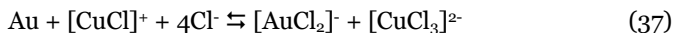
Glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) has recently received increased interest as an alternative gold leaching media, glycine being an α -amino acid with a carboxylic group and an amine group. Glycine leaching is carried out in neutral or alkaline (typically pH 10 – 11) solutions, using oxygen or hydrogen peroxide as oxidant. Also, copper(II) (0.06 – 0.6 g/L) is used as an oxidation reagent with oxygen or hydrogen peroxide (0.01 – 1%) to increase gold extraction. (Eksteen and Oraby, 2015; Oraby and Eksteen, 2015b; Eksteen and Oraby, 2016) It has been stated that gold leaching kinetics increases at higher pHs (Oraby and Eksteen, 2015b) due to the increasing formation of hydrogen ions and oxygen generation as a result of hydrogen peroxide decomposition or the production of hydrogen radicals (Süss *et al.*, 1997). The glycine concentration used is typically investigated in a concentration range of 7.5 – 150 g/L, and the applied temperature is 30 – 75 °C (Eksteen and Oraby, 2015; Eksteen and Oraby, 2016). Dissolved gold forms a strong complex (Table 1) with glycine when using hydrogen peroxide as oxidant (Eq. 35) and when using oxygen as oxidant, Eq. (36) (Tauetsile *et al.*, 2018a).



Gold can be recovered from glycine by activated carbon. It is suggested that the gold loading capacity of activated carbon increases with increasing copper concentration in solution (Tauetsile *et al.*, 2018a). On the other hand, a higher copper concentration decreases the gold adsorption kinetics (Tauetsile *et al.*, 2018b).

2.4.5 Chloride leaching

In gold chloride leaching, gold can be dissolved into the solution by a dissolved oxidant such as copper(II) or iron(III), with chloride acting as the complexing reagent. The gold dissolution kinetics is faster in chloride solutions compared to cyanide solutions. In chloride solutions, gold dissolves as gold(I) and gold(III) chloride complexes. (Marsden and House, 2006) The reaction in chloride solution with copper(II) can result in monovalent gold(I) Eq. (37) (Senanayake, 2004) and/or gold(III) chloride complex formation Eq. (38) (Leppinen *et al.*, 2010). Similarly, leaching with iron(III) can result in gold dissolution in monovalent form Eq. (39) (Senanayake, 2004) and/or as gold(III) Eq. (40) (Seisko *et al.*, 2019). An external oxidant such as oxygen is required to oxidize the reduced species: copper(I) to copper(II) Eq. (41) or iron(II) to iron(III) Eq. (42) (Abe and Hosaka, 2010). Further, the dissolved iron and copper may also react with each other. When the oxidation potential is <1.2 V vs. SHE (standard hydrogen electrode) (0.911 V vs. Ag/AgCl) at pH <0.5 (Nicol, 1980) or <0.8 V vs. SCE (saturated calomel electrode) (0.755 V vs. Ag/AgCl) at pH 1 (Frankenthal and Siconolfi, 1982; Diaz *et al.*, 1993), gold(I) ($[\text{AuCl}_2]^-$) prevails, whereas at potentials of >1.2 V vs. SHE (0.911 V vs. Ag/AgCl) at pH <0.5 (Nicol, 1980), >0.8 V vs. SCE (0.755 V vs. Ag/AgCl) at pH 1 (Diaz *et al.*, 1993) or >1.1 V vs. SCE (1.055 V vs. Ag/AgCl) (Frankenthal and Siconolfi, 1982), gold(III) ($[\text{AuCl}_4]^-$) prevails.



Gold chloride complexes have lower stability compared to cyanide (Table 1), which is strongly dependent on the redox potential (Hasab *et al.*, 2013). A high solution redox potential helps to keep gold in solution, whereas gold reduces/re-precipitates upon contact with a reductant e.g., sulfidic minerals, metals (Mikhlin and Romanchenko, 2007), silicates (Mohammadnejad *et al.*, 2013), or

carbon (Sibrell *et al.*, 1990) at lower redox potentials. Redox potential, on the other hand, is highly dependent on the concentrations of copper(II) and/or iron(III) in the solution (Seisko, 2020). Copper(II) and iron(III) concentrations are affected by the pH: pH >2 precipitates iron(III) species and pH >3 precipitates copper(II) as atacamite. Gold chloride leaching has been reported to be favored by low pH, high chloride concentration, increased temperature, and high ore surface area (Hilson and Monhemius, 2006).

Several processes have been developed for chloride leaching such as Platsol™, the Intec process, Nippon N-Chlo, Dundee Sustainable Technologies, and Outotec's gold chloride process. In many of the development stage processes, bromide is added as an additive to chloride leaching. The advantages of bromide can be related either to oxidation or stability of gold complex. Bromide can be used to support the stability of the gold bromide complexes vs. gold chloride complex to decrease the gold losses. Also, it can act as a catalyst for the oxidation reagent, or as a chemical compound with chlorine (Halex, [BrCl₂]⁻) that have high oxidation potential.

The Platsol™ process was developed in collaboration with the University of British Columbia, Kane Consultants Ltd., and SGS Lakefield Research (Aylmore, 2016). It operates at high temperature (>200 °C) and increased oxygen pressure (e.g., 700 kPa) (Dreisinger *et al.*, 2005). The sodium chloride concentration in the autoclave feed is low, 5 – 10 g/L, i.e., chloride is used as an additive in pressure oxidation (Fleming, 2002). However, this low amount of chlorides is enough to dissolve and complex gold and PGM, and they can be recovered from the autoclave discharge slurry onto activated carbon (CIP) or after solid-liquid separation from solution by sulfide (NaHS) precipitation. Gold and PGM recovery can also be carried out using activated carbon in the autoclave. Instead of activated carbon, an ion exchange resin (e.g., Purolite A500 and Cognic AuRIX® 100) can also be used to recover gold after solid-liquid separation. (Ferron *et al.*, 2003). Base metals can be recovered from the solution after PGM recovery by industrially applied methods (Dreisinger *et al.*, 2005). The Platsol™ process is not suitable for preg-robbing ores due to gold losses during autoclave leaching (Ferron *et al.*, 2003).

The Intec gold process uses a mixed halides as the lixiviant in the process (a chlorine-bromine complex, [BrCl₂]⁻, named Halex) (Aylmore, 2016). In the process, copper sulfide oxidation is carried out at a temperature range of 85 – 95 °C with 213 – 284 g/L chloride, 479 – 639 g/L bromide (6 – 8 M chloride/bromide) and 20 – 60 g/L of cupric-containing solution. The residence time is 3 – 10 h depending on the leach kinetics and mineral composition in the feed. Gold is recovered onto activated carbon or ion exchange resin. The process has been developed for copper-bearing gold concentrates. Highly carbonaceous feeds are not directly suitable for the Intec gold process due to preg-robbing behavior during leaching. (Intec Ltd., 2009)

The N-Chlo process was developed by Nippon Mining & Metals. The process was developed for simultaneous copper and gold recovery from sulfide (e.g., chalcopyrite) and silicate minerals. The leaching is carried out in bromide ([Br]_{aq} >100 g/L) or chloride-bromide ([Br]_{aq} <100 g/L) media. If chloride is

added to the leaching, the chloride to bromide ratio will be 1:3 or less. The chemical composition of the leaching solution is 50–80 g/L bromide, 0–25 g/L chloride, <50 g/L copper, and 0.01–30 g/L iron. The temperature range is 45–95 °C. (Yoshimura and Abe; 2017) Copper(II) is used as an oxidation reagent to transfer oxygen from the air to the gold surface (Aylmore, 2016).

Dundee Sustainable Technologies, formerly Nicromet Extraction, has developed a chlorination-based gold process (Dundee Sustainable Technologies, 2014). Gold leaching is carried out as vat leaching at atmospheric pressure and ambient temperature, typically using free-milling or roasted (sulfur-free) raw materials (Aylmore, 2016). Bromine is used as a catalyst for the oxidation agent (Dundee Sustainable Technologies, 2014). Unlike previous processes, the oxidant is not copper(II) or iron(III) chloride or a bromide complex, but the chlorine/bromine gas that is generated in situ from hypohalides (NaOCl and NaOBr) with addition of acid. The hypohalides are regenerated in an electrolytic cell. (Lalancette *et al.*, 2015)

Neomet Technologies Inc. has developed the Neomet gold process. The process was developed to recover gold from gold ore; however, it has been suggested that it is also able to recover gold from refractory and carbonaceous ores. The leaching is carried out in chloride media with the addition of nitric acid at high temperatures (80–160 °C). Hydrochloric acid is recovered and regenerated in the process. Gold is leached as a gold chloride complex using nitric acid and hydrochloric acid as oxidants. (Harris and White, 2011)

Outotec's gold chloride process is based on the HydroCopper™ process, which was developed to recover copper, silver, and gold from sulfidic copper concentrates (Hyvärinen *et al.*, 2004; Leppinen *et al.*, 2010). The development of Outotec's gold process has been continued for gold-bearing materials (Miettinen *et al.*, 2013; Miettinen *et al.*, 2014; Lundström *et al.*, 2014; Lundström *et al.*, 2015; Lundström *et al.*, 2016) and also for double refractory materials (Lundström *et al.*, 2017). In addition, a gold recovery process by solvent extraction for chloride solution has been developed and patented by Outotec (Paatero and Haapalainen, 2011; Haapalainen and Karonen, 2015; Haapalainen and Miettinen, 2016; Haapalainen, 2016). In addition, an alternative gold recovery route directly from a gold-bearing copper chloride solution has been presented, a direct electrochemical recovery by electrodeposition-redox replacement (EDRR) (Lundström and Yliniemi, 2017).

The gold chloride complex ($[\text{AuCl}_4]^-$) can also be recovered using activated carbon. Unlike in cyanide solutions, gold has a tendency to reduce on activated carbon as metallic gold due to its electrochemical nature. (McDougall and Hancock, 1981) Mass transfer limits gold reduction (gold(I) and gold(III)) on activated carbon (Hughes and Linge, 1989). Gold reduces mainly on the activated carbon surface and only randomly inside the pores of activated carbon (Wojnicki *et al.*, 2015). The impurities (e.g., copper and iron) only have a small effect on gold reduction on activated carbon (Sun and Yen, 1993).

2.5 Process simulation and environmental analysis

Steady-state mass and energy balance is the most commonly used simulation method in the fields of engineering and design (Smith, 2005). There are several applications for the models in engineering: research and development, process design, planning and scheduling, process optimization, and prediction and control (Roffel and Betlem, 2006). In addition, the model output can be used to evaluate not only the economic but also the environmental feasibility of the process (Reuter, 1998; Elomaa *et al.*, 2019). The modeling type and detail level of the model depend greatly on the application (Roffel and Betlem, 2006). The process simulation may cover only a single area of the process or the whole process. The input flows indicate quantities of chemical feed in the real world. The same goes for output flows. With modeling, it is possible to test various ideas and options to improve the understanding of the process operation in different scenarios. (Smith, 2005)

Models can be classified according to their properties: dynamic model, static/steady-state model, mechanistic models, and empirical model. Dynamic models are time dependent and often presented as differential (or difference) equations. Steady-state models are not time dependent and represent operation at a steady operation point. Mechanistic models are based on the actual or assumed mechanisms of the studied phenomenon, whereas empirical models are based on observations. (Smith, 2005; Seppälä *et al.*, 2014)

The comparison of process options is often challenging. The mass and energy balance presents the resources required and the outputs generated to perform the process operation. (Llamas *et al.*, 2019) To produce a simulation of a metallurgical process requires a lot of understanding about chemistry and industrial metallurgical process operations in the applied unit processes (Reuter *et al.*, 2015). In metallurgical systems, resources of a different nature and the residues produced have a wide variation, and generic and average values or simplifications create “black box models”. Therefore, comparison of the processes and sustainability assessment is challenging. (Reuter, 1998; Llamas *et al.*, 2019; Segura-Salazar *et al.*, 2019) In general, the target of the simulation is to produce accurate, verified, and detailed data from a metallurgical process for a life cycle inventory (Reuter 1998). General data for the hydrometallurgical gold process simulation (process conditions and material specific characterizations) can be found from the published literature, and consequently this data can be used to produce general flowsheets. The life cycle inventory for metallurgical processes can be collected from a simulated mass and energy balance. (Elomaa, 2020)

Life cycle inventory analysis is a data collection and calculation procedure to quantify the relative inputs and outputs of the process (ISO 14040, 2006). From the simulation model, energy, raw material, ancillary and other physical inputs, products, co-products and waste, releases to air, water and soil, and other environmental aspects are collected for an LCI (ISO 14044, 2006). An LCI can be used for an LCA, which is the standardized method to evaluate environmental impacts of processes (ISO 14040, 2006). Environmental impacts evaluated by LCA can be classified in different impact categories, such as global

warming potential, human toxicity, ecotoxicity, acidification potential, and eutrophication potential (Curran, 2012).

3. Experimental method

This Chapter describes the conditions of the batch leaching experiments, experimental set-up, analysis methods, and calculation methods used in Publications I - IV. In addition, the methodology of simulation is presented, and consequently the results of simulation are presented solely in the compendium section of the thesis.

3.1 Batch leaching experiments

The conditions of the selected batch leaching tests from Publications I – IV are presented in Table 2. The leaching parameters were originally selected based on the literature, that highlights that high chloride, bromide and oxidant concentration as well as temperature is required for gold dissolution. Also, industrially relevant high solid concentration was used when appropriate. However, in the course of the research it became evident that milder and less aggressive leaching conditions could allow for sufficient gold extractions. Therefore, chloride concentration, copper(II) and iron(III) concentrations as well as bromide concentration were brought down to find the lower limits that could allow gold dissolution of free gold in chloride media. The experiments were carried out at Outotec Research Center in Pori, Finland. The relationships of Tests 1 – 25 related to the findings and objectives are presented in Figure 3.

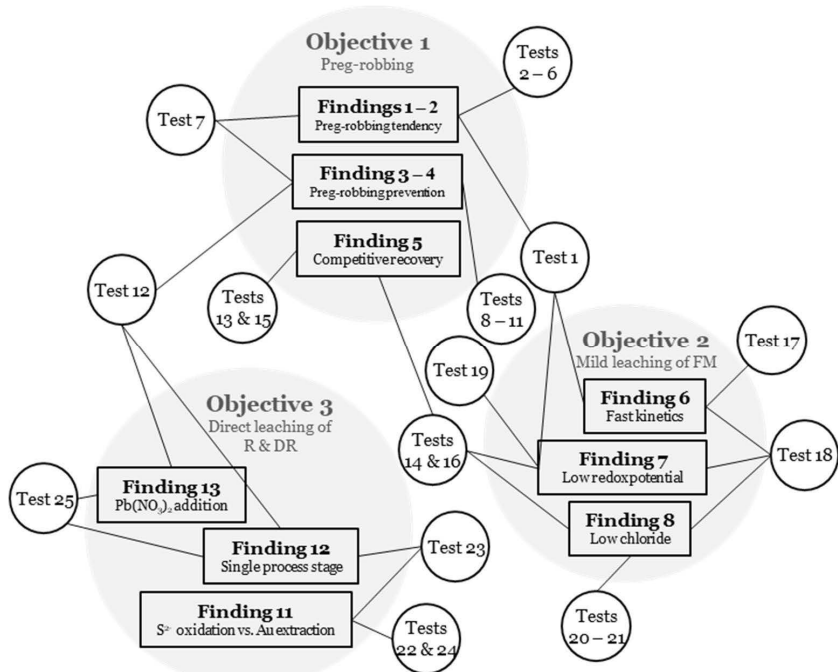


Figure 3. The relationship of Tests 1 – 25 to findings 1 – 8 and 11 – 13 and to objectives 1 – 3. FM stands for free-milling gold ore, R refractory, and DR double refractory gold concentrate.

Table 2. Experimental parameters of gold batch leaching tests from Publications I – IV. S/L = solid concentration, DR = double refractory concentrate, R = refractory concentrate, and FM = free-milling ore.

Test Nr.	Publication/ Test Nr	S/L, g/L	[Cl] ₀ , g/L	[Br] ₀ , g/L	[Cu] ₀ , g/L	[Fe] ₀ , g/L	[HCl], g/L	pH, -	[Act. C] ₀ , g/L	T, °C	t, h	Other, -
1	I/Test 1	400	150	6.2	15	-	10	-	-	98	10	*0% w/w
2	I/Test 2	400	150	6.2	15	-	10	-	-	98	10	*0.01% w/w
3	I/Test 3	400	150	6.2	15	-	10	-	-	98	10	*0.1% w/w
4	I/Test 4	400	150	6.2	15	-	10	-	-	98	10	*1% w/w
5	I/Test 5	400	150	6.2	15	-	10	-	-	98	10	*5% w/w
6	I/Test 6	400	150	6.2	15	-	10	-	-	98	10	*10% w/w
7	II/Test 8	220	150	6.2	15	-	10	-	-	98	12	DR POX
8	II/Test 9	100	150	6.2	15	-	10	-	-	98	12	DR POX + Cl ₂
9	IV/Test 5	262	225	78	100	-	-	1.7	-	98	12	DR POX
10	IV/Test 6	86	225	78	100	-	10	-	30	98	24	DR POX
11	IV/Test 8	122	234	78	100	-	-	0.5	-	95	60	DR
12	IV/Test 9	119	225	78	100	-	-	1.7	25	98	40	DR
13	III/Test 9	360	100	-	5	-	10	-	-	98	30	FM
14	III/Test 10	360	100	-	5	-	10	-	18	95	30	FM
15	III/Test 11	360	100	-	-	5	10	-	-	98	30	FM
16	III/Test 12	360	100	-	-	5	10	-	18	94	30	FM
17	II/Test CN	500	-	-	-	-	-	11	-	22	24	FM, NaCN**
18	III/Test 2	360	225	78	100	-	-	1.7	-	98	4	FM
19	III/Test 17	360	100	-	-	-	10	-	18	95	30	FM
20	III/Test 18	240	20	-	18	-	-	<3	19	98	40	FM
21	III/Test 19	240	10	-	9	-	-	<3	19	98	40	FM
22	IV/Test 1	28	225	78	100	-	-	1.7	-	98	12	R POX
23	IV/Test 3	211	225	78	100	-	-	1.7	-	98	60	R
24	IV/Test 4	198	225	78	100	-	-	1.7	-	98	36	R
25	IV/Test 10	110	225	78	100	-	-	1.7	25	98	40	DR, Pb(NO ₃) ₂ ***

* Activated powder addition into free-milling gold ore before leaching test.

** [NaCN]_{aq} = 3 g/L

*** [Pb(NO₃)₂]_{aq,0} = 224 g/t_{feed}

Three different gold-containing raw materials were investigated in the thesis. Non-preg-robbing silicate based on free-milling gold ore (FM) was used in Tests 1 – 6 and 13 – 21. Main minerals are quartz (56.2%), clay minerals (21.1%), micas (15.6%) and, feldspars (4%) in free-milling gold ore. Its more detailed mineralogical composition is presented in Publication III. Double refractory gold concentrate (DR) was also investigated and POX leaching residue was used in Tests 7 – 8 (Publication II). The double refractory concentrate consists of 33.1% pyrite and 12.5% arsenopyrite. In this raw material, arsenopyrite was the main carrier of gold (69.5%), while arsenic-bearing pyrite carried the rest (30.5%). Double refractory gold concentrate was also used in Tests 11 – 12 and 25 as such and as a POX leach residue in Tests 9 – 10 (Publication IV). The third investigated raw material was refractory gold concentrate (R), where arsenopyrite was the main carrier of gold (82.1%), and pyrite contained the remaining 17.9% of gold. This material mainly consists of pyrite (52.6%) and arsenopyrite (14.8%). Its POX residue was used in Test 22 and the concentrate in Tests 23 – 24. More detailed mineralogical composition of the double refractory and refractory gold concentrates are presented in Publication IV. Table 3 summarize the main metal contents of the investigated raw materials.

Table 3. Chemical composition of free-milling gold ore, double refractory and refractory gold concentrates.

	Free-milling ore (FM)	Double refractory concentrate (DR)	Refractory concentrate (R)
Au, g/t	4.8	38.7	18.5
Ag, g/t	1.6	42.6	28.4
Al, %	8.7	-	-
As, %	<0.003	6.1	6.8
C_{total}, %	0.11	3.6	-
Ca, %	<0.05	3	0.66
Cu, %	0.023	0.14	0.06
Fe, %	0.8	22.5	31.3
Mg, %	0.3	1.6	0.15
Mn, %	0.006	0.09	0.11
Na, %	0.34	-	-
Pb, %	<0.002	0.05	0.57
S, %	0.26	20.1	31
SiO₂, %	75.3	19.3	12
Zn, %	0.002	0.03	0.4

Copper(II) chloride and iron(III) chloride were used as an oxidant source, regenerated by oxygen gas during the experiments, Publications I – IV. Calcium chloride and sodium bromide were used as the ligand source for dissolved gold complexation, Publications I – IV. Hydrochloric acid and calcium hydroxide were used for pH control during the tests, Publications I – IV. The adsorption material (CICl tests) was activated carbon (Act. C) Norit RO 3515, Publications III – IV. The effect of lead (lead(II) nitrate) on gold extraction was investigated in Test 25, Publication IV. Sodium cyanide was used as a source of cyanide and

pressured air was used as an oxidant in Test 17, Publications I – II. Chlorination was investigated as a method for preventing preg-robbing phenomena in the pre-treatment of Test 8, Publication II. Sodium hypochlorite and chlorine gas were used as oxidants in chlorination pre-treatment, but not in the gold leaching experiments. Sulfuric acid was used as an initial acid addition in the acidification pre-treatment tests and pressure oxidation pre-treatment tests (if initial acid was added).

3.1.1 Leaching set-up

The batch gold chloride leaching experiments were carried out in a titanium (Publications I – IV) or glass reactor (Publications I – IV). The schematics of the experimental leaching set-up are presented in Figure 4. The titanium reactor was equipped with baffles and a reflux condenser and the glass reactor was equipped with a reflux condenser. An a45 type (pitch blade, OKTOP 1000 series) or GLS (gas liquid solid) type (OKTOP 2000 series) impeller was used. The a45 type impeller was used with a lower mixing speed to create more gentle agitation to avoid grinding the activated carbon. The redox potential was measured with an Ag/AgCl vs. Pt electrode. Oxygen gas was fed under the impeller. The temperature was adjusted automatically and verified with a thermometer. Hydrochloric acid or calcium hydroxide slurry was fed automatically based on the pH or manually based on the acid concentration. The acid concentration was measured with an automatic titrator.

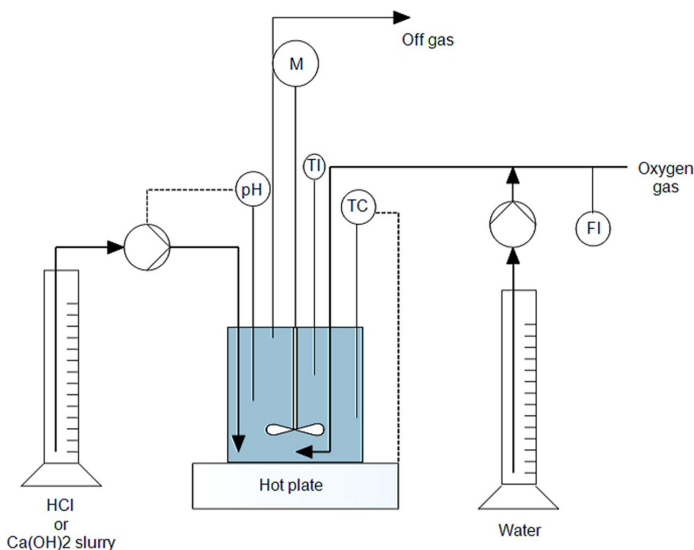


Figure 4. Schematics of the leaching set-up.

The cyanide leaching test, Test 17, (Publications I – II), was carried out in the same kind of experimental set-up without automatic pH control, water feed, or heating system. Control of the pH was carried out manually, with the addition of solid calcium hydroxide. The cyanide concentration was titrated, and the

consequent cyanide addition was made based on the analyzed cyanide concentration.

The pressure oxidation tests (Publications II and IV) were carried out in a one gallon autoclave. The autoclave was equipped with heating elements and cooling coils. The agitator had an upper impeller (a45) and lower impeller (GLS), and oxygen was fed below to the lower impeller. Samples were taken from the autoclave through the pipe below the lower impeller.

The slurry sample was taken from the reactor by syringe with an excess pipe. The excess pipe was added to the syringe hub so that the sample could be taken from inside the slurry. However, this is not the optimal sampling method due to the possible classify of solid in the excess pipe. The solid samples could not be taken when activated carbon was used for gold recovery during the leaching. The activated carbon particles block the excess pipe, and therefore the solid sample would be even more classified than in the absence of activated carbon. The solid sample (if taken) was filtered, washed with water, and dried. The solution sample was diluted to avoid precipitation at ambient temperature.

3.1.2 Analysis of solution and solid samples

Solution samples were diluted with 10% hydrochloric acid and the base metals (e.g., copper, iron, sodium, calcium, and arsenic) were analyzed by inductive coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6000). Gold was analyzed by graphite furnace atomic absorption spectrometry (GFAAS, Varian Spectra) after gold extraction into dibutyl sulfide with hydrochloric acid or by inductive coupled plasma mass spectrometry (ICP-MS, Thermo Scientific iCAP Q). Chloride and bromide were analyzed by ion chromatography (IC, Dionex DX-120). The samples for ICP-MS and IC were diluted with 5 g/L of nitric acid. The GFAAS sample was not diluted due to the pre-treatment analysis method.

For the solid samples, base metals analysis was conducted after total dissolution by ICP-OES. Total carbon and total sulfur were analyzed by a combustion method (Leco TC-136), whereas elemental sulfur was titrated after sodium sulfite treatment. The sulfate content of the solid samples was analyzed by IC after sodium carbonate treatment. The sulfide content of the sample was calculated from the total sulfur, elemental sulfur, and sulfate content. Gold was analyzed by the fire assay method (FA) with a lead collector (in a third-party laboratory). The concentration of gold was analyzed by flame emission spectrometry (FAAS), ICP-OES, or gravimetrically, depending on the gold and silver concentration in the sample.

The activated carbon sample was incinerated before analysis. The incinerated activated carbon was divided: base metals analysis (if needed) was conducted by ICP-OES after total dissolution, whereas gold analysis was conducted by GFAAS or ICP-MS after selective gold dissolution. Silver was analyzed by ICP-OES or ICP-MS after selective silver dissolution.

3.1.3 Calculation of extraction

Gold extraction was predominantly calculated based on solid analysis, i.e., leach residue gold analysis, Eq. (43) (Publications I – IV). This provides high accuracy owing to the possibility of using a large sample size (5 – 20 g) and taking parallel samples for analysis. However, gold recovery to solution can also be calculated based on the solution analysis of the final leach solution, Eq. (44). It was observed that the selection of sampling tube material (not plastic) as well as diluent was critical due to the unstable nature of the gold chloride complex in the solution samples.

Recovery on activated carbon was calculated based on the gold content in the loaded activated carbon, Eq. (45). This calculation result was shown to be the most uncertain, due to the properties of activated carbon and the analysis method used. The incinerated activated carbon was electrostatic and the solid was fine, which made the handling of solid difficult.

The mass balance of the leaching test can be evaluated with accountability, analyzing all the solid and solution fractions and their gold content. The accountability describes accuracy and reliability of the test. In Publication II, the accountability was calculated for gold, Eq. (46). In this thesis, the accountability values were analyzed as presented in Publication II: 90 – 110% suggesting excellent, and 85 – 90% and 110 – 115% good accountability for gold. Gold amount in feed and outputs are equal when accountability is 100%. Accountability value higher than 100% indicates that higher amount of gold is analyzed in the outputs compared to feed material. Values below 100% indicates lower quantity of gold analyzed in the outputs compared to feed material.

$$E_{\text{Au}} = \frac{m_{s,0}c_{s,0,\text{Au}} - m_{s,\text{res}}c_{s,\text{res},\text{Au}} - \sum m_{s,\text{sample}}c_{s,\text{res},\text{Au}}}{m_{s,0}c_{s,0,\text{Au}}} \cdot 100 \quad (43)$$

where E_{Au} represents gold extraction (%), $m_{s,0}$ the mass of solid at the beginning (g), $m_{s,\text{res}}$ the mass of leach residue (g), $m_{s,\text{sample}}$ the mass of solid sample (g), $c_{s,0,\text{Au}}$ the gold content in the feed material (g/t), and $c_{s,\text{res},\text{Au}}$ the solid content in the leach residue (g/t).

$$R_{\text{aq,Au}} = \frac{V_{\text{aq,final}}c_{\text{aq,final,Au}} + \sum V_{\text{aq,sample},i}c_{\text{aq,sample},i,\text{Au}}}{m_{s,0}c_{s,0,\text{Au}}} \cdot 100 \quad (44)$$

where $R_{\text{aq,Au}}$ represents the gold recovery to solution (%), $V_{\text{aq,final}}$ the volume of the final solution (L), $c_{\text{aq,final,Au}}$ the gold concentration in the final solution (g/L), $V_{\text{aq,sample},i}$ the volume of solution sample at time i (L), and $c_{\text{aq,sample},i,\text{Au}}$ the gold concentration in the solution sample at time i (g/L).

$$R_{\text{C,Au}} = \frac{m_{\text{C,loaded}}c_{\text{C,loaded,Au}}}{m_{s,0}c_{s,0,\text{Au}}} \cdot 100 \quad (45)$$

where $R_{\text{C,Au}}$ represents the gold recovery onto activated carbon (%), $m_{\text{C,loaded}}$ the mass of loaded activated carbon (g), and $c_{\text{C,loaded,Au}}$ the gold content of loaded activated carbon (g/t).

$$AC_{Au} = \frac{\sum m_{s,sample,i} c_{s,res,Au} + \sum V_{aq,sample,i} c_{aq,sample,i,Au} + m_{s,res} c_{s,res,Au} + V_{aq,final} c_{aq,final,Au}}{m_{s,0} c_{s,0,Au}} \cdot 100 \quad (46)$$

where AC_{Au} represents the accountability of gold (%).

3.2 Simulation

Findings 9 and 10 (in objective 2) of the work are related to the results achieved by process simulation. Based on significant experimental results, simulation cases with free-milling (FM) gold ore were carried out in chloride media. The chemical and mineralogical composition of the ore is presented in Publication III. The simulation was carried out for five separate gold leaching processes:

- *high copper* ($[Cl]_{aq} = 225$ g/L, $[Cu]_{aq} = 100$ g/L), Figure 5
- *low copper* ($[Cl]_{aq} = 100$ g/L, $[Cu]_{aq} = 5$ g/L), Figure 6
- *low iron* ($[Cl]_{aq} = 100$ g/L, $[Fe]_{aq} = 5$ g/L), Figure 6
- *sea water* ($[Cl]_{aq} = \sim 20$ g/L, $[Cu]_{aq} = 18$ g/L), Figure 7
- *cyanide* ($[NaCN]_{aq} = 3$ g/L), Figure 8.

The aim of the simulations was to investigate the effect of chloride and copper(II) concentrations on the mass and energy balance of the chloride process. Additionally, the difference between copper and iron as oxidation reagents was investigated. The cyanide process was simulated as a reference process for chloride processes. These results (unpublished) are presented solely in the compendium section of the thesis.

The simulation part of the current thesis is based on the presented experimental results, literature, and factors used in industrial process modeling. The simulation was carried out using the Sim module (HSC-Sim) of HSC Chemistry 10.0.0.5 software. HSC Chemistry software has been developed by Outotec Oy, and can be used for the design of metallurgical processes. The Sim module is a simulation platform for hydrometallurgical, pyrometallurgical, minerals processing, and physical recycling system models. Based on simulation it is possible to determine the size and price of equipment, select construction materials and evaluate the initial costs related to consumed resources, as presented in the literature (Reuter, 1998; Roffel and Betlem, 2006; Elomaa *et al.*, 2019). The Sim module can also be combined with LCA functionality or with third-party software (e.g., GaBi). (Outotec 2019) The actual LCA evaluation was out of the scope of the current thesis as well as economical evaluation of the processes. The simulations were limited only to the hydrometallurgical unit processes on the assumption that mining and material preparation e.g., crushing and grinding before leaching process, are similar for all each investigated cases. The simulation results were evaluated and used to produce LCI data. This LCI data can be later used to produce an LCA. The Sim module has been used in mass and energy balance calculations for characterizing process behavior (Seppälä *et al.*, 2014; Michaux *et al.*, 2019; Palacios, 2019; Michaux *et al.*, 2020) and as a basis for LCA analysis (Teir *et al.*, 2016; Pell *et al.*, 2019; Ghodrat *et al.*, 2017; Elomaa *et al.*, 2017; Elomaa, 2020) in several metallurgical applications.

3.2.1 Parameters in chloride process simulations

The feed input used was 100 t/h of free-milling gold ore, and the solid concentration used was 20% in the chloride leaching cases for *high copper* (Figure 5), *low copper* (Figure 6), *low iron* (Figure 6), and *sea water* (Figure 7). The water used in grinding was separated by thickening and filtration (not needed in the *sea water* case). The moisture of the ground ore fed to the pulping reactor was 8%. Water accumulation in the chloride leaching circuit was avoided by adding an evaporation unit.

The main parameters used in the simulations are presented in Table 4. The expected extractions of gold, silver, and impurities as well as recovery onto activated carbon are based on the chloride leaching test results of the current thesis (Test 18, 14, 16, and 20, Table 2). The copper and iron concentrations were controlled by the addition of copper(II) sulfate and iron(II) sulfate. In the process, oxygen purging allows for iron(II) oxidation to iron(III). The chloride concentration was controlled by the addition of calcium chloride and/or by removing sodium chloride by crystallization. In the *sea water* case, the chloride concentration was controlled by internal solution circulation and fresh sea water feed. The composition of the sea water used is presented in Table 5. Solid concentration in the gold chloride leaching was controlled by evaporation. Gold recovery onto activated carbon was counter-current to the slurry feed in the leach reactor series.

Table 4. Gold leaching (CICl) conditions applied in the gold chloride process simulations.

	<i>High copper</i>	<i>Low copper</i>	<i>Low iron</i>	<i>Sea water</i>
[Cu] _{aq} , g/L	100	5	No control	17
[Fe] _{aq} , g/L	No control	No control	5	No control
[Cl] _{aq} , g/L	225*	100	100	19
[HCl] _{aq} , g/L	10	10	10	-
pH, -	-	-	-	3
[Act.C], g/L	20	20	20	20
S/L, g/L	360	360	360	235
E _{Au} , %	98	94	85	72
c _{C,loaded,Au} , g/t	3 532	3 496	3 572	3 636
Test nr.	18	14	16	20

* Sodium bromide was not used in the model.

Table 5. Chemical composition of sea water used in the *sea water* case (Anderson, 2003).

[Mg ²⁺] _{aq} , g/kg	[K ⁺] _{aq} , g/kg	[Ca ²⁺] _{aq} , g/kg	[HCO ₃ ⁻] _{aq} , g/kg	[Br ⁻] _{aq} , g/kg	[Na ⁺] _{aq} , g/kg	[SO ₄ ²⁻] _{aq} , g/kg	[Cl ⁻] _{aq} , g/kg
1.295	0.39	0.416	0.145	0.066	10.752	2.701	19.345

The slurry was fed to the thickener after chloride leaching. The overflow of the thickener was circulated to pulping, whereas the underflow was fed to the first leach residue filter. Acidic ([HCl]_{aq} = 4 g/L in *high copper*, *low copper*, and *low*

iron cases and pH = 3 in *sea water* case) wash water was used to wash the soluble copper and iron out of the leach residue. Before the second leach residue filter, the leach residue was pulped to the wash water from the second leach residue filter. The target of re-pulping was to ensure the removal of chloride and copper/iron from the leach residue. The filtrate from the second leach residue filter was used as wash water in the first leach residue filter, after the addition of acid.

The bleed treatment differed between the simulated models. In the *high copper* case, the copper concentration was high (100 g/L). The bleed from the bleed treatment was taken from the filtrate flow from the first leach residue filter. Due to the high copper concentration, copper was precipitated (pH = 3) and recovered separately as atacamite. In the atacamite precipitation, not only copper but also some of iron and aluminum were precipitated. The precipitate was dissolved with sulfuric acid and recycled to gold leaching to avoid copper losses. Gypsum was formed during the atacamite precipitation and leaching, which is why the slurry from atacamite leaching was fed to the gold leaching thickener to avoid feeding gypsum to the leaching reactors. After atacamite precipitation, the remaining solution was further purified by hydroxide precipitation (pH = 11.5) to remove other impurities (e.g., remaining aluminum, iron, and magnesium), after which the solution was routed to evaporation. The bleed from evaporation was fed to crystallization to control the chloride concentration in the leaching circuit, if needed. The concentrated solutions from the evaporator and crystallizer were routed to pulping.

In the *low copper* and *low iron* cases, the concentration of copper or iron (5 g/L) was much lower than in the *high copper* case (100 g/L), which allowed the atacamite precipitation and re-leaching to be omitted. Then, the bleed could be fed directly to hydroxide precipitation. In the *sea water* case, the solutions from the first leach residue filter were fed to hydroxide precipitation. There was no evaporation and/or crystallization for chloride, as the water and chloride balance were managed directly by the necessary amount of bleeding. Therefore, the process solution was not circulated back to the process, but removed from the process after hydroxide precipitation. Extra purification (e.g., sodium and chloride removal) of the solution was not investigated in this thesis but was assumed to be directly returned back to natural sea waters.

Activated carbon was incinerated in a furnace at 400 °C in all cases (Halkola *et al.*, 2019). Further gold extraction from the incinerated activated carbon was conducted by two-step leaching in chloride solutions: first, most of the impurities such as copper and iron were dissolved (S/L = 200 g/L and $[\text{HCl}]_{\text{aq},0} = 50 \text{ g/L}$), after which the gold was dissolved under more aggressive conditions with hydrogen peroxide and hydrogen chloride (S/L = 250 g/L, $[\text{HCl}]_{\text{aq},0} = 300 \text{ g/L}$ and $T = 80 \text{ °C}$) (Virtanen and Schmachtel, 2015). Silver was precipitated as silver chloride. Gold was reduced in two stages with sodium metabisulfite (SMBS) (Mooiman and Simpson, 2005; Haapalainen, 2016). In the first stage, the gold concentration in solution was decreased to 1.5 g/L. Solid-liquid separation was carried out, the solid material (gold product) was dried and smelted into bars and the solution was fed to the second gold reduction

stage. In the second stage, the rest of the gold was reduced and after solid-liquid separation, the solid gold was circulated back to the gold leaching of the incinerated activated carbon.

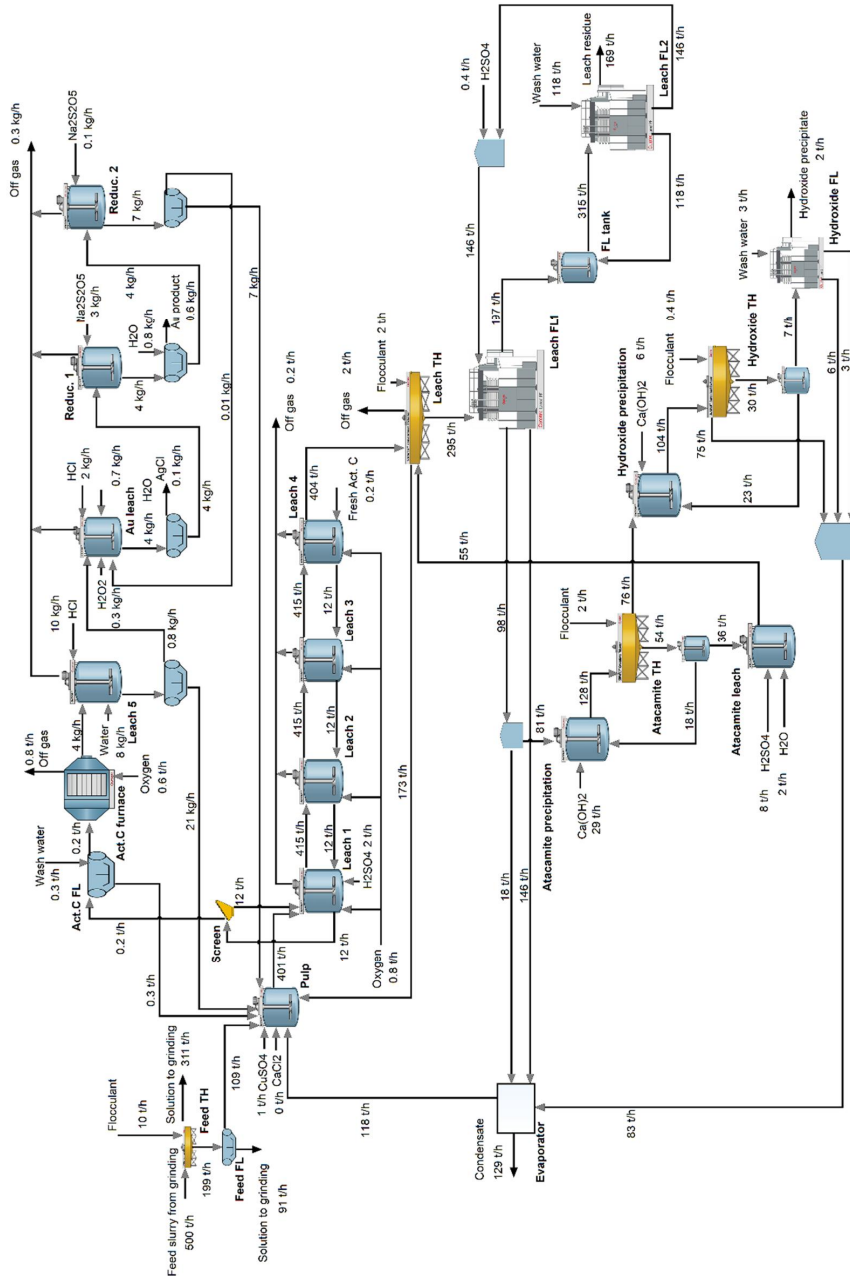


Figure 5. Flowsheet of the simulated high copper case.

3.2.2 Parameters in cyanide process simulation

The gold extraction and leaching time of the *cyanide* case are based on Test 17 results, Figure 8. The chemical composition, mineralogy, feed (100 t/h solid), and solid concentration of the feed (20%) were kept the same in the *cyanide* case as in the chloride leaching cases of *high copper*, *low copper*, *low iron*, and *sea water*. The slurry was fed to the feed thickener. The overflow from the feed thickener was circulated back to grinding (not included in the simulation). The underflow (solid concentration 50%) was routed to the pulping reactor. In the pulping reactor, the pH was set to 10 and the solid concentration to 35%. Sodium cyanide ($[\text{NaCN}]_{\text{aq}} = 3 \text{ g/L}$) was added in the next reactor and the pH increased to 11. The slurry continued to the first CIL reactor. A sodium cyanide concentration of 3 g/L was maintained in the first CIL reactor. The pH was kept at 11 during the cyanide leaching. Air was fed as an oxidant to all the CIL reactors. Gold extraction was adjusted to 98% and the gold concentration in the loaded activated carbon was 9 737 g/t. The activated carbon concentration was 15 g/L in cyanide leaching. The activated carbon was fed counter-currently against the slurry.

The slurry from the last CIL reactor was routed to detoxification. The detoxification was carried out by the Inco type process. Sodium metabisulfite was used as a source of sulfur dioxide. Copper was added (10 mg/L) to catalyze the cyanide oxidation. The air flow rate was 1.5 L/min/L_{solution}. (Marsden and House, 2006) The detoxified solution was pumped from the pond to pulping where 50% of the required water feed was circulated.

Gold was recovered from activated carbon by Zadra elution (Marsden and House, 2006). The loaded activated carbon from gold leaching was transferred to the acid wash column. The carbon was washed with 3% hydrochloric acid (1 bv, bed volume) and water (4 bv). The washed carbon was then transferred to the elution column. Elution was carried out with 20 g/L of sodium cyanide solution at 130 °C. Then, 40 bv of cyanide solution was circulated through the column during elution. Cyanide solution was rinsed out from the activated carbon with water (2 bv). Gold was recovered from the cyanide solution by electrowinning. The solid gold was filtered, dried, and melted into bars (gold product). The eluted activated carbon was fed to the carbon regeneration furnace after removal of fine particles. Carbon was regenerated at 730 °C in the presence of steam and was circulated back to the last CIL reactor.

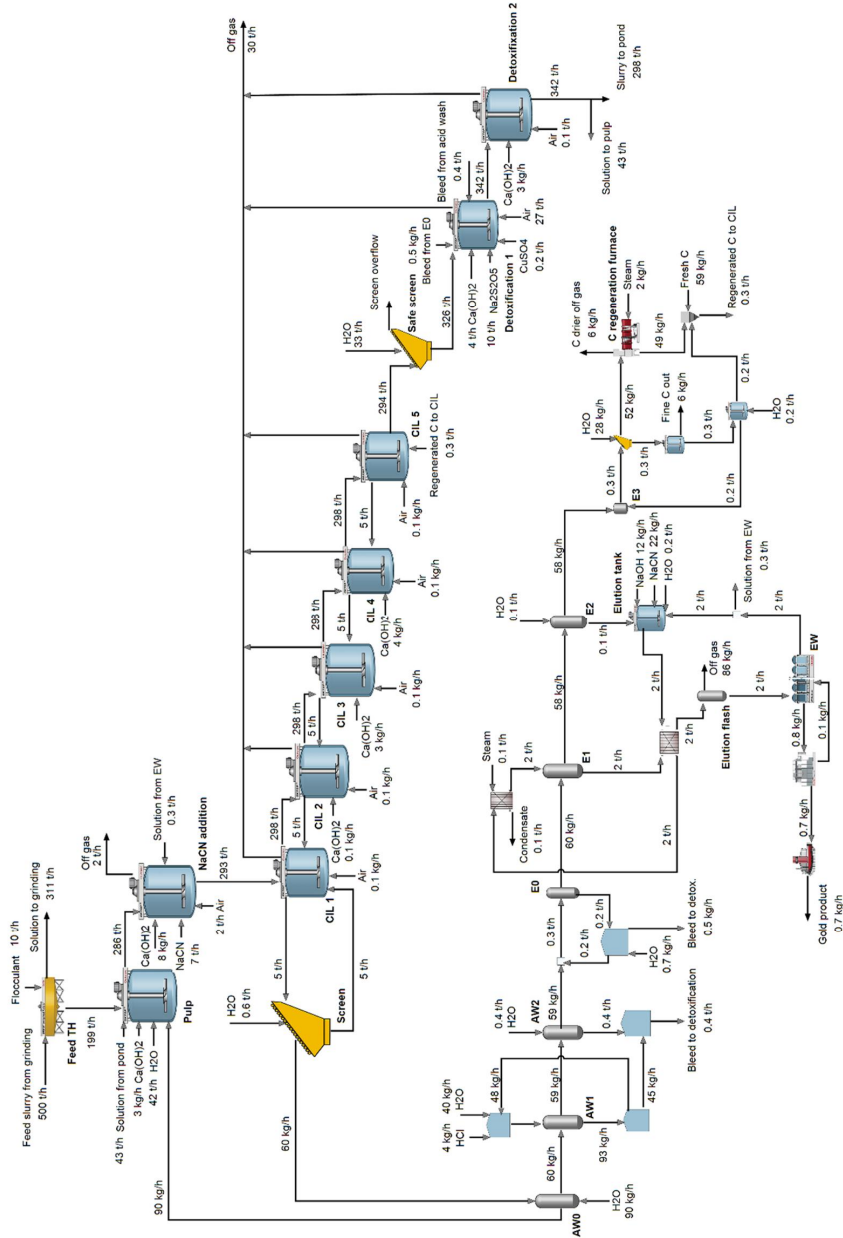


Figure 8. Flowsheet of the simulated cyanide case.

4. Results

The current Chapter summarizes the main results of the thesis. Section 4.1 represents the preg-robbing phenomena in chloride-bromide solutions (Publications I – IV), whereas section 4.2 focuses on the leaching of gold from free-milling gold ore in mild chloride leaching conditions and determines the optimal leaching conditions (Publications I – III). Section 4.3 compares the effects of process parameters, process flowsheets, and conditions based on the simulation of different process scenarios, which are the unpublished, new results of this thesis. Section 4.4 reveals the nature of refractory and double refractory gold concentrate, where gold leaching in chloride-bromide media takes place simultaneously with sulfide oxidation (Publications II and IV).

4.1 Preg-robbing phenomena in chloride-bromide leaching

The preg-robbing phenomena in gold chloride-bromide leaching were investigated by the addition of activated carbon powder to free-milling (FM) gold ore with a natural carbon content of 0.12% ($[\text{Cl}]_{\text{aq,o}} = 150 \text{ g/L}$, $[\text{Br}]_{\text{aq,o}} = 6.2 \text{ g/L}$ and $[\text{Cu}]_{\text{aq,o}} = 15 \text{ g/L}$). In the absence of the external addition of preg-robbing elements –in this case fine carbon powder– the gold extraction achieved was 92% (Table 6). However, gold extraction decreased to 70% with only an increase of 0.01% carbon content and was as low as 1% with 10% addition of fine activated carbon, Figure 9. The strong correlation between carbon content and preg-robbing is one of the findings of the thesis (finding 1). Verification Test 7 with a naturally preg-robbing material (POX-treated double refractory gold concentrate with 3.3% of carbonaceous matters), resulted in a gold extraction of 2%. Based on the results in Figure 9, gold extraction seems to be lower with the naturally preg-robbing material, as expected (finding 2). Nevertheless, it is obvious that the graphite carbon naturally present in double refractory gold concentrate causes intensive preg-robbing, analogously to the synthetically added activated carbon in chloride-bromide media. The accountabilities of all Tests 1 – 7 conducted for preg-robbing demonstration were “excellent”, with one exception of “good” (Test 4), in which the total amount of analyzed gold (concentration in the final solution, gold content in the leach residue, mass of the leach residue, and/or volume of the final solution) exceeded a higher value (110%) when compared to the initially analyzed gold content of the ore, Table 6.

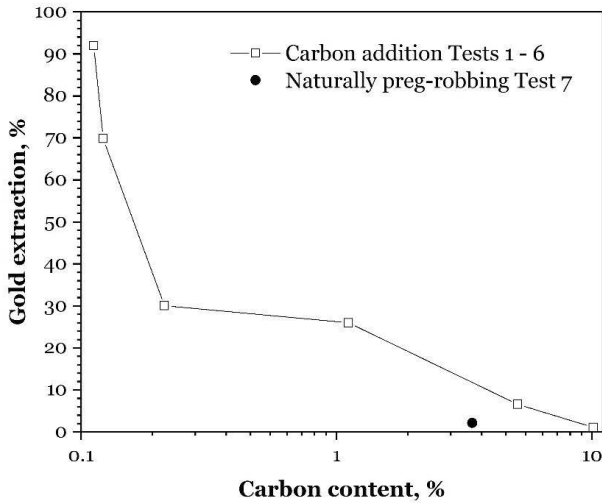


Figure 9. Gold extraction as a function of carbon content in solid in Tests 1 – 7. Tests 1 – 7: $[\text{Cl}]_{\text{aq},0} = 150 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 6.2 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 15 \text{ g/L}$ and $[\text{HCl}]_{\text{aq}} = 10 \text{ g/L}$ (Publications I – II).

Table 6. Gold extraction (E_{Au}) Eq. (43), recovery to solution ($R_{\text{aq,Au}}$) Eq. (44), and accountability (Ac_{Au}) Eq. (46) in Tests 1 – 7, the equations are presented in section 3.1.3. Tests 1 – 7: $[\text{Cl}]_{\text{aq},0} = 150 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 6.2 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 15 \text{ g/L}$ and $[\text{HCl}]_{\text{aq}} = 10 \text{ g/L}$. Test 7 is considered as a verification test with real POX-treated DR raw material.

Test	E_{Au} , %	$R_{\text{aq,Au}}$, %	Ac_{Au} , %
1	92	98	105
2	70	73	105
3	30	27	100
4	26	29	114
5	7	<0.5	98
6	1	<0.5	103
7	2	0.8	96

4.1.1 Prevention of preg-robbing in chloride leaching

The prevention of preg-robbing was investigated using chlorination pre-treatment (Tests 7 – 8, Publication II) and with the addition of activated carbon in chloride leaching (CICl) (Tests 9 – 12, Publication IV). Test 7 was used as a reference test for Test 8. In both tests, double refractory gold concentrate after pressure oxidation with an initial 3.3% carbon content was used. The chlorination (Cl_2 treatment) was carried out before the actual chloride-bromide leaching of gold ($[\text{Cl}]_{\text{aq},0} = 150 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 6.2 \text{ g/L}$ and $[\text{Cu}]_{\text{aq},0} = 15 \text{ g/L}$). During the chlorination, the carbon content was shown to decrease from 3.3% to 3.1%. However, the gold extraction increased from 2% to 45% (Test 8), when compared to the reference test with no chlorination (finding 3). The accountability value of 67% (Test 8, Table 7) shows that the gold accountability in that experiment was relatively poor, which suggests that the effect of

chlorination might not be as significant as suggested by the gold extraction value calculated by solid analysis. Based on the solution analysis, the extraction would have increased only up to 11% using chlorination as pre-treatment. However, the increase in gold recovery could not be solely explained by the decrease in carbon content (i.e., hypothetical carbon oxidation).

In the state-of-the-art cyanide processing, gold recovery onto activated carbon during leaching (CIL) is used to prevent preg-robbing (Marsden and House, 2006). In this thesis (Publication IV), the same method was investigated in chloride-bromide leaching, denoted carbon in chloride leach (CICl). Tests 9 and 10 were carried out with POX-treated double refractory gold concentrate (DR), in the absence and presence of carbon. No gold extraction was observed in Test 9 (Table 7). On the other hand, as high as 80% extraction was achieved when activated carbon i.e., CICl, was used (Test 10). In Test 12, gold extraction increased from 18% (Test 11) to 67% (Test 12) by the use of CICl, owing to the fact that gold was recovered onto activated carbon rather than being lost to the carbonaceous matter of the feed material (finding 4 of the thesis). The results of this thesis suggest that CICl can provide a highly efficient way to prevent preg-robbing in chloride-bromide leaching, as this method is substantially more effective than chlorination.

Table 7. Gold extraction (E_{Au}) Eq. (43), recovery to solution ($R_{aq,Au}$) Eq. (44) and to activated carbon ($R_{C,Au}$) Eq. (45), and accountability (Ac_{Au}) Eq. (46) in Tests 8 – 12 with POX leach residue of double refractory concentrate (Tests 8 – 11) or double refractory concentrate (Tests 11 – 12), the equations are presented in section 3.1.3. Test 8: $[Cl]_{aq,o} = 150$ g/L, $[Br]_{aq,o} = 6.2$ g/L, $[Cu]_{aq,o} = 15$ g/L and $[HCl]_{aq} = 10$ g/L. Test 9 – 12: $[Cl]_{aq,o} = 225$ g/L (Tests 9, 10 and 12), $[Cl]_{aq,o} = 234$ g/L (Test 11), $[Br]_{aq,o} = 78$ g/L, $[Cu]_{aq,o} = 100$ g/L, $[Act.C]_o = 30$ g/L (Test 10), $[Act.C]_o = 25$ g/L (Test 12), $pH = 1.7$ (Tests 9 and 12), $pH = 0.5$ (Test 11) and $[HCl]_{aq} = 10$ g/L (Test 10).

Test	E_{Au} , %	$R_{aq,Au}$, %	$R_{C,Au}$, %	Ac_{Au} , %
8	45	11	-	67
9	-2	0	-	102
10	80	<0.2	67	87
11	18	2	-	83
12	67	0.8	51	85

4.1.2 Gold chloride complex in chloride solution

A gold chloride complex is a relatively unstable complex compared to e.g., a gold cyanide complex (Table 1). However, the current thesis addresses the problematics of aggressive leach solutions by also investigating options for gold dissolution in less aggressive leaching conditions. Gold chloride leaching tests (Tests 13 – 16) were carried out at lower chloride (100 g/L), copper(II) (5 g/L), or iron(III) (5 g/L) concentrations with free-milling gold ore. Test 13 was carried out with copper(II) as oxidant without activated carbon and Test 14 with activated carbon. Correspondingly, Test 15 was carried out with iron as oxidant without activated carbon and Test 16 with activated carbon. It is evident that the experiments where no carbon was used had a higher gold concentration in solution, Figure 10. Gold concentration varied from 0.1 mg/L to 1.5 mg/L in Test 13 and from 0.03 mg/L to 0.5 mg/L in Test 15. However, the final gold

extraction was higher in the presence of activated carbon, as the extraction could be increased from 78% to 94% when copper(II) was used as oxidant, and from 41% to 85% when iron(III) was used as oxidant, Table 8 (finding 5 of the thesis). At lower chloride concentrations, the ability of gold to stay dissolved in solution decreased, as gold had a higher tendency to become reduced in the raw material. In the observed tests, the accountability was mostly “excellent” (Tests 13 – 16), however Test 15 suffered from poor accountability, reflecting possibly a larger number of error sources in the experiment with iron(III) chloride leaching without gold activated carbon recovery.

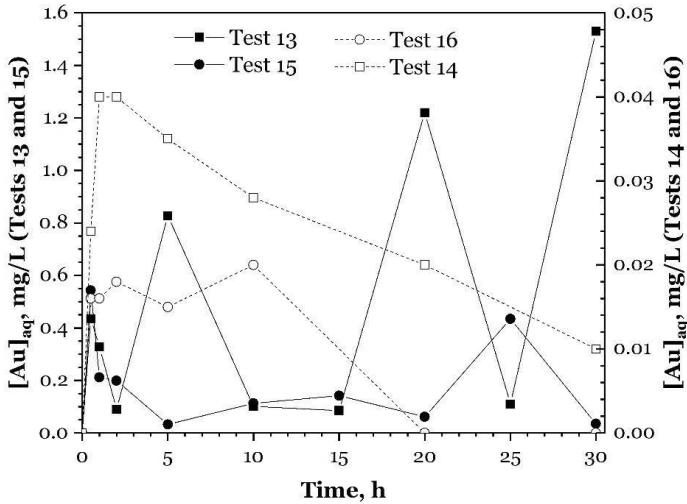


Figure 10. Gold concentration in chloride leaching Tests 13 – 16 at $[Cl]_{aq,0} = 100$ g/L, $[Cu]_{aq,0} = 5$ g/L (Tests 13 – 14), $[Fe]_{aq,0} = 5$ g/L (Tests 15 – 16), $[Act.C]_o = 18$ g/L (Tests 14 and 16) and $[HCl]_{aq} = 10$ g/L with free-milling gold ore (Publication III).

Table 8. Gold extraction (E_{Au}) Eq. (43), recovery to solution ($R_{aq,Au}$) Eq. (44) and activated carbon ($R_{C,Au}$) Eq. (45), and accountability (AC_{Au}) Eq. (46) in Tests 13 – 16, the equations are presented in section 3.1.3. Tests 13 – 16: $[Cl]_{aq,0} = 100$ g/L, $[Cu]_{aq,0} = 5$ g/L (Tests 13 – 14), $[Fe]_{aq,0} = 5$ g/L (Tests 15 – 16), $[Act.C]_o = 18$ g/L (Tests 14 and 16) and $[HCl]_{aq} = 10$ g/L with free-milling gold ore.

Test	E_{Au} , %	$R_{aq,Au}$, %	$R_{C,Au}$, %	AC_{Au} , %
13	78	76	-	97
14	94	0.6	91	97
15	41	15	-	74
16	85	0.1	89	104

4.2 Free-milling ore

In this section, the most relevant results with free-milling gold ore are presented. More experiments with free-milling material are presented in Publication III. Gold leaching kinetics for free-milling gold ore was shown to be extremely fast under the most aggressive chloride-bromide leach conditions. The highest extraction (98%) was achieved in as little as half an hour, Test 18 ($[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 78 \text{ g/L}$ and $\text{pH} = 1.7$). Under milder conditions (Test 1, $[\text{Cl}]_{\text{aq},0} = 150 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 6.2 \text{ g/L}$ and $[\text{Cu}]_{\text{aq},0} = 15 \text{ g/L}$), five hours was required to achieve maximum extraction. The extraction (92%) was lower than in aggressive leaching conditions (Test 18). In cyanide leaching ($[\text{NaCN}]_{\text{aq}} = 3 \text{ g/L}$, Test 17), the gold leaching kinetics was shown to be substantially slower and the highest gold concentration, corresponding to 98% extraction, was reached at 24 hours. It can be summarized that the gold leaching kinetics in gold chloride-bromide leaching was faster compared to cyanide leaching, Figure 11 (finding 6), which has also been stated in the existing literature (Aylmore, 2005; Marsden and House, 2006; Lampinen *et al.*, 2017; Seisko *et al.*, 2019). The accountability was either excellent or good in all of the related tests: 105% in Test 1 (Table 6), 86% in Test 17 (Table 9), and 107% in Test 18 (Table 9).

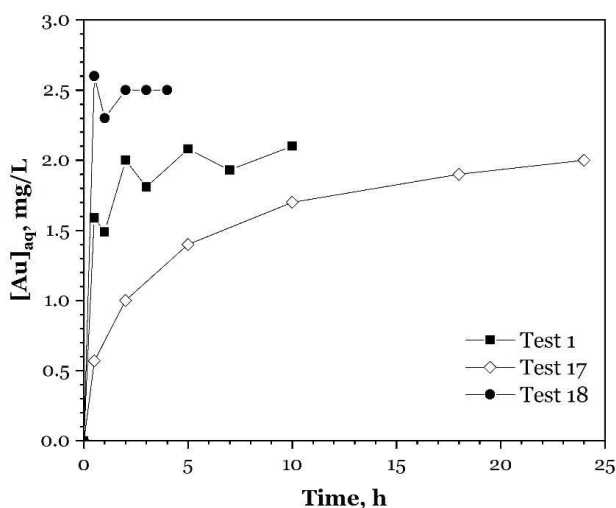


Figure 11. Gold concentration in chloride leaching Tests 1 and 18 and in cyanide leaching Test 17. (Publication I – III) Test 1: $[\text{Cl}]_{\text{aq},0} = 150 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 6.2 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 15 \text{ g/L}$ and $[\text{HCl}]_{\text{aq}} = 10 \text{ g/L}$. Test 17: $[\text{NaCN}]_{\text{aq}} = 3 \text{ g/L}$ and $\text{pH} = 11$. Test 18: $[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 78 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$ and $\text{pH} = 1.7$.

Table 9. Gold extraction (E_{Au}) Eq. (43), recovery to solution ($R_{aq,Au}$) Eq. (44), and accountability (Ac_{Au}) Eq. (46) in chloride leaching Test 18 and in cyanide leaching Test 17, the equations are presented in section 3.1.3. Test 17: $[NaCN]_{aq} = 3$ g/L and $pH = 11$. Test 18: $[Cl]_{aq,o} = 225$ g/L, $[Br]_{aq,o} = 78$ g/L, $[Cu]_{aq,o} = 100$ g/L and $pH = 1.7$.

Test	E_{Au} , %	$R_{aq,Au}$, %	Ac_{Au} , %
17	98	80	86
18	98	93	107

In milder leaching conditions, low (5 g/L) or zero initial concentrations of copper and iron (oxidants) were used in ClCl mode, at a chloride concentration of 100 g/L. These were compared to the aggressive leaching results i.e., to tests at high chloride concentrations with bromide (Test 1 and Test 18).

It can be seen that all of Tests 1 (Table 6, 92%), 14 (Table 8, 94%), 16 (Table 8, 85%), 18 (Table 9, 98%), and 19 (Table 10, 87%) resulted in high gold extraction, the highest being achieved in the most aggressive conditions (Test 18) with the highest amount of oxidant present (100 g/L). However, it is notable that even in the absence of any initially added copper(II) or iron(III) (Test 19), the naturally dissolving oxidants, copper (up to 59 mg/L, Figure 12A) and iron (up to 1.5 g/L, Figure 12B), present in the ore could increase gold extraction up to 87%, although the redox potential (vs. Ag/AgCl) was lower than 580 mV, and the initial redox potential only 460 mV, Figure 13. This is one of the notable findings of the thesis (finding 7). The total amount of oxidants, i.e., the amount of copper and iron in Tests 1, 14, 16, and 18 – 19 are presented in Figure 12.

Table 10. Gold extraction (E_{Au}) Eq. (43), recovery to solution ($R_{aq,Au}$) Eq. (44) and to activated carbon ($R_{C,Au}$) Eq. (45), and accountability (Ac_{Au}) Eq. (46) in Test 19 with free-milling gold ore, the equations are presented in section 3.1.3. Test 19: $[Cl]_{aq,o} = 100$ g/L, $[Act.C]_o = 18$ g/L and $[HCl]_{aq} = 10$ g/L.

Test	E_{Au} , %	$R_{aq,Au}$, %	$R_{C,Au}$, %	Ac_{Au} , %
19	87	0	78	91

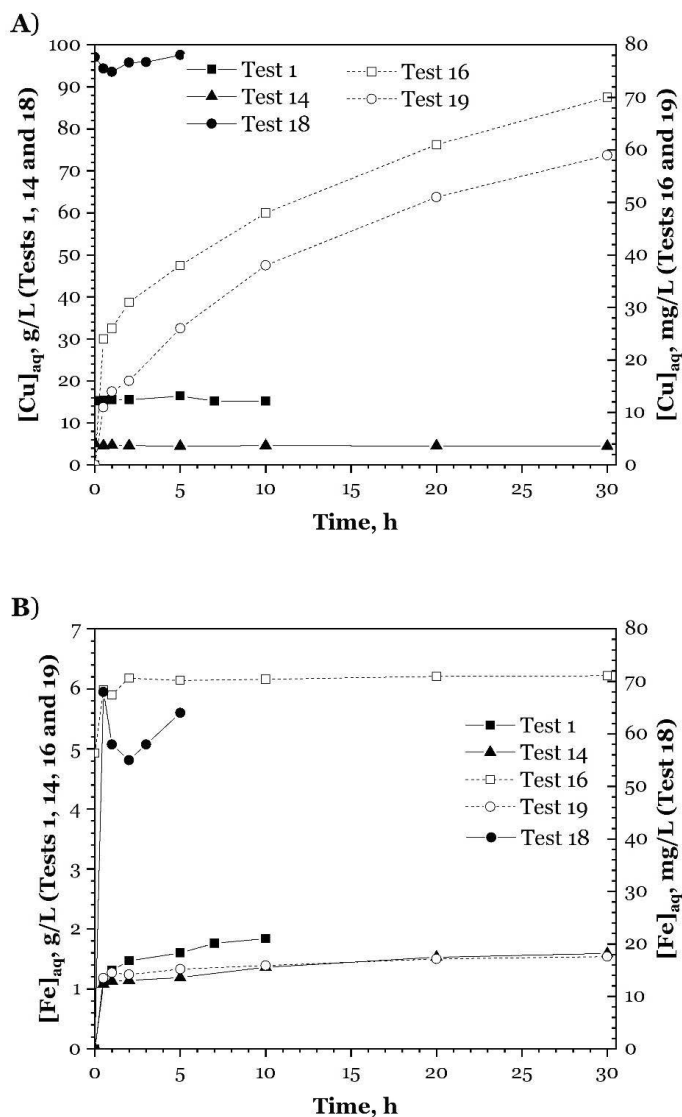


Figure 12. A) copper concentration and B) iron concentration in Tests 1, 14, 16, and 18 – 19 with free-milling gold ore (Publications I and III). Test 1: $[\text{Cl}]_{\text{aq},0} = 150 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 6.2 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 15 \text{ g/L}$ and $[\text{HCl}]_{\text{aq}} = 10 \text{ g/L}$. Tests 14, 16 and 19: $[\text{Cl}]_{\text{aq},0} = 100 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 5 \text{ g/L}$ (Test 14), $[\text{Fe}]_{\text{aq},0} = 5 \text{ g/L}$ (Test 16), $[\text{Act.C}]_0 = 18 \text{ g/L}$ and $[\text{HCl}]_{\text{aq}} = 10 \text{ g/L}$. Test 18: $[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 78 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$ and $\text{pH} = 1.7$.

The redox potentials (vs. Ag/AgCl) in Tests 1, 14, 16, and 18 – 19 are presented in Figure 13. The redox potential of the solution generally decreases as the raw material is subjected for leaching. This is due to consumption of oxidative species (such as iron(III) and copper(II) species) as well as exposure of species with lower oxidation power to the solution along dissolution. With increasing time and no exposure of new solid raw material, continuous oxygen purging allowed more of species to be oxidized. For example, iron(II) species oxidize to iron(III) and copper(I) to copper(II), which further increases the concentration

of species with higher oxidation power, and therefore also the redox potential of the solution. The highest redox potential (~ 650 mV) was evident in Tests 1 and 18. In those tests, the gold extraction was over 90%, Table 6 and Table 9. The gold extraction was also higher than 90% in Test 14 (94%), despite the lower redox potential (~ 600 mV), Table 8. The redox potential was at the same level in Test 14 ($[\text{Cu}]_{\text{aq},0} = 5$ g/L) and Test 16 ($[\text{Fe}]_{\text{aq},0} = 5$ g/L). Nevertheless, the gold extraction remained at 85% in Test 16.

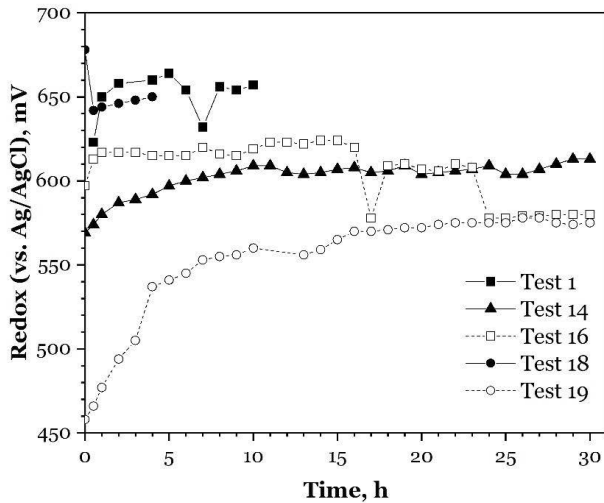


Figure 13. Redox potential (vs. Ag/AgCl) in Tests 1, 14, 16, and 18 – 19 with free-milling gold ore (Publications I and III). Test 1: $[\text{Cl}]_{\text{aq},0} = 150$ g/L, $[\text{Br}]_{\text{aq},0} = 6.2$ g/L, $[\text{Cu}]_{\text{aq},0} = 15$ g/L and $[\text{HCl}]_{\text{aq}} = 10$ g/L. Tests 14, 16 and 19: $[\text{Cl}]_{\text{aq},0} = 100$ g/L, $[\text{Cu}]_{\text{aq},0} = 5$ g/L (Test 14), $[\text{Fe}]_{\text{aq},0} = 5$ g/L (Test 16), $[\text{Act.C}]_0 = 18$ g/L and $[\text{HCl}]_{\text{aq}} = 10$ g/L. Test 18: $[\text{Cl}]_{\text{aq},0} = 225$ g/L, $[\text{Br}]_{\text{aq},0} = 78$ g/L, $[\text{Cu}]_{\text{aq},0} = 100$ g/L and $\text{pH} = 1.7$.

Very mild chloride concentrations (20 – 10 g/L) were investigated in Tests 20 and 21 with free-milling gold ore. An amount as low as 20 g/L of chlorides was investigated in Test 20, corresponding to chloride levels typical of sea water. An even lower chloride concentration (10 g/L) was investigated in Test 21. Chloride was added as copper(II) chloride, so that the copper concentration was 18 g/L in Test 20 and 9 g/L in Test 21 ($\text{pH} < 3$).

The measured redox potentials (vs. Ag/AgCl) in these experiments were low (< 560 mV in Test 21) and even lower than 520 mV in Test 20. The redox was higher in Test 21 despite the lower copper concentration than in Test 20, Figure 14. The higher redox potential can be explained by the dissolved iron: in Test 21 the iron concentration increased up to 500 – 650 mg/L, but in Test 20 only to 40 – 80 mg/L. Despite such low redox potentials, 72% gold extraction was achieved in Test 20 and 64% in Test 21, Table 11, i.e., a higher total oxidant concentration was shown to contribute to higher final gold extraction, regardless of the lower redox potential levels during leaching. The accountability was higher in Test 21, whereas Test 20 displayed a slightly poorer accountability, Table 11. It is still truly notable that gold could be dissolved at such low chloride concentrations and redox potentials, using ClCl . This is maybe the most notable finding of the thesis, as such low chloride

concentrations or redox potentials have been conventionally considered as unsuitable for gold leaching (finding 8). However, only partial gold recovery was achieved in such mild conditions.

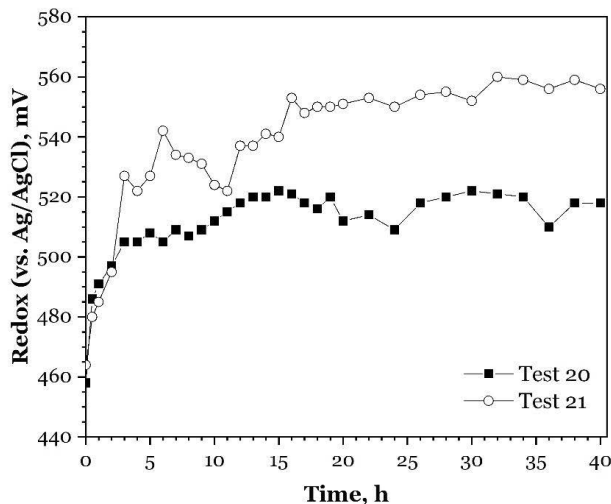


Figure 14. Redox potential (vs. Ag/AgCl) in chloride leaching Tests 20 – 21 with free-milling gold ore (Publication III). Test 20: $[Cl]_{aq,0} = 20$ g/L, $[Cu]_{aq,0} = 18$ g/L, $[Act.C]_0 = 19$ g/L and $pH < 3$. Test 21: $[Cl]_{aq,0} = 10$ g/L, $[Cu]_{aq,0} = 9$ g/L, $[Act.C]_0 = 19$ g/L and $pH < 3$.

Table 11. Gold extraction (E_{Au}) Eq. (43), recovery to solution ($R_{aq,Au}$) Eq. (44) and to activated carbon ($R_{C,Au}$) Eq. (45), and accountability (Ac_{Au}) Eq. (46) in Tests 20 – 21 with free-milling gold ore, the equations are presented in section 3.1.3. Test 20: $[Cl]_{aq,0} = 20$ g/L, $[Cu]_{aq,0} = 18$ g/L and $pH < 3$. Test 21: $[Cl]_{aq,0} = 10$ g/L, $[Cu]_{aq,0} = 9$ g/L and $pH < 3$.

Test	E_{Au} , %	$R_{aq,Au}$, %	$R_{C,Au}$, %	Ac_{Au} , %
20	72	<0.6	58	86
21	64	<0.8	65	102

4.3 Comparison of process models for free-milling gold ore

Section 4.2. presented novel findings based on the experimental work, gold leaching in very mild solutions. This section addresses the question from a process point of view: “Does it provide any holistic process advantage if gold can be dissolved in less aggressive conditions, even similar to sea water?” This section presents five process simulations in order to determine the effect of chloride and copper concentration on chloride leaching (*high copper*, *low copper*, and *sea water*). Additionally, iron (*low iron*) as an oxidation chemical instead of copper (*low copper*) was investigated. The chloride cases were compared to the reference *cyanide* case.

The flowsheets of the investigated and simulated processes are presented in Figure 5 – Figure 8. In the gold chloride models, gold is recovered by CICI during gold leaching. In contrast, in the *cyanide* model (Figure 8), gold is recovered by

CIL, which increases the comparability with the chloride models. The feed to each process is 100 t/h free-milling gold ore (with mineralogy presented in Publication III), with a 20% solid concentration.

4.3.1 Gold leaching and recovery

Gold extraction in the models was based on the experimental results achieved in Tests 18 (*high copper*), 14 (*low copper*), 16 (*low iron*), and 20 (*sea water*). In the *high copper* case, the simplification was made that gold extraction is the same as in Test 18, though no bromide addition is conducted, and CICI is applied in the model. In the *sea water* case, the sulfate concentration used in the model is higher than in Test 20, because copper is added as sulfate to avoid excess chloride accumulation in the process. Gold adsorption to activated carbon is modeled in counter-currently to the slurry flow. In the models, activated carbon is transferred continuously, compared to real industrial operations where it is transferred in batches. The feed of activated carbon was set to reach the target gold loading onto activated carbon of $\sim 3\,500 \text{ g}_{\text{Au}}/\text{t}_{\text{carbon}}$ in the chloride leaching cases, and $\sim 9\,700 \text{ g}_{\text{Au}}/\text{t}_{\text{carbon}}$ in the *cyanide* leaching case. In the *cyanide* case, initial gold loading was $100 \text{ g}_{\text{Au}}/\text{t}_{\text{carbon}}$ in eluted activated carbon.

Gold extraction (based on the test results) and gold recovery over the holistic process (simulation results) are presented in Table 12. The remaining gold concentration in solution was set to 0.05 mg/L in the chloride cases and 0.01 mg/L in the *cyanide* case. The gold loss was notably low due to the solution circulation in the *high copper*, *low copper*, and *low iron* cases. In the *sea water* case, the solution does not require circulation, which increases gold losses and decreases gold recovery. The same situation is evident in the *cyanide* case as no solution is circulated. Gold can also be lost with the ground/fine activated carbon in the *cyanide* case. However, gold loss with ground carbon is estimated to be insignificant in the chloride cases, as will be explained below. A carbon consumption of 40 – 60 g/t is expected in the CIL process (Marsden and House, 2006). In the *cyanide* case, the estimated carbon loss is 59 g/t. In the literature it has been presented that 40% carbon loss occurs in adsorption, 6% in carbon transfer, 7% in elution, and 47% in carbon regeneration. Despite a 23.6 g/t carbon loss in the leaching reactors, the gold loss with fine carbon in the residue was estimated to be zero. This is based on the assumption that fine carbon particles pass through the CIL circuit quickly with slurry and that the gold loading in fine carbon particles remains low. (Marsden and House, 2006) In the *cyanide* case, gold is also lost with the carbon in elution and regeneration stages, which increases the gold loss in *cyanide*. In the chloride leaching cases (*high copper*, *low copper*, *low iron*, and *sea water*), gold is not lost with activated carbon due to incineration of the loaded activated carbon.

Table 12. Gold extraction (based on test results) and recovery (simulation result) in the simulated cases.

	<i>High copper</i>	<i>Low copper</i>	<i>Low iron</i>	<i>Sea water</i>	<i>Cyanide</i>
$E_{Au}, \%$	98	94	85	72	98
$R_{Au}, \%$	97.9	93.9	84.9	70.7	97.6

4.3.2 Water balance

Controlling the water balance is challenging in hydrometallurgical processes. Especially in the *high copper* case but also in the *low copper* case and the *low iron* case, the circulation of chloride- and copper-containing solutions back to leaching must be conducted to decrease the total chemical consumption, as well as to manage the chloride concentrations in the bleed solutions. It needs to be noted that one major challenge of hydrometallurgical processing is the creation of bleed streams that cannot be directly integrated with the surrounding environment, but instead may cause an environmental burden. In the current thesis, this is more of an issue with the *high copper*, *low copper*, and *low iron* cases, whereas with the *sea water* and *cyanide* cases the bleed is expected to be suitable for natural waters. In the *sea water* and *cyanide* cases, the target is to process the gold ore with such solutions that have a concentration similar to natural levels (*sea water*). In the *cyanide* case, slurries are pumped to a pond after detoxification, thus aiming at high integrability with natural waters after a certain time.

In all the simulated chloride processes, the overflow from the thickener is circulated back to the gold chloride leaching stage. This enables high chloride and copper/iron circulation back to the leaching stage, i.e., reuse of the chemicals. This also allows the remaining dissolved gold to be further subjected to gold recovery (CICl in leaching), when gold remains in the solution. The solutions from leach residue filtration are fed to the evaporator in the *high copper*, *low copper*, and *low iron* cases, i.e., in such situations where higher a chloride concentration is required in the leaching and therefore also chlorides need to be circulated back to leaching.

Evaporation is required to control the water balance and to keep a high solid concentration in leaching (finding 9 of the thesis). The excess water entering the process originates mostly from the washing waters (in Leach FL 2 the wash water feed is 118 t/h in the *high copper* case and 105 t/h in the *low copper* and *low iron* cases) as well as from the chemical feed (with calcium hydroxide, 21.5 t/h of water enters the atacamite precipitation stage in the *high copper* case and 8.4 t/h and 8.7 t/h of water enters the hydroxide precipitation stage in the *low copper* and *low iron* cases). The simulation suggests that the need for evaporation is 129 t/h (234 t/kg_{Au}) in the *high copper* case, and 89 t/h in the *low copper* (168 t/kg_{Au}) and the *low iron* (186 t/kg_{Au}) cases, Table 13. In the *high copper* case, atacamite precipitation and leaching bring more water and increase the need for evaporation up to a higher level compared to the *low copper* and *low iron* cases. Some water will be removed from the *high copper*, *low copper*, and *low iron* cases along with the filtration cakes as moisture (leach

residue having 30% moisture, and hydroxide cake 35%). The evaporated water is condensed and re-used in the process, e.g., for chemical preparation and washing waters.

In the *sea water* case, no highly costly evaporation was required, as the water balance could be controlled with the bleed. In the *sea water* case, the advantage can be assumed to be a similar chloride content in the bleed compared to natural sea water. Therefore, the bleed is better suited for direct bleeding to natural sea waters. Bleed treatment is explained in more detail in the following section. The bleed in the *sea water* case was found to be 240 t/h, Table 13. Although the bleed is very high, it is notable that in the *sea water* case no high cost evaporation is needed for reagent circulation, due to the lower chloride concentrations used.

In the *cyanide* case, the excess water is also bled out after detoxification (341.5 t/h slurry). The simulation suggests that 43.2 t/h of this can be circulated from ponds to leaching and 197 t/h (not containing solid material) bled permanently out of the process area (Table 13). The bleed from the *cyanide* case is lower, due to the higher solid concentration in leaching: 500 g/L was used in the *cyanide* case, whereas 230 g/L was used in the *sea water* case.

Table 13. Main water effluents from the processes.

	<i>High copper</i>	<i>Low copper</i>	<i>Low iron</i>	<i>Sea water</i>	<i>Cyanide</i>	Unit
Leach residue	51	45	45	42	-	t/h
Hydroxide cake	0.6	1.1	1.0	7.3	-	t/h
Evaporation	129	89	89	-	-	t/h
Bleed	-	-	-	240	197	t/h

4.3.3 Bleed treatment

The bleed treatment varied between process options due to the different lixivants (chloride vs. cyanide) and ion concentration in the chloride cases. In the bleed treatment of the chloride cases, the impurity metals (aluminum, manganese, manganese, silver (that remained in solution), copper, and iron) were removed by hydroxide precipitation, before circulation to evaporation (*high copper*, *low copper*, and *low iron*) or bleeding the water out (*sea water*). The free-milling ore investigated contained a very small amount of soluble impurities (e.g., copper 0.02%, iron 0.8%, aluminum 8.7%, and magnesium 0.3%). Therefore, impurity levels originating from the raw material were found to be relatively low, and the flow requirement for the bleed smaller than it would be with a raw material with high impurity concentrations.

In the *high copper* case, the chloride (225 g/L) and copper (100 g/L) concentrations used were high. These conditions allowed high gold extraction in leaching but also high copper concentration, so the copper also needed to be precipitated as atacamite before the bleed treatment by hydroxide precipitation (e.g., copper, aluminum, magnesium, and iron hydroxides). Consequently, in the holistic process, atacamite is dissolved in a separate unit with sulfuric acid and circulated back to leaching. The slurry from atacamite leaching is fed to a

leach thickener in order to remove the gypsum formed. The required solution feed to atacamite precipitation was found to be 80.6 t/h in the *high copper* case and the feed to hydroxide precipitation 75.5 t/h.

In the *low copper* and *low iron* cases, no separate atacamite precipitation was required, but the hydroxide precipitation was carried out for the bleed solution directly. Then, the flow to hydroxide precipitation was found to be slightly lower compared to the *high copper* case; 71.8 t/h in the *low copper* case, and 71.7 t/h in the *low iron* case. However, the amount of hydroxide precipitate was found to be higher in the *low copper* and *low iron* cases compared to the *high copper* case, Table 16. This can be explained by the fact that in these processes all of the copper and iron precipitation occurs in the hydroxide precipitation stage (as no atacamite precipitation unit exists). Further, in the *low copper* case, the amount of hydroxide precipitate formed was found to be higher than in the *low iron* case, Table 16, mostly due to the presence of both higher quantities of copper and iron, and thus a higher total amount of species to be neutralized. Copper concentration before hydroxide precipitation is 4.8 g/L and the iron concentration 2.4 g/L in the *low copper* case, whereas it is 0.2 g/L and 4.9 g/L in the *low iron* case, respectively.

The situation in the *sea water* case is different as the solution is circulated to leaching only from the leach residue thickener, but not from the residue filtration or bleed treatment. Therefore, the flow to hydroxide precipitation is drastically higher (204.1 t/h) than e.g., in the *low copper* case (71.8 t/h). The amount of hydroxide precipitate formed was found to be higher in the *sea water* case than in the *low copper* case due to the higher copper (13 g/L vs. 4.8 g/L) and sulfate (40.4 g/L vs. 1.2 g/L) concentrations. Calcium hydroxide is used as a neutralization chemical, allowing gypsum formation as well. Therefore, the gypsum content in hydroxide precipitate in the *sea water* case is 54.7%.

In the *cyanide* case, bleed treatment differs from the chloride leaching cases. Cyanide leaching is operated at pH 11, so the concentrations of the dissolved ions are much lower than in the chloride cases. Therefore, the slurry from CIL is fed directly (326.3 t/h) to detoxification. This operation is carried out by the addition of sodium metabisulfite (Inco process). During the detoxification, the cyanide and WAD complexes are oxidized to cyanate. In the *cyanide case* too, no reagent circulation nor evaporation is needed, making the process straightforward. The slurry feed to the pond was found to be 341.5 t/h, and from the pond 43.2 t/h solution is circulated back to the process, to pulping.

4.3.4 Consumptions of chemicals and auxiliaries

The residence time cannot be taken into account in steady-state HSC-Sim simulation. Nevertheless, residence time is based on the experimental leaching tests of current work, and consequently the flow rates are based on the simulations, Table 14. This allows the determination of the number of leaching reactors. Size of 400 m³ was used for the reactors. The number of reactors and the other equipment have a direct effect on the required power consumption of the plant. In the current investigation, the power consumption is only

approximate and does not take into account auxiliary equipment such as pumps, Table 15.

Table 14. Residence time, slurry flow, total volume, and number of reactors in the simulated cases.

	<i>High copper</i>	<i>Low copper</i>	<i>Low iron</i>	<i>Sea water</i>	<i>Cyanide</i>	Unit
Residence time	4	30	30	40	24	h
Slurry feed	288	287	286	438	228	m ³ /h
Total volume	1 152	8 610	8 580	17 520	5 472	m ³
Number of reactors	3	22	21	44	14	pc

The quantities of resources consumed are presented in Table 15. The operation time in each process option is expected to be 8 000 h/a. An addition of chloride (CaCl₂) is needed only in the *low copper* case, whereas in the *high copper* and *low iron* cases the chloride addition is zero. This is explained by the fact that chloride is partially precipitated by atacamite in the *low copper* case, binding some of the chlorides, and is not circulated to leaching in the *low copper* case, unlike in the *high copper* case. On the other hand, the circulation of atacamite increases the consumption of sulfuric acid. The sulfuric acid consumption is lower in the *sea water* case due to the higher pH in the leaching operation compared to the other chloride processes ($[HCl]_{aq} = 10 \text{ g/L}$). Copper sulfate feed was found to be highest in the *sea water* case due to water management by bleeding (and no evaporation), causing a higher copper loss in the bleed treatment, i.e., hydroxide precipitation.

In chloride processes, the activated carbon consumption is higher compared to the *cyanide* case. In the *cyanide* case, the activated carbon is circulated (eluted and regenerated), and consequently only a small amount is added to replace carbon losses due to attrition (fines). In contrast, in the chloride cases, carbon is incinerated, thus only fresh activated carbon is fed to chloride leaching. Chemical consumption in gold recovery from the activated carbon stage depend on the gold extraction and recovery to activated carbon, due to approximately the same gold loading onto activated carbon.

Steam is used to heat the leaching solution to 98 °C in the chloride cases. Consumption of steam and cooling water was found to be higher in the *high copper*, *low copper*, and *low iron* cases, due to the need for an evaporation unit. After evaporation, the steam formed is condensed and used as process water. This decreases the need for fresh water compared to the *sea water* case and even compared to the *cyanide* case.

Table 15. Quantities consumed in the simulated processes.

	<i>High copper</i>	<i>Low copper</i>	<i>Low iron</i>	<i>Sea water</i>	<i>Cyanide</i>	Unit
Concentrate	800	800	800	800	800	kt/a
CaCl₂	0	1 978	0	-	-	t/a
CuSO₄·5H₂O	9 590	9 065	-	80 659	143	t/a
FeSO₄·7H₂O	-	-	6 667	-	-	t/a
NaCN	-	-	-	-	13 079	t/a
HCl (36%)	101	89	114	46	30	t/a
H₂SO₄ (95%)	88 897	27 052	25 851	276	-	t/a
Ca(OH)₂	71 866	23 360	24 120	60 934	6 289	t/a
NaOH	-	-	-	-	50	t/a
H₂O₂ (50%)	2.1	2.0	1.9	1.3	-	t/a
Na₂S₂O₅	2.2	2.1	1.9	1.6	16 175	t/a
Flocculant	96	83	83	92	40	t/a
Act. C	1 307	1 268	1 117	920	47	t/a
Water	167	79	71	1 226	742	kt/a
Steam	317	287	284	157	1	kt/a
Cooling water	24 730	18 531	18 702	0	-	kt/a
O₂ gas	11 375	5 561	4 778	3 697	-	t/a
Air	-	-	-	-	237 950	t/a
Power	10 270	15 870	14 990	20 350	6 190	MW/a

4.3.5 Products and emissions

The amount of gold ore feed is the same (100 t/a) in all of the simulated models, therefore the amount of gold produced in each case depends on the gold extraction and recovery onto activated carbon in each simulated process, Table 12. Gold production was found to be the highest in the *high copper* and *cyanide* cases, and the lowest in the *sea water* case. 4 414 kg/a gold is produced in the *high copper* case and 3 184 kg/a in the *sea water* case. In addition, silver chloride is considered as a by-product; it is recovered as an impure solid (main impurities are copper and iron). Only a small part of the dissolved silver (20%) is recovered onto activated carbon in chloride process simulations. In the *cyanide* case, silver recovery (59%) is higher due to higher adsorption onto activated carbon. Silver is recovered with gold in doré bars.

The quantity of the leach residue produced is highest in the *high copper* case, Table 16. This is explained by the gypsum formed due to the use of calcium hydroxide in atacamite precipitation and use of sulfuric acid in atacamite leaching. Less gypsum is formed in the *sea water* case due to the low calcium concentration compared to other chloride processes. In the *low copper* and *low iron* cases, the quantity of leach residue is at the same level as the leaching conditions are quite similar: the main components in the residue being silicate, aluminum, and calcium, Table 17. The mineralogical composition of silicate containing minerals is expected to be the same in feed and the leach residue.

The quantity of hydroxide precipitates is highest in the *sea water* case, due to the high flow rate through hydroxide precipitation and higher sulfate

concentrate compared to the other chloride cases. The quantity and quality of the hydroxide precipitate (precipitate from the bleed solution) depends on the acid concentration in leaching (gypsum formation), copper concentration, and iron concentration, Table 17. The quantity of solid had a direct effect on the quantity of solution removed as moisture in solid. The use of air as oxidant in gold leaching (in the *cyanide* case) instead of oxygen (in the chloride cases) increased the off gas flow although the efficiency of oxygen and oxygen in air was the same (80%). The temperature decreased from 98 °C to 86 °C in the leach thickener. Energy was released as steam (evaporation) in the leach thickener. The highest steam formation was found in the *sea water* case because the slurry flow was higher (and the solid concentration lower). The steam is the main component in off gas due to high operation temperature in the investigated chloride cases. The emission to air contains also some carbon dioxide due to activated carbon incineration in the gold recovery stage and the carbon dioxide amount was 5 – 20% of the emissions to air. 19% of the emissions are carbon dioxide in *high copper* case, whereas 10% in *low copper* and *low iron* cases, and 5% in *sea water* case. Leaching in the *cyanide* case takes place in ambient temperature and, therefore, water loss by evaporation is negligible.

Table 16. Quantities of products, emissions to industrial soil, waterways, and to air from the simulated processes.

	<i>High copper</i>	<i>Low copper</i>	<i>Low iron</i>	<i>Sea water</i>	<i>Cyanide</i>	Unit
Emissions to industrial soil						
Leach residue	944	845	842	788	811*	kt/a
Hydroxide cake	8 536	16 177	14 358	174 219	-	t/a
Products						
AgCl cake	794	5 029	508	139	843**	kg/a
Gold product	4 414	4 234	3 827	3 184	4 397	kg/a
Emissions to waterways						
Solids moisture	409	371	369	396	-	t/a
Solution out	-	-	-	1 923	1 577	kt/a
Emissions to air						
Off gas	22 999	29 875	34 867	58 527	231 709	t/a

* Solid material in slurry.

** Metallic silver in doré bar with gold.

The amount of solution bled out from the *sea water* process is the highest of the chloride processes as explained earlier; 240 t/h with 9.7 g/L chloride, 1.1 g/L calcium, 6.7 g/L sodium, and 1.1 g/L sulfate. Solution from the *cyanide* case contains 6.8 g/L sulfate, 6.5 g/L sodium, 0.01 g/L chloride, 0.6 g/L calcium and the WAD is 5 mg/L, with the total bleed out of the process to tailing 197 t/h.

Table 17. Main chemical content of leach residue and hydroxide precipitate, and concentration of moisture in solids.

	<i>High copper</i>	<i>Low copper</i>	<i>Low iron</i>	<i>Sea water</i>	<i>Cyanide</i>	Unit
Leach residue						
Al	7.4	8.3	8.3	8.4	9.9	%
Ca	4.4	1.7	1.6	0.3	0.6	%
Cu	0.3	0.01	0.01	0.01	0.03	%
Fe	0.7	0.6	0.8	0.8	0.8	%
Si	31.4	35.2	35.2	37.8	34.4	%
Solution with leach residue						
Cl	0.1	0.1	0.1	0.01	0.01	g/L
Cu	0.1	0.01	0.00	0.01	0.01	g/L
Fe	0	0	0.01	0	0	g/L
pH	3.4	3.4	3.4	3.9	8.8	-
Hydroxide cake						
Al	27.2	13.8	15.5	3.2	-	%
Ca	8.9	10.8	12.8	17.8	-	%
Cl	0	4.6	0.2	0.7	-	%
Cu	2.2	16.3	0.8	11.8	-	%
Fe	0.6	7.8	18.7	0.2	-	%
Solution with hydroxide cake						
Ca	1.3	0.9	0.9	0.01	-	g/L
Cl	2.2	1.6	1.6	0.2	-	g/L
Na	0.01	0.01	0.01	0.01	-	g/L
pH	10.7	10.7	10.7	10.5	-	-

4.3.6 Life cycle inventory, LCI

The life cycle inventory data is collected in Table 18 (inputs) and Table 19 (outputs) as normalized data to 1 kg of Au. The data was produced with HSC-Sim software for the five process cases investigated.

Each process option has its own characteristic consumption profile of chemicals and utilities. The addition of calcium chloride during the process is only required for the *low copper* case. In all the other cases, hydrochloric acid addition in gold recovery from activated carbon is sufficient make-up for chloride or is not needed at all (*cyanide* case). The copper sulfate requirement is by far the highest in the *sea water* case because of the high copper losses in bleed treatment when compared to the *high copper* and *low copper* cases. In the *cyanide* case, copper sulfate is added only as small amounts as a catalyst for detoxification. The *low iron* case does not need any addition of copper, but an addition of iron sulfate is necessary. Also, sodium cyanide addition is required only in the *cyanide* case due to the different lixiviant used in leaching.

Hydrochloric acid is used in all the process options. In the *cyanide* case, hydrochloric acid is used in the loaded carbon wash and the consumption is the lowest compared to the chloride cases. In the chloride cases, hydrochloric acid is used for incinerated carbon leaching, to leach gold and impurities out of the material. Sulfuric acid consumption is significantly higher in the *high copper* case compared to the other chloride cases due to atacamite dissolution. A higher process pH decreases the sulfuric acid consumption in the *sea water* case

compared to the *low copper* and *low iron* cases. The *cyanide* case does not need sulfuric acid addition. Calcium hydroxide consumption is high in the *sea water* and *high copper* cases, due to the higher copper concentration compared to the *low copper* and *low iron* cases. In the *cyanide* case, the ion concentration is much lower than in the chloride cases, which decreases the calcium hydroxide consumption. Sodium hydroxide is used for sodium cyanide solution preparation to keep the solution pH at 11, whereas in the chloride cases no sodium hydroxide is required.

Hydrogen peroxide consumption is dependent on the amount of gold in the incinerated activated carbon. Therefore, it is at the same level in all the chloride cases investigated. Similarly, sodium metabisulfite consumption for gold reduction is at the same level in the chloride processes. In the *cyanide* case, sodium metabisulfite is used in detoxification. Therefore, the high sodium cyanide concentration used in the simulation is shown to increase the sodium metabisulfite consumption too. Flocculant consumption depends on the amount of raw material feed, leach residue, hydroxide cake, and atacamite precipitate (*high copper* case), Table 16. Therefore, flocculant consumption is highest in the *sea water* case. Flocculant is only used in the raw material thickener in the *cyanide* case, which decreases the flocculant consumption in that process. Carbon incineration increases the consumption of fresh activated carbon in the chloride process compared to the *cyanide* case. In the *cyanide* case, activated carbon is circulated and only addition of make-up activated carbon is carried out to replace the lost fines of activated carbon.

The addition of water is lower in cases where the water balance is controlled by evaporation (*high copper*, *low copper*, and *low iron*) compared to the *sea water* and *cyanide* cases, where the water balance is controlled by the bleed. In the *sea water* case, 64% of total water consumption is sea water (used in leaching) and the rest is fresh water (used for filter wash waters, and chemical preparation). The evaporation used in the *high copper*, *low copper*, and *low iron* cases also increases the consumption of steam and cooling water compared to the *sea water* and *cyanide* cases. Steam consumption is almost zero in the *cyanide* case, where it is used only in loaded carbon elution and activated carbon regeneration. Lower solid concentration in *sea water* leaching compared to the other chloride cases increases the steam consumption in leaching reactor heating. Cooling is not needed in the *sea water* and *cyanide* cases.

In the *high copper* case, oxygen consumption is higher, due to more oxidative leaching conditions compared to the other chloride leaching cases. The *cyanide* case does not need oxygen addition as air is sufficient to provide the oxidative power. In the chloride cases, no air is needed. The consumption of power is the highest in the *sea water* case because it has the longest leaching time (40 h). Hydroxide precipitation and several solid-liquid separations (thickeners and filters) also increase the power consumption in the *high copper*, *low copper*, *low iron*, and *sea water* cases compared to the *cyanide* case.

It is evident that the development-stage chloride processes are more complicated than cyanide leaching, and therefore more process steps and equipment are needed. The residence time is short in aggressive chloride

leaching conditions; however, in milder conditions it is even longer compared to cyanide leaching. This has an impact on the total volume and number of reactors and agitators, as well as power inputs. Thus, the longer leaching time also increases the power consumption, but on the other hand the steam consumption is relatively low in the *sea water* case compared to the other chloride cases. Consequently, the power consumption in the chloride processes is higher. This is one of the findings of this thesis (finding 10).

Table 18. LCI of consumed resources from HSC-Sim in simulated processes as normalized amounts to 1 kg of gold.

	<i>High copper</i>	<i>Low copper</i>	<i>Low iron</i>	<i>Sea water</i>	<i>Cyanide</i>	Unit
Concentrate	181	189	209	251	182	t/kg _{Au}
CaCl₂	0	0.5	0	0	-	t/kg _{Au}
CuSO₄·5H₂O	2.2	2.1	-	25	0.03	t/kg _{Au}
FeSO₄·7H₂O	-	-	1.7	-	-	t/kg _{Au}
NaCN	-	-	-	-	3.0	t/kg _{Au}
HCl (36%)	23	21	30	14	6.8	kg/kg _{Au}
H₂SO₄ (95%)	20	6.4	6.8	0.1	-	t/kg _{Au}
Ca(OH)₂	16	5.5	6.3	19	1.4	t/kg _{Au}
NaOH	-	-	-	-	11	kg/kg _{Au}
H₂O₂ (50%)	0.5	0.5	0.5	0.4	-	kg/kg _{Au}
Na₂S₂O₅	0.5	0.5	0.5	0.5	3 679	kg/kg _{Au}
Flocculant	22	20	22	29	9.1	kg/kg _{Au}
Act. C	0.3	0.3	0.3	0.3	0.01	t/kg _{Au}
Water	38	19	19	385	169	t/kg _{Au}
Steam	72	68	74	49	0.2	t/kg _{Au}
Cooling water	5 602	4 377	4 887	0	-	t/kg _{Au}
O₂ gas	2.6	1.3	1.2	1.2	-	t/kg _{Au}
Air	-	-	-	-	54	t/kg _{Au}
Power	2 327	3 748	3 917	6 391	1 408	kW/kg _{Au}

The output flows from all the simulated cases are presented in Table 19. The effect of gold production can be seen in the normalized numbers. The amount of solid waste compared to the gold produced was highest in the *sea water* case and lowest in the *cyanide* case. This is mainly due to the high extraction and thus high gold production in the *cyanide* process (98%, Table 9), whereas the *sea water* process suffered from low total gold recovery (72%, Table 11).

It is evident that the amount of solution bled out of the process is the highest in the *sea water* case, whereas in the other chloride processes water is managed by evaporation. In evaporation, 92% of total steam consumption and total cooling water consumption were required in the *high copper* case and 80 – 82% of the total steam consumption and 96 – 97% of total cooling water consumption were required in the *low copper* and *low iron* cases. However, the *sea water* process also aims at utilizing chloride solution, which can be directly discharged into natural sea waters without environmental impact (Table 5).

Table 19. LCI of emissions from HSC-Sim as normalized amounts to 1 kg of gold.

	<i>High copper</i>	<i>Low copper</i>	<i>Low iron</i>	<i>Sea water</i>	<i>Cyanide</i>	<i>Unit</i>
Emissions to industrial soil						
Leach residue	214	200	220	247	184*	t/kg _{Au}
Hydroxide cake	1.9	3.8	3.8	55	-	t/kg _{Au}
Products						
AgCl cake	0.2	1.2	0.1	0.04	0.2**	kg/kg _{Au}
Gold product	1.0	1.0	1.0	1.0	1.0	kg/kg _{Au}
Emissions to waterways						
Solids moisture	93	88	96	124	-	t/kg _{Au}
Solution out	-	-	-	604	359	t/kg _{Au}
Emissions to air						
Off gas	5.2	7.1	9.1	18.4	52.7	t/kg _{Au}

* Solid in slurry to pond

** Metallic silver in doré bar with gold.

4.4 Refractory and double refractory concentrates

Experiments with refractory (R) and double refractory (DR) gold concentrates are presented in Publication IV. In this section, the most relevant results are summarized.

Arsenopyrite was the main carrier of gold (82.1%) and pyrite carried the rest of the gold in the investigated refractory concentrate. During POX treatment, 98% of sulfide was oxidized and 99% of gold dissolved from POX residue in the following chloride-bromide leaching ($[Cl]_{aq,0} = 225$ g/L, $[Br]_{aq,0} = 78$ g/L, $[Cu]_{aq,0} = 100$ g/L and $pH = 1.7$), Table 20. Sulfide oxidation (pyrite and arsenopyrite) can also be carried out directly by chloride leaching (Marsden and House, 2006). Then, sulfide is oxidized, and gold is liberated and dissolved simultaneously from refractory gold concentrate. Direct gold chloride-bromide leaching (Tests 23) showed that sulfide oxidation for refractory concentrate was 67%, and simultaneously 81% gold extraction was achieved. In Test 24, the sulfide oxidation was even lower (46%), and this also resulted in lower gold extraction (67%). The gold extraction was shown to be linearly dependent on the sulfide oxidation with the investigated refractory concentrate, Figure 15 (finding 11).

Table 20. Gold extraction (E_{Au}) Eq. (43), recovery to solution ($R_{aq,Au}$) Eq. (44), and accountability (Ac_{Au}), Eq. (46) in Tests 22 – 23 at $[Cl]_{aq,0} = 225$ g/L, $[Br]_{aq,0} = 78$ g/L, $[Cu]_{aq,0} = 100$ g/L and $pH = 1.7$, the equations are presented in section 3.1.3.

Test	E_{Au} , %	$R_{aq,Au}$, %	Ac_{Au} , %
22	99	99	99
23	81	84	103
24	67	61	94

Eqs. (23) – (24) suggest that elemental sulfur is formed during the direct chloride leaching of pyrite and arsenopyrite. However, the analyzed elemental sulfur content in the leach residue was only 0.88% in Test 23 and 1% in Test 24.

This indicates that elemental sulfur further oxidizes to sulfates during chloride-bromide leaching at redox potentials of 529 – 650 mV vs. Ag/AgCl, simplified as Eq. (47).

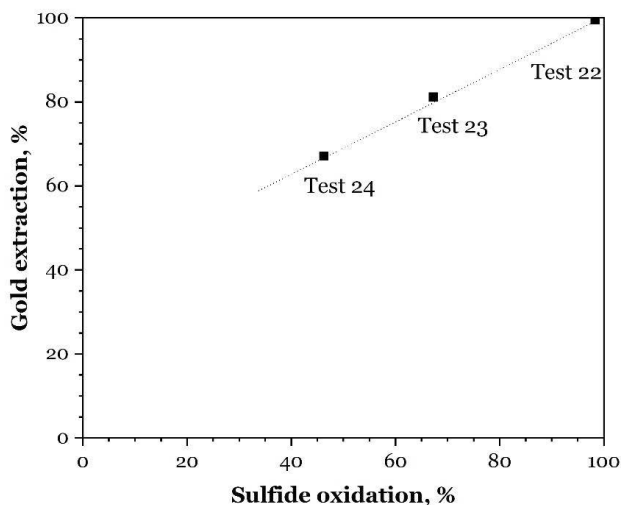
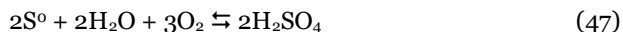


Figure 15. Gold extraction as a function of sulfide oxidation for refractory gold concentrate in Tests 22 – 24 at $[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 78 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$ and $\text{pH} = 1.7$ (Publication IV).

Lead (lead(II) nitrate) addition has been earlier used to increase gold extraction with some carbonaceous material in cyanide leaching (Marsden and House, 2006). The effect of lead(II) nitrate ($224 \text{ g/t}_{\text{feed}}$) on chloride-bromide leaching ($[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 78 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$, $[\text{Act.C}]_{\text{aq}} = 25 \text{ g/L}$ and $\text{pH} = 1.7$) was also investigated in the current thesis with double refractory concentrate (Publication IV). The redox potentials (vs. Ag/AgCl) were approx. 630 mV in Test 12 without addition of lead(II) nitrate and slightly lower ($\sim 590 \text{ mV}$) in Test 25 with lead(II) nitrate addition, Figure 16. Iron concentration was found to be higher in Test 25 (200 – 300 mg/L) compared to Test 12 (50 – 100 mg/L).

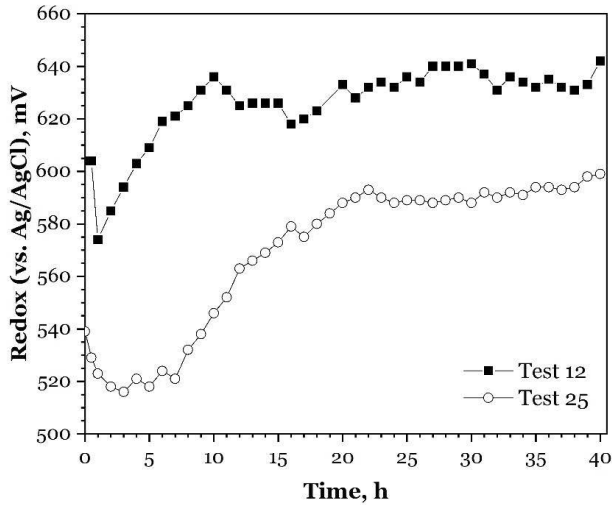


Figure 16. Redox potential (vs. Ag/AgCl) in chloride-bromide leaching of double refractory gold concentrate in Tests 12 (no lead(II) nitrate addition) and 25 (lead(II) nitrate addition, 224 g/t_{feed}). Tests 12 and 25: [Cl]_{aq,0} = 225 g/L, [Br]_{aq,0} = 78 g/L, [Cu]_{aq,0} = 100 g/L, [Act.C]₀ = 25 g/L and pH = 1.7. (Publication IV)

The experiments showed that gold extraction could be increased from 67% (Test 12, Table 7) to 88% (Test 25, Table 21) with an addition of lead(II) nitrate (224 g/t_{feed}) using carbon in leaching (CICl) (finding 13). Activated carbon was used during the leaching, because of the preg-robbing nature of the investigated double refractory concentrate. The accountability was good in Test 12 (85%, Table 7) but only 71% in Test 25 (Table 21). The low recovery on activated carbon (Table 21) suggests that there may have been an error in the activated carbon analysis or in the mass of activated carbon.

Table 21. Gold extraction (E_{Au}) Eq. (43), recovery to solution ($R_{aq,Au}$) Eq. (44) and activated carbon ($R_{C,Au}$) Eq. (45), and accountability (Ac_{Au}) Eq. (46) in Test 25: [Cl]_{aq,0} = 225 g/L, [Br]_{aq,0} = 78 g/L, [Cu]_{aq,0} = 100 g/L, pH = 1.7, [Act.C]₀ = 25 g/L and [Pb(NO₃)₂]_{aq,0} = 224 g/t_{feed}, the equations are presented in section 3.1.3.

Test	E_{Au} , %	$R_{aq,Au}$, %	$R_{C,Au}$, %	Ac_{Au} , %
25	88	0.7	58	71

The dissolved gold concentrations (Tests 12, 23, and 25) are presented in Figure 17. It can be clearly seen that the dissolved gold concentration increases in chloride-bromide leaching without activated carbon to a much higher level in Test 23 than in Tests 12 and 25 with activated carbon. These results confirmed that sulfide oxidation (gold liberation), gold extraction, and reduction onto activated carbon is possible in a single process stage, (finding 12).

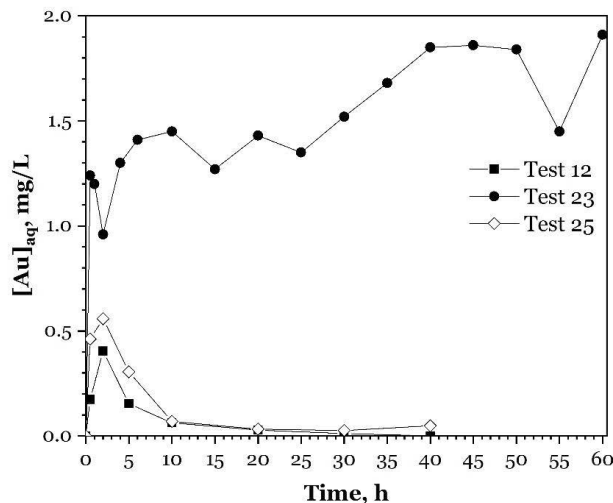


Figure 17. Gold concentration in double refractory concentrate leaching in Tests 12 and 25 (simultaneous ClCl recovery) and refractory gold concentrate leaching in Test 23 (no ClCl) (Publication IV). Tests 12, 23 and 25: $[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 78 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$, $\text{pH} = 1.7$, $[\text{Act.C}]_0 = 25 \text{ g/L}$ (Tests 12 and 25) and $[\text{Pb}(\text{NO}_3)_2]_{\text{aq},0} = 224 \text{ g/t}_{\text{feed}}$ (Test 25).

To summarize the previous sections: the results showed that 67% (Table 7) gold extraction from double refractory gold concentrate could be achieved with 81% sulfide oxidation with ClCl. Gold extraction was further increased to 88% (Table 21) by the addition of lead(II) nitrate ($224 \text{ g/t}_{\text{feed}}$), with as low as 45% sulfide oxidation. These findings show clearly that gold dissolution is highly dependent on the mineralogy of the sample; almost all of the gold could be liberated from the double refractory concentrate with only half of the sulfides being oxidized. However, in the case of refractory concentrate, almost full oxidation was required for full gold extraction. This further highlights the necessity of mineralogical analysis and experimental leaching tests when considering the most appropriate gold leaching and recovery options.

5. Discussion

This thesis investigated chloride and chloride-bromide leaching as an alternative cyanide-free option for gold hydrometallurgical processing. In the current research, three different gold materials were used: free-milling gold ore (Publications I – III), double refractory gold concentrate (Publications II and IV), and refractory gold concentrate (Publication IV).

5.1 Leaching of free-milling gold ore

Based on the findings of this study (Publication I), it is clear that the preg-robbing tendency in a chloride-bromide environment in the presence of carbon is strong. The tendency was low with 0.01% carbon content (gold extraction >70%), moderate with a content of 0.1 – 1%, and very high with a content of 5 – 10% (gold extraction <10%) for free-milling ore ($[Cl]_{aq,0} = 150 \text{ g/L}$, $[Br]_{aq,0} = 6.2 \text{ g/L}$ and $[Cu]_{aq,0} = 15 \text{ g/L}$). This result was verified with the POX residue of naturally preg-robbing double refractory gold concentrate, which contained 3.3% of graphitic carbon, resulting in as low as 2% gold extraction (Publication II). In the literature, it has been presented that the preg-robbing activity of graphite carbon is lower than that of amorphous and native carbon (Mohammadnejad *et al.*, 2013). However, in the current study, the analyzed gold extraction was even lower than expected based on the tests with addition of activated carbon powder, although the carbon in the natural raw material was graphitic. Also, the preg-robbing tendency in chloride media was shown to be higher than that in cyanide leaching when compared to the existing literature (Helm *et al.*, 2011).

Through the use of chlorination (pre-treatment), preg-robbing could be slightly prevented, with gold extraction in the consequent chloride-bromide leaching increasing from 2% to 45% (Publication II). According to the literature, chlorination is suggested to modify the carbon surface, by forming a chlorhydrocarbon layer or composed carboxyl groups. These surface groups have been suggested to block the active adsorption sites of carbon, and this way prevent preg-robbing in cyanide leaching. (Marsden and House, 2006) It can be speculated that in the historical gold chlorination process in the 19th century (Mears and Thies processes) (Rose 1898), the chlorine gas used in wooden reactors may also have had a simultaneous advantageous effect on preg-robbing prevention, via the formation of active groups on natural carbon, preventing the adoption or reduction of dissolved gold chloride complexes. Also, the use of

carbon in chloride leach (CICl) has been shown to prevent or decrease the effect of preg-robbing. In aggressive chloride-bromide leaching ($[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 78 \text{ g/L}$ and $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$) of double refractory gold concentrate, the gold extraction could be increased from 0% to 80% (POX treated concentrate) and from 18% to 67% (direct leaching of refractory concentrate) by the application of CICl (Publication IV).

In a milder leaching environment ($[\text{Cl}]_{\text{aq},0} = 100 \text{ g/L}$), the gold chloride complex was relatively unstable in the produced leach solutions (Publication III), even though the raw material was not classified as preg-robbing as such. Gold extractions from free-milling ore to solution were 78% and 41% ($[\text{Cl}]_{\text{aq},0} = 100 \text{ g/L}$ and 5 g/L oxidant copper(II) or iron(III), respectively). The measured redox potentials in these tests were below 630 mV (vs. Ag/AgCl), mostly even below 580 mV, which is lower compared to the standard gold reduction potentials of gold(I) chloride 0.821 V vs. Ag/AgCl (1.11 V vs. SHE) and gold(III) chloride 0.711 V vs. Ag/AgCl (1.00 V vs. SHE) (Aylmore, 2005). However, using simultaneous gold recovery by CICl, gold extraction could be increased substantially, to 94% and 84%, respectively. This suggests that gold leaching in mild chloride media can be strongly supported by providing a competitive adsorbent during leaching in the vicinity of the dissolved gold chloride complex, and this not only prevents preg-robbing but also supports gold extraction (and recovery) under less oxidative leaching conditions. This may challenge the conventional thinking of the necessity for highly aggressive chloride media for gold dissolution (Intec Ltd., 2009; Lalancette *et al.*, 2015).

In the current thesis the highest and fastest gold extraction (98%) was achieved by the most aggressive chloride-bromide leaching ($[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 78 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$) at very high kinetics ($t = 0.5 \text{ h}$), as hypothesized (von Bonsdorff *et al.*, 2005; Lampinen *et al.*, 2017). Conventional cyanide leaching could reach equally high gold extraction, but at slower kinetics ($t = 24 \text{ h}$). Under slightly milder chloride-bromide leaching conditions ($[\text{Cl}]_{\text{aq},0} = 150 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 6.2 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 15 \text{ g/L}$), 92% gold extraction was achieved at $t = 5 \text{ h}$. Milder leaching conditions ($[\text{Cl}]_{\text{aq},0} = 100 \text{ g/L}$, with no initially added copper(II) or iron(III) as oxidant, were still shown to allow 87% gold with the help of naturally dissolvent oxidants only ($[\text{Cu}^{2+}]_{\text{aq}} = 60 \text{ mg/L}$ and $[\text{Fe}^{3+}]_{\text{aq}} = 1.5 \text{ g/L}$), supported by the use of CICl, even though the redox potential was as low as 460 – 580 mV. This is notable, as the results indicate that gold leaching can be performed only by the addition of chloride-containing water, when a sufficiently high temperature ($T = 98 \text{ }^\circ\text{C}$) and oxygen purging are provided. Finally, gold chloride leaching was investigated at chloride concentrations similar to those typical for sea water ($[\text{Cl}]_{\text{aq},0} = 20 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 18 \text{ g/L}$), and even at lower concentrations ($[\text{Cl}]_{\text{aq},0} = 10 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 9 \text{ g/L}$). The redox potential was 550 mV (vs. Ag/AgCl) in the test with sea water chloride concentrations, and yielded 72% gold extraction. The gold extraction decreased to 64% when the chloride concentration was decreased to 10 g/L and that of copper to 9 g/L (redox potential 520 mV vs. Ag/AgCl). These results truly provide new horizons for gold chloride leaching, as in the state-of-the-art literature, sea water has not been considered as a potential leaching

environment for gold, but rather the necessity for high chloride concentration and oxidant concentration has been emphasized (Nicol, 1980).

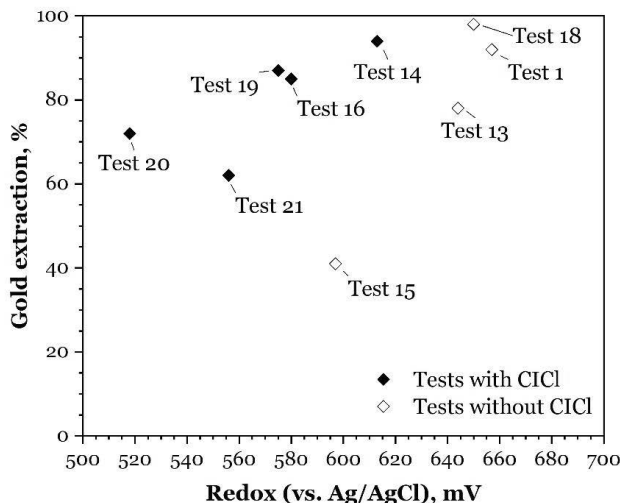


Figure 18. Gold extraction as a function of redox at the end of the tests (vs. Ag/AgCl) in free-milling chloride and chloride-bromide leaching tests with and without gold recovery by CICI. Test 1: $[\text{Cl}]_{\text{aq},0} = 150 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 6.2 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 15 \text{ g/L}$ and $[\text{HCl}]_{\text{aq}} = 10 \text{ g/L}$. Test 13 – 16 and 19: $[\text{Cl}]_{\text{aq},0} = 100 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 5 \text{ g/L}$ (Tests 13 – 14), $[\text{Fe}]_{\text{aq},0} = 5 \text{ g/L}$ (Tests 15 – 16), $[\text{Act.C}]_0 = 18 \text{ g/L}$ (Tests 14, 16 and 19) and $[\text{HCl}]_{\text{aq}} = 10 \text{ g/L}$. Test 18: $[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$, $[\text{Br}]_{\text{aq},0} = 78 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$ and $\text{pH} = 1.7$. Test 20: $[\text{Cl}]_{\text{aq},0} = 20 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 18 \text{ g/L}$, $[\text{Act.C}]_0 = 19 \text{ g/L}$, and $\text{pH} < 3$. Test 21: $[\text{Cl}]_{\text{aq},0} = 10 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 9 \text{ g/L}$, $[\text{Act.C}]_0 = 19 \text{ g/L}$ and $\text{pH} < 3$.

Figure 18 shows the matrix of final redox potentials in the chloride leaching experiments vs. the gold extraction achieved in the experiments where the gold-containing raw material investigated was free-milling ore. The dependency between redox potential and final gold extraction indicates that the gold leaching behavior is more dependent on the solution redox potential in the absence of carbon (open symbols), compared to experiments where carbon was present (closed symbols). As an example, 41% gold extraction was achieved with a final redox potential of 597 mV (vs. Ag/AgCl), Test 15. At approximately the same final redox potential (580 mV), the gold extraction was substantially higher, 85%, with CICI, Test 16. However, under more aggressive leaching conditions, the dependency is not equally clear, as almost identical gold extraction (92% in Test 1 and 94% in Test 14) could be achieved with and without CICI (657 mV in Test 1 and 613 mV in Test 14). The tendency shown in Figure 18 may partially explain the claimed necessity for highly oxidative leach conditions for gold, emphasized in the existing literature (Dreisinger *et al.*, 2005; Intec Ltd., 2006; Harris and White, 2011; Miettinen *et al.*, 2014; Lalancette *et al.*, 2015; Aylmore, 2016), as gold stability is higher in more aggressive solutions. However, this thesis reveals that aggressive leach conditions as such are not a necessity for actual gold extraction (if CICI or potential and alternative adsorption/reduction sites are provided). It should be noted that the final redox potential does not solely explain the final gold extraction (as for example leaching time and other process parameters varied in

the experiments), and therefore Figure 18 needs to be considered as indicative rather than a comprehensive explanation of the relationship between gold extraction and redox potential.

5.2 Holistic processing of free-milling ore in chloride media

Process modeling was carried out for five different process scenarios: *high copper* ($[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$ and $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$), *low copper* ($[\text{Cl}]_{\text{aq},0} = 100 \text{ g/L}$ and $[\text{Cu}]_{\text{aq},0} = 5 \text{ g/L}$), *low iron* ($[\text{Cl}]_{\text{aq},0} = 100 \text{ g/L}$ and $[\text{Fe}]_{\text{aq},0} = 5 \text{ g/L}$), *sea water* ($[\text{Cl}]_{\text{aq},0} = \sim 20 \text{ g/L}$ and $[\text{Cu}]_{\text{aq},0} = 18 \text{ g/L}$), and *cyanide* ($[\text{NaCN}]_{\text{aq}} = 3 \text{ g/L}$) as reference. The simulation models were based on experimental test results with free-milling gold ore and supported by the literature values; known industrial design values were applied.

Gold was recovered onto activated carbon during leaching (CICl or CIL) in all of the simulated cases. However, the mechanism of gold recovery from activated carbon differs in chloride and cyanide processes. In cyanide leaching, the gold cyanide complex is adsorbed onto activated carbon (Goodall *et al.*, 2005) whereas in chloride leaching it preferentially reduces on it (McDougall and Hancock, 1981; Hughes and Linge, 1989). Therefore, in cyanide leaching, gold is eluted, whereas in chloride-based processes it is assumed that activated carbon will be incinerated. In the chloride process, a new batch of fresh activated carbon is always fed to the last gold leaching reactor, whereas in the cyanide process carbon is circulated and fresh carbon is needed only for make-up. This increases the fresh carbon consumption in chloride processes vs. cyanide, also in so doing increasing the direct carbon dioxide emissions related to the gold recovery step.

The chloride balance control was shown to vary in the processes. Chlorides were fed to the leaching stage (when needed), and to the gold recovery from incinerated activated carbon. In the *high copper* and *low iron* cases, no calcium chloride feed to leaching was required. In the case of *low copper*, some calcium chloride addition was required to replace lost chloride. In the case of *sea water*, addition of chloride by fresh sea water was required as chlorides were bled out of the process. The outflows of chlorides from the process were leach residue and hydroxide precipitate in the *high copper*, *low copper*, and *low iron* cases. An additional outflow of chlorides is bled out in the *sea water* case. In none of the chloride cases was crystallization needed to control chloride concentrations.

Chloride and copper/iron circulation in the chloride process was shown to decrease the chemical additions required. The amount of impurities was controlled by hydroxide precipitation. In the *high copper* case, copper was recovered separately as atacamite, and then dissolved and circulated back into gold leaching to provide copper and chloride as circulated chemicals. In the *low copper* or *sea water* cases, copper could not be recovered separately but was precipitated into the hydroxide precipitate with other impurities. Correspondingly, iron was not recovered in the *low iron* case. The circulation of chloride-containing solution was shown to decrease the chemical and solid concentrations in leaching, if no water removal unit process was used. Also,

water accumulated in the process via chemical additions and the wash waters used in filters. Therefore, it was evident that control of the water balance is relatively difficult in chloride-based processes. In the *high copper*, *low copper*, and *low iron* cases, there was a need to evaporate excess water to control the water balance, and to circulate chlorides back into leaching. The drawback of this processing route is that evaporation is a relatively costly process step. The alternative option to control the water balance is to bleed solution out from the process, specifically in the *sea water* and *cyanide* cases. The location and country-specific legislations may limit the bleed solution composition allowed, e.g., regulating the maximum concentration of chlorides or sulfates in the bleed solution. However, it can be assumed that in the *sea water* case and *cyanide* case (after detoxification) the bleed solution composition is closer to the disposable content as such. The current thesis presented the bleed composition in the *sea water* and *cyanide* cases, but the need for additional bleed purification was not evaluated.

Overall, the process modeling undertaken highlighted the challenges and advantages of the chloride processes. Depending on the environmental legislation and geographical location, water balance is an issue to be addressed. Modeling suggests that the *high copper*, *low copper*, and *low iron* processes require the least evaporation. In contrast, in the *low copper* and *low iron* processes, chemical consumptions are lower due to chemical circulation and the lower copper/iron and chloride concentration. However, evaporation increases the costs related to energy consumption. In the *sea water* process, the relatively high copper concentration used increases chemical consumption, but the gold extraction is also lower compared to other chloride processes, decreasing the overall feasibility. The *cyanide* process is straightforward, no evaporation is needed and gold extraction is high; however, the main challenge is not the techno-economic feasibility, but the toxicity of cyanide.

The process modeling for free-milling ore suggests that, although low chloride (20 g/L) concentration leaching of gold by sea water can be conducted, a higher gold extraction is achieved with a slightly higher chloride concentration (100 g/L). In the *low copper* case, the gold extraction is still relatively high (94%) and the atacamite management stage can be avoided (vs. the *high copper* case). Also, a smaller amount of water needs to be evaporated (89 t/h in *low copper* vs. 129 t/h in *high copper*), decreasing the consumption of steam and cooling water. Overall, the chemical and utility consumptions are mainly smaller than in the *high copper* case. It is clear that the *sea water* case needs more investigation and experimental testwork to determine the possibilities of decreasing the copper concentration, increasing gold extraction, and improving the water balance issue. The aim should be to decrease the copper concentration to a lower level, i.e., similar to the *low copper* (5 g/L) case, and definitely shorter leaching times and higher gold extraction (if possible) would increase interest in the *sea water* process. The lack of evaporation is a significant advantage of the *sea water* case compared to the other chloride cases. Overall, in this stage of process development, it seems that the *low copper* case is the most promising of the investigated chloride processes.

5.3 Leaching of refractory gold concentrates

In the current thesis, one of the main targets was to leach gold directly from refractory and double refractory gold concentrates, with simultaneous sulfide oxidation and gold extraction in aggressive leaching media (Publication IV). The experimental research showed a linear dependency between sulfide oxidation and gold dissolution with the refractory gold concentrate investigated. With 60 h leaching time, 67% of sulfides could be oxidized and 81% gold was dissolved. With 46% sulfide oxidation, 67% of gold could be dissolved in the test with the same leaching conditions using a leaching time of 36 h. However, with double refractory gold concentrate, 97% of sulfides could be oxidized, but the gold extraction was only 18%, due to preg-robbing. With the use of ClCl , 67% of gold could be dissolved with 81% sulfide oxidation. This shows that mineralogy has a significant effect on gold dissolution, and it is not necessarily linear to the sulfide oxidation in the case of partially refractory, refractory, or double refractory ores.

Surprisingly, the highest gold extraction (88%) was reached with as low as 45% sulfide oxidation from the double refractory gold concentrate with lead(II) nitrate ($224 \text{ g/t}_{\text{feed}}$) and the use of ClCl (24 g/L). In cyanide leaching, it has been suggested that lead(II) nitrate reduces or prevents the formation of sulfide ions layers on gold by coating the sulfide minerals and reducing the dissolution of sulfide minerals (Deschênes, 2005). Sulfide oxidation is mandatory in the approach presented and therefore, this suggestion may not be relevant in the leaching approach used. Lead precipitation as lead sulfate is possible during the leaching due to sulfide oxidation to sulfate. Therefore, it may be speculated that nitrate ions could affect the gold extraction as well. The mechanism of lead(II) nitrate was not further studied in the current thesis, and no clear explanation of the mechanism can be provided. However, the use of lead would not be environmentally the most favorable method to be developed further.

The experimental results presented in this thesis provide novel and comparative values for the state-of-the-art refractory gold raw material processes (e.g., roasting, pressure oxidation, or bio-oxidation). These processes typically have high capital expenditure (CAPEX) and operating expenditure (OPEX), which highlights the importance of the development of alternative oxidation methods for refractory gold raw materials.

5.4 Recommendations for future work

It seems that gold chloride leaching has a very high tendency for preg-robbing, especially in low chloride concentrations. Therefore, the optimization of gold recovery onto activated carbon is a necessity that was not thoroughly investigated in this study. Also, the type and amount of activated carbon may affect the recovery parameters, e.g., gold loading, gold reduction kinetics, and impurity (e.g., silver, copper, and iron) levels in loaded activated carbon. Furthermore, the silver content can be relatively high compared to the gold content in gold concentrates. In process development, the focus should be on silver dissolution and recovery.

Gold leaching kinetics, specifically in mild leaching conditions, should be investigated further not only with free-milling but also with pre-oxidized material. Gold can be liberated from sulfide minerals in several ways, e.g., POX, bio-oxidation, or roasting. After sulfide oxidation, materials behave in a similar way to free-milling materials from the gold leaching point of view. The results suggest that the presence of bromide is not a necessity for gold leaching, therefore mild leaching for pre-oxidized material (POX) in mild conditions should also be further investigated. Additionally, testwork with direct leaching of refractory materials is needed to optimize the leaching conditions, as the current thesis had only limited scope to investigate this phenomenon. The use of lead(II) nitrate as an additive in direct leaching of refractory materials needs further research. Determination of mechanism of lead(II) nitrate would help to e.g., evaluate amount of addition and effects of lead to environment.

Flowsheet development is a necessity for all future gold leaching processes that are already in the development stage. In particular, direct refractory and double refractory gold concentrates processes need to be simulated, and the mass and energy balance determined. It is also necessary to evaluate the CAPEX and OPEX regarding the profitability of the chloride process compared to the cyanide leaching process. In addition, LCA examination should be carried out for the LCI data presented in the current thesis as well as for all the novel processes to be developed in future to quantify the environmental impact.

6. Conclusions

The aim of this study was to investigate gold leaching related phenomena and processes in chloride and chloride-bromide media. Three different primary gold materials were investigated: free-milling gold ore, refractory gold concentrate, and double refractory gold concentrate.

It was found that the preg-robbing tendency in chloride-bromide leaching can be roughly divided into three categories: low (92 – 70% gold extraction with 0 – 0.01% carbon content), moderate (30 – 20% gold extraction with 0.1 – 1% carbon content), and very high (10 – 0% gold extraction with 5 – 10% carbon content). Naturally occurring graphite carbon (3.3%) in the POX residue of double refractory concentrate was noticed to have at least an equally strong tendency for preg-robbing as the activated carbon powder added to the raw material. Of the methods to prevent preg-robbing, simultaneous gold recovery onto activated carbon (CICl) during chloride-bromide leaching was found to be more efficient than chlorination (separate Cl_2 treatment before gold leaching). With CICl, gold extraction could be increased from 0% to 80% with the POX residue of double refractory gold concentrate and from 18% to 67% with the direct leaching of double refractory gold concentrate.

Gold dissolution kinetics was found to be faster in chloride-bromide media (0.5 – 5 h, depending leaching conditions) compared to cyanide media (24 h) for the free-milling ore. As high as 94% ($[\text{Cu}]_{\text{aq},0} = 5 \text{ g/L}$) or 85% ($[\text{Fe}]_{\text{aq},0} = 5 \text{ g/L}$) gold extraction could be achieved with relatively low (100 g/L) chloride concentrations, when using CICl for gold recovery. In these tests the measured redox potential was ~600 mV vs. Ag/AgCl.

Furthermore, efficient gold leaching was evident even at lower redox potential leaching conditions; 87% of gold could be dissolved at redox potentials of 460 – 580 mV vs. Ag/AgCl, without any initial addition of copper(II) or iron(III) apart from the oxidants originating from the free-milling ore (copper 59 mg/L and iron 1.5 g/L). At even lower chloride concentrations, similar to sea water ($[\text{Cl}]_{\text{aq},0} = 20 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 18 \text{ g/L}$ and $\text{pH} < 3$), an extraction as high as 72% gold could be reached. At even lower concentrations ($[\text{Cl}]_{\text{aq},0} = 10 \text{ g/L}$, $[\text{Cu}]_{\text{aq},0} = 9 \text{ g/L}$ and $\text{pH} < 3$), gold extraction was still possible, with 64% extraction. It is notable that in the current thesis, gold could be dissolved at such mild concentrations, supported by CICl recovery.

Process simulations were carried out for free-milling gold ore in different leaching conditions with HSC Chemistry software's Sim module: *high copper* ($[\text{Cl}]_{\text{aq},0} = 225 \text{ g/L}$ and $[\text{Cu}]_{\text{aq},0} = 100 \text{ g/L}$), *low copper* ($[\text{Cl}]_{\text{aq},0} = 100 \text{ g/L}$ and

[Cu]_{aq,o} = 5 g/L), *low iron* ([Cl]_{aq,o} = 100 g/L and [Fe]_{aq,o} = 5 g/L), *sea water* ([Cl]_{aq,o} = ~20 g/L and [Cu]_{aq,o} = 18 g/L), and *cyanide* ([NaCN]_{aq} = 3 g/L). Gold was recovered onto activated carbon simultaneously (CICl or CIL) in all simulated cases. The consumption of chemicals could be decreased by internal process circulations of solution, and by decreasing the chloride used, as well as the copper/iron and acid concentrations in leaching. Evaporation was used to control the water balance in the *high copper*, *low copper*, and *low iron* cases to avoid a decrease in the chloride, copper, or iron and solid concentrations in leaching. The evaporation unit is a relatively costly process step; however, it is necessary to avoid water accumulation in most of the chloride processes. The other option to control the water balance is to bleed solution out of the process, as conducted in the *sea water* and *cyanide* cases. The location and country-specific legislations limit and determine the required bleed solution composition in regard to chloride concentration as well as other species present.

The direct one-stage hydrometallurgical gold extraction from refractory gold concentrate investigated was found to be linearly dependent on sulfide oxidation. The highest gold extraction (99%) was achieved with 98% sulfide oxidation. However, the investigated double refractory concentrate showed a different mineralogy, and thus leaching behavior, with only 45% sulfide oxidation allowing 88% gold extraction (with lead(II) nitrate (224 g/t_{feed}) and CICl (24 g/L)). This shows that mineralogy has a major effect on gold dissolution, and it is not necessarily linear to sulfide oxidation in the case of partially refractory, refractory, or double refractory ores. The work conducted shows that the oxidation of arsenopyrite and/or pyrite in atmospheric pressure with simultaneous gold dissolution and even with simultaneous gold recovery onto activated carbon can be conducted in chloride-bromide leaching without any pre-treatment. In future, this can provide an alternative treatment route for refractory gold ores, when compared to the state-of-the-art POX, bio-oxidation, and roasting routes.

References

- Abe, Y. and Hosaka, H. (2010). Method for leaching gold, US 7,682,420 B2, Retrieved on March 23, 2010.
- Adams, M.D. and Burger, A.M. (1998). Characterization and blinding of carbonaceous preg-robberts in gold ores, *Minerals engineering*, 11, pp. 919 – 927.
- Afenya, P.M. (1991). Treatment of carbonaceous refractory gold ore, *Minerals engineering*, 4, pp. 1043 – 1055.
- Anderson, G. (2003). Cited 6.3.2020 : <https://www.marinebio.net/marinescience/o2ocean/swcomposition.htm>.
- Angelov, A.T. and Groudev, S.N. (2002). Treatment of gold-bearing solutions by cementations with zinc, *Annual of the University of Mining and Geology*, 44 – 45, pp. 125 – 129.
- Arslan, F. and Duby, P.F. (1997). Electro-oxidation of pyrite in sodium chloride solutions, *Hydrometallurgy*, 46, pp. 157 – 169.
- Aylmore, M.G. and Muir, D.M. (2001). Thiosulfate leaching of gold – a review, *Minerals Engineering*, 14, pp. 135 – 174.
- Aylmore, M.G. (2005). *Chapter 21: Alternative lixivants to cyanide for leaching gold ores* in *Advances in Gold Ore Processing*, 1st ed., Adams, M.D., Elsevier, B.V., Amsterdam, Netherlands, pp. 501 – 539.
- Aylmore, M.G. (2016). *Chapter 27: Alternative Lixivants to Cyanide for Leaching Gold Ores*, in *Gold Ore Processing: Project Development and Operations*, 2nd ed., Adams, M.D., Elsevier B.V., Amsterdam, Netherlands, pp. 447 – 484.
- Barric. (2016). Processing innovation nets metallurgy award. Cited 24.3.2020: <https://www.barrick.com/news/news-details/2016/processing-innovation-nets-metallurgy-award/default.aspx>.
- Bas, A.D., Koc, E., Yazici, E.Y. and Deveci, H. (2015). Treatment of copper-rich gold ore by cyanide leaching, ammonia pretreatment and ammoniacal cyanide leaching, *Transactions of Nonferrous Metals Society of China*, 25, pp. 597 – 607.
- Blight, K., Ralph, D.E. and Thurgate, S. (2000). Pyrite surface after bio-leaching: a mechanism for bio-oxidation, *Hydrometallurgy*, 58, pp. 227 – 237.
- von Bonsdorff, R.C., Aromaa, J., Forsén, O. and Hyvärinen, O. (2005). Dissolution of gold in cupric chloride solutions. Proceedings of EMC 2005, Dresden, Germany, pp. 237 – 245.
- Ciftci, H. and Akcil, A. (2010). Effect of biooxidation conditions on cyanide consumption and gold recovery from a refractory gold concentrates, *Hydrometallurgy*, 104, pp. 142 – 149.

- Cohen, B., Shipley, D.S., Tong, A.R., Casaroli, S.J.G. and Petrie, J.G. (2005). Precipitation of iron from concentrated chloride solutions: Literature observations, challenges and preliminary experimental results, *Minerals Engineering*, 18, pp. 1344 – 1347.
- Cole, J., Dunne, R. and Giblett, A. (2012). Review of current enhanced gravity separation technologies and applications. Proceedings of Separation Technologies for Minerals, Coal and Earth Resources, Perth, Australia, pp. 163 – 175.
- Corrans, I.J. and Angove, J.E. (1991). Ultra fine milling for the recovery of refractory gold, *Minerals Engineering*, 4, pp. 763 – 776.
- Curran, M.A. (2012). Life cycle assessment handbook: A guide for environmentally sustainable products, Salem, Massachusetts, Scrivener Publishing LLC, John Wiley & Sons Inc, Hoboken, New Jersey, USA.
- Deschênes, G. (2005). *Chapter 20: Advances in the cyanidation of gold* in Advances in Gold Ore Processing, 1st ed., Adams, M.D., Elsevier, B.V., Amsterdam, Netherlands, pp. 479 – 500.
- Diaz, M.A., Kelsall, G.H. and Welham, H.J. (1993). Electrowinning coupled to gold leaching by electrogenerated chlorine: I. Au(III)...Au(I)/Au kinetics in aqueous Cl₂/Cl⁻ electrolysis, *Journal of Electroanalytical Chemistry*, 361, pp. 25 – 28.
- Donato, D.B., Nichols, O., Possingham, H., Moore, M., Ricci, P.F. and Noller, B.N. (2007). A critical review of the effect of gold cyanide-bearing tailings solutions on wildlife, *Environment International*, 33, pp. 974 – 984.
- Donato, D.B., Madden-Hallett, D.M., Smith, G.B. and Gursansky, W. (2017). Heap leach cyanide irrigation and risk to wildlife: Ramifications for the international cyanide management code, *Ecotoxicology and Environmental Safety*, 140, pp. 271 – 278.
- Dong, Z., Zhu, Y., Han, Y., Gu, X. and Jiang, K. (2019). Study of pyrite oxidation with chlorine dioxide under mild conditions, *Minerals Engineering*, 133, pp. 106 – 114.
- Doucet, D., Girard, D., Grondin, L. and Matte, P. (2010). Technical Report on the December 31, 2009, Mineral Resource and Mineral Reserve Estimation and the Extension Project, Kittila Mine, Finland. Cited 20.3.2020: https://s21.q4cdn.com/374334112/files/doc_downloads/operations/kittila/March4-KittilaMine-Technical-Report-2010_v001_d1j74l.pdf.
- Dreisinger, D., Murray, W., Hunter, D., Baxter, K., Ferron, J. and Fleming, C. (2005). *The Application of the Platsol™ Process to Copper-Nickel-Cobalt-PGE/PGM Concentrates from Polymet Mining's Northmet Deposit*. Proceedings of ALTA 2005 Nickel/Cobalt Sessions, Perth, Australia.
- Dundee Sustainable Technologies. (2014). Cited 25.3.2020: <https://www.911metallurgist.com/blog/wp-content/uploads/2015/08/Alternative-to-Cyanide.pdf>.
- Eksteen, J.J. and Oraby, E.A. (2015). The leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide: Effect of catalytic ions, sulphide minerals and amino acid type, *Minerals Engineering*, 70, pp. 36 – 42.
- Eksteen, J.J. and Oraby, E.A. (2016). A process for copper and/or precious metal recovery, US2016/0194734 A1, Retrieved on July 7, 2016.
- Elomaa, H., Rintala, L. and Lundström, M. (2017). Process simulation and environmental footprint of gold chlorination and cyanidation process. Proceedings of *European Metallurgical Conference 2017*, 3, pp. 1293 – 1310.

- Elomaa, H., Rintala, L., Aromaa, J. and Lundström, M. (2018). Open circuit potential and leaching rate of pyrite in cupric chloride solution, *Canadian Metallurgical Quarterly*, 57, pp. 416 – 421.
- Elomaa, H., Sinisalo, P., Rintala, L., Aromaa, J. and Lundström, M. (2019). Process simulation and gate-to-gate life cycle assessment of hydrometallurgical refractory gold concentrate processing, *The International Journal of Life Cycle Assessment*, 25, pp. 456 – 477.
- Elomaa, H. (2020). Simulation based life cycle assessment method for evaluation of hydrometallurgical cyanide-free gold processes. Doctoral dissertation. Aalto University, Helsinki, Finland.
- Ferron, C.J., Fleming, C.A., Dreisinger, D. and O’Kane, T. (2003). Chloride as an Alternative to Cyanide for the Extraction of Gold – Going Full Circle?, *SGS Minerals Service Technical Bulletin*, 2003-01.
- Fleming, C.A. (2002). Platsol™ Process Provides a Viable Alternative to Smelting, *SGS Minerals Service Technical Bulletin*, 2002-01.
- Fleming, C.A. (2010). Basic iron sulfate – a potential killer in the processing of refractory gold concentrates by pressure oxidation, *Minerals & Metallurgical Processing*, 27, pp. 81 – 88.
- Fleming, C.A., Mazei, A., Bourrocaudy, E., Canizares, M. and Ashbury, M. (2011). Factors influencing the rate of gold cyanide leaching and adsorption on activated carbon, and their impact on the design of CIL and CIP circuits, *Minerals Engineering*, 24, pp. 282 – 494.
- Frankenthal, R.P. and Siconolfi, D.J. (1982). The anodic corrosion of gold in concentrated chloride solution, *Journal of The Electrochemical Society*, 129, pp. 1192 – 1196.
- Fraser, K.S., Walton, R.H. and Wells, J.A. (1991). Processing of refractory gold ores, *Minerals Engineering*, 4, pp. 1029 – 1041.
- Garrels, R.M. and Thompson, M.E. (1960). Oxidation of pyrite by iron sulfate solutions, *American Journal of Science*, 258-A, pp. 57 – 67.
- Ghodrat, M., Rhamdhani, M.A., Brooks, G., Rashidi, M. and 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.
- Goodall, W.R., Leatham, J.D. and Scales, P.J. (2005). A new method for determination of preg-robbing in gold ores, *Minerals engineering*, 18, pp. 1135 – 1141.
- Griffiths, S.R., Donato, D.B., Lumsden, L.F. and Coulson, G. (2014). Hypersalinity reduce the risk of cyanide toxicosis to insectivorous bats interacting with wastewater impoundments at gold mines, *Ecotoxicology and Environmental Safety*, 99, pp. 28 – 34.
- Ha, V.H., Lee, J.-C., Huynh, T.H., Jeong, J. and Pandey, B.D. (2014). Optimization the thiosulfate leaching of gold from printed circuit boards of discarded mobile phone, *Hydrometallurgy*, 149, pp. 118 – 126.
- Haapalainen, M. and Karonen, J. (2015). Gold solvent extraction, WO2015/185803 A1, Retrieved on December 10, 2015.
- Haapalainen, M. (2016). Recovery of gold from solutions, WO2016/146892 A1, Retrieved on September 22, 2016.
- Haapalainen, M. and Miettinen, V. (2016). Method for gold recovery from solution, WO2016/181039 A1, Retrieved on November 17, 2016.

- Habashi, F. (2005). *Gold – An Historical Introduction*, in *Advances in Gold Ore Processing*, 1st ed., Adams, M.D., Elsevier, B.V., Amsterdam, Netherlands, pp. xxv – xlvii.
- Halkola, J., Kurki, S. and Lillkung, K. (2019). Rotary bed-type electric furnace, WO2019/016428 A1, Retrieved on January 24, 2019.
- Harris, B. and White, C. (2011). Process for the Recovery of Gold from an Ore in Chloride Medium with a Nitrogen Species, WO2011/100821 A1, Retrieved on August 25, 2011.
- Hasab, M.G., Rashchi, F. and Raygan, S. (2013). Chloride-hypochlorite oxidation and leaching of refractory sulfide gold concentrate, *Physicochemical Problems of Mineral Processing*, 49, pp. 61 – 70.
- Helm, M.M., Vaughan, J.P. and Staunton, W.P. (2011). Evaluation of preg-robbing in Goldstrike carbonaceous ore using raman spectroscopy, in *Proceeding World Gold 2011*, pp. 595 – 606.
- Henao, D.M.O. and Godoy, M.A.M. (2010). Jarosite pseudomorph formation from arsenopyrite oxidation using *Acidithiobacillus ferrooxidans*, *Hydrometallurgy*, 104, pp. 162 – 168.
- Holmes, P.R., Fowler, T.A. and Crundwell, F.K. (1999). The mechanism of bacterial action in the leaching of pyrite by *Thiobacillus ferrooxidans*, *Journal of The Electrochemical Society*, 146, pp. 2906 – 2912.
- Hilson, G. and Monhemius, A.J. (2006). Alternatives to Cyanide in the Gold Mining Industry: What Prospects for the Future?, *Journal of Cleaner Production*, 17, pp. 1158 – 1167.
- Hughes, H.C. and Linge, H.G. (1989). The kinetics of gold loading from gold(III) chloride solution onto fresh activated coconut carbon, *Hydrometallurgy*, 22, pp. 57 – 65.
- Hyvärinen, O., Hämäläinen, M., Lamberg, P. and Liipo, J. (2004). Recovering gold from copper concentrate via the HydroCopper™ process, *JOM*, 56, pp. 57 – 59.
- Intec Ltd. (2009). Cited 2.3.2020: <http://www.intecip.com.au/intec-gold-process.pdf>.
- ISO 14040. (2006). Environmental management, Life cycle assessment, Principles and framework, Finnish Standards Association.
- ISO 14044. (2006). Environmental management, Life cycle assessment, Requirements and guidelines, Finnish Standards Association SFS.
- Jiang, T., Li, Q., Yang, Y.-B., Li, G.-H. and Qui, G.-Z. (2008). Bio-oxidation of arsenopyrite, *Transactions of Nonferrous Metals Society of China*, 18, pp. 1433 – 1438.
- Kadioğlu, Y., Karaca, S. and Bayrakceken, S. (1995). Kinetics of pyrite oxidation in aqueous suspension by nitric acid, *Fuel Processing Technology*, 41, pp. 273 – 287.
- Kuyucak, N. and Akcil, A. (2013). Cyanide and removal options from effluents in gold mining and metallurgical processes, *Minerals Engineering*, 50 – 51, pp. 13 – 29.
- La Brooy, S.R., Linge, H.G. and Walker, G.S (1994). Review of gold extraction from ores, *Minerals engineering*, 7, pp. 1213 – 1241.
- Laitos, J.G. (2013). Cyanide, Mining, and the Environment, *Pace Environmental Law Review*, 30, pp. 869 – 949.

- Lalancette, J.-M., Dubreuil, B. and Lemieux, D. (2015). An Improvement Closed Loop Method for Gold and Silver Extraction by Halogens, WO2015/135053 A1, Retrieved on September 17, 2015.
- Lampinen, M., Seisko, S., Forsström, O., Laari, A., Aromaa, J., Lundström, M. and Koironen, T. (2017). Mechanism and kinetics of gold leaching by cupric chloride, *Hydrometallurgy*, 169, pp. 103 – 111.
- Leppinen, J., Hyvärinen, O., Heimala, S., Palosaari, V., Hämäläinen, M. and Hämäläinen, T. (2010). Method for the recovery of gold from sulphide concentrate, US 7,785,395 B2, Retrieved on August 31, 2010.
- Li, C., Li, H., Yang, X., Wang, S. and Zhang, L. (2015). *Gold leaching from a refractory gold concentrate by the method of liquid chlorination* in Rare Metal Technology 2015, 1st ed., Neelamegghan, N., Alam, S., Oosterhof, H., Jha, A., Dreisinger, D., Wang, S., Springer, Cham, pp. 71 – 77.
- Liu, Q., Yang, H.-Y., Tong, L.-I., Jin, Z.-N. and Sand., W. (2016). Fungal degradation of elemental carbon in carbonaceous gold ore, *Hydrometallurgy*, 160, pp. 90 – 97.
- Llamas, A.A., Delgado, A.V., Capilla, A.V., Cuadra, C.T., Hultgren, M., Peltomäki, M., Roine, A., Stalter, M. and Reuter, M.A. (2019). Simulation-based energy, thermo-economic and environmental footprint analysis of primary copper production, *Minerals Engineering*, 131, pp. 51 – 65.
- Logsdon, M.J., Hagelstein, K. and Mudder, T.I. (1999). *The Management of Cyanide in Gold Extraction*, 1st ed. International Council on Metals and the Environment (ICME), Ottawa, Canada, pp. 5 – 13.
- Lundström, M., Ahtiainen, R., Haakana, T. and O'Callaghan, J. (2014). Techno-Economical Observations Related to Outotec Gold Chloride Process. Proceedings of ALTA 2014 Gold-Precious Metals Sessions, Melbourne, Australia, pp. 89 – 104.
- Lundström, M., Ahtiainen, R., Laihonon, P. and Lindgren, M. (2015). Possibilities and Challenges in Gold Chloride Processing. Proceedings of ALTA 2015 Gold-Precious Metals Sessions, Melbourne, Australia, pp. 259 – 268.
- Lundström, M., O'Callaghan, J., Haakana, T., Ahtiainen, R. and Karonen, J. (2016). Process for Recovering Gold, WO2016/066905 A1, Retrieved on May 6, 2016.
- Lundström, M. and Yliniemi, K. (2017). A method of recovering gold from a gold-bearing concentrated copper chloride solution, WO2017/216417 A1, Retrieved on December 21, 2017.
- Lundström, M., Ahtiainen, R. and O'Callaghan, J. (2017) Method for Recovering Gold, WO2017/072411 A1, Retrieved on May 4, 2017.
- Macdonald, E.H. (2007). *Handbook of Gold Exploration and Evaluation*, 1st ed. Woodhead Publishing Limiting, Cambridge, England and CRC Press LLC, Boca Raton, USA.
- Marchevsky, N., Barroso Quiroga, M.M., Giaveno, A. and Donati, E. (2017). Microbial oxidation of refractory gold sulfide concentrate by a native consortium, *Transactions of Nonferrous Metals Society of China*, 27, pp. 1142 – 1149.
- Mariano, R.A. and Evans, C.L. (2018). The effect of breakage energies on the mineral liberation properties of ores, *Minerals Engineering*, 126, pp. 184 – 193.
- Márquez, M., Gaspar, J., Bessler, K.E. and Magela, G. (2006). Process mineralogy of bacterial oxidized gold ore in São Bento Mine (Brazil), *Hydrometallurgy*, 83, pp. 114 – 123.

- Marsden, J.O. and House, C.I. (2006). *The Chemistry of Gold Extraction*, 2nd ed., Society for Mining, Metallurgy and Exploration, Inc. (SME), Colorado, USA.
- McDougall, G.J. and Hancock, R.D. (1981). Gold complexes and activated carbon, *Gold Bulletin*, 14, pp. 138 – 152.
- Michaux, B., Hannula, J., Rudolph, M., Reuter, M.A., van der Boogaart, K.G., Möckel, R., Kobylin, P., Hultgren, M., Peltomäki, M., Roine, A. and Remes, A. (2019). Water-saving strategies in the mining industry – The potential of mineral processing simulators as a tool for their implementation, *Journal of Environmental Management*, 234, pp. 546 – 553.
- Michaux, B., Hannula, J., Rudolph, M. and Reuter, M.A. (2020). Study of process water recirculation in a flotation plant by means of process simulation, *Minerals Engineering*, 148, 106181.
- Miettinen, V., Haapalainen, M., Ahtiainen, R. and Karonen, J. (2013). Development of Gold Chloride Process. Proceedings of ALTA 2013 Gold Sessions, Melbourne, Australia, pp. 187 – 202.
- Miettinen, V., Ahtiainen, R., Valkama, K., Paatero, E., Hietala, K. and Haapalainen, M. (2014). Method of Preparing a Gold-Containing Solution and Process Arrangement for Recovering Gold and Silver, WO2014/17765 A1, Retrieved on November 6, 2014.
- Mikhlin, Y.L. and Romanchenko, A.S. (2007). Gold deposition on pyrite and the common sulfide minerals: An STM/STS and SR-APS study of surface reactions and Au nanoparticles, *Geochimica et Cosmochimica Acta*, 71, pp. 5985 – 6001.
- Miller, P. and Brown, A. (2005). *Chapter 16: Bacterial oxidation of refractory gold concentrates* in *Advances in Gold Ore Processing*, 1st ed., Adams, M.D., Elsevier, B.V., Amsterdam, Netherlands, pp. 371 – 402.
- Miller, J.D., Wan, R.-Y. and Diaz, X. (2005). *Chapter 38: Preg-robing gold ores*, in *Advances in Gold Ore Processing*, 1st ed., Adams, M.D., Elsevier, B.V., Amsterdam, Netherlands., pp. 937 – 972.
- Mohammadnejad, S., Provis, J.L. and van Deventer, J.S.J. (2013). Reduction of gold(III) chloride to gold(0) on silicate surfaces, *Journal of Colloid and Interface Science*, 389, pp. 252 – 259.
- Mooiman, M.B. and Simpson, L. (2005). *Chapter 34: Refining of gold- and silver-bearing Doré*, in *Gold ore processing: Project development and operations*, 2nd ed., Adams, M.D., Elsevier, B.V., Amsterdam, Netherlands, pp. 595 – 618.
- Moses, C.O., Nordstrom, D.K., Herman, J.S. and Mills, A.L. (1987). Aqueous pyrite oxidation by dissolved oxygen and by ferric iron, *Geochimica et Cosmochimica Acta*, 51, pp. 1561 – 1571.
- Muir, D.M. (2002). Basic principles of chloride hydrometallurgy, in *Chloride Metallurgy 2002 International Conference on the Practice and Theory of Chloride/Metal Interaction 32nd Annual Hydrometallurgy Meeting, Volume II*, 1st ed., Peek, E. and Van Weert, G., The Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Canada, pp. 759 – 778.
- Muir, D.M. and Aylmore, M.G. (2005). *Chapter 22: Thiosulfate as an alternative lixiviant to cyanide for gold ores*, in *gold ore processing: Project development and operations*, 2nd ed., Adams, M.D., Elsevier, B.V., Amsterdam, Netherlands, pp. 371 – 402.
- Nan, X.-Y., Cai, X. and Kong, J. (2014). Pretreatment process on refractory gold ores with As, *ISIJ International*, 54, pp. 543 – 547.

- Nicol, M.J. (1980). The anodic dissolution of gold. Part I. Oxidation in acidic solutions, *Gold Bulletin*, 145, pp. 70 – 75.
- Nicol, M., Zhang, S. and Tjandrawan, V. (2018) The electrochemistry of pyrite in chloride solutions, *Hydrometallurgy*, 178, pp. 116 – 123.
- Ofori-Sarpong, G. and Osseo-Asare, K. (2013). Preg-robbing of gold from cyanide and non-cyanide complexes: effect of fungi pretreatment of carbonaceous matter, *International Journal of Mineral Processing*, 119, pp. 27 – 33.
- Ofori-Sarpong, G., Amankwah, R.K. and Osseo-Asare, K. (2013). Reduction of preg-robbing by biomodified carbonaceous matter – a proposed mechanism, *Minerals Engineering*, 42, pp. 29 – 35.
- Oraby, E.A. and Eksteen, J.J. (2015a). Gold leaching in cyanide starved copper solutions in the presence of glycine, *Hydrometallurgy*, 156, pp. 81 – 88.
- Oraby, E.A. and Eksteen, J.J. (2015b). 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). Cited 5.3.2020:
https://www.outotec.com/globalassets/products/digital-solutions/hsc/ote_outotec_hsc_chemistry_eng_web.pdf.
- Paatero, E. and Haapalainen, M. (2011) Method for recovering gold by solvent extraction, WO2011/154603 A1, Retrieved on December 15, 2011.
- Palacios, J.-L., Abadias, A., Valero, A. and Reuter, M.A. (2019). Producing metals from common rocks: The case of gold, *Resources, Conservation & Recycling*, 148, pp. 23 – 35.
- Pell, R., Wall, F., Yan, X., Li, J. and Zeng, X. (2019). Mineral processing simulation based-environmental life cycle assessment for rare earth project development: A case study in the Songwe Hill project, *Journal of Environmental Management*, 249, 109353.
- Rabieh, A., Eksteen, J.J. and Albijanic, B. (2017). The effect of grinding chemistry on cyanide leaching of gold in the presence of pyrrhotite, *Hydrometallurgy*, 173, pp. 115 – 124.
- Rawlings, D.E., Tributsch, H. and Hansford, G.S. (1999). Reasons why *Leptospirillum*-like species rather than *Thiobacillus ferrooxidans* are the dominant iron-oxidizing bacteria in many commercial processes for the biooxidation of pyrite and related ores, *Microbiology*, 145, pp. 5 – 13.
- Reuter, M.A. (1998). The simulation of industrial ecosystems, *Minerals Engineering*, 11, pp. 891 – 918.
- Reuter, M.A., Van Schaik, A. and 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, *The International Journal of Life Cycle Assessment*, 20, pp. 671 – 693.
- Rimstidt, J.D. and Vaughan, D.J. (2003). Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism, *Geochimica et Cosmochimica Acta*, 67, pp. 873 – 880.
- Riveros, P.A. and Dutrizac, J.E. (1997). The precipitation of hematite from ferric chloride media, *Hydrometallurgy*, 46, pp. 85 – 104.
- Roffel, B. and Betlem, B. (2006). *Process Dynamics and Control Model for Control and Prediction*, John Wiley & Sons Ltd. Sussex, England, pp. 1 – 25.

- Rose, T. (1898). *The Metallurgy of Gold*, 3rd ed. Roberts-Austen, W., The Royal School of Mines, Charles Griffin and Company, Limited, London.
- Rusanen L., Aromaa, J and Forsén, O. (2013). Pressure oxidation of pyrite-arsenopyrite refractory gold concentrate, *Physicochemical Problems of Mineral Processing*, 49, pp. 101 – 109.
- Schmitz, P.A., Duyvesteyn, S., Johnson, W.P., Enloe, L. and McMullen, J. (2001). Ammoniacal thiosulfate and sodium cyanide leaching of preg-robbing Goldstrike ore carbonaceous matter, *Hydrometallurgy*, 60, pp. 25 – 40.
- Segura-Salazar, J., Lima, F.M. and 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. and Lundström, M. (2019). Features affecting the cupric chloride leaching of gold, *Minerals Engineering*, 137, pp. 94 – 101.
- Seisko, S. (2020). Electrochemical studies of gold dissolution in cupric and ferric chloride solutions. Doctoral dissertation. Aalto University, Helsinki, Finland.
- Senanayake, G. (2004). Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications, *Minerals Engineering*, 17, pp. 785 – 801.
- Seppälä, P., Sorsa, A., Paavola, M., Remes, A., Ruuska, J. and Leiviskä, K. (2014). Pilot plant simulation as a tool for more efficient mineral processing, *Proceeding of IFAC The International Federation of Automatic Control 2014*, pp. 11506 – 11511.
- Sibrell, P.L., Wan, R.Y. and Miller, J.D. (1990). Spectroscopic analysis of passivation for carbonaceous matter from Carling trend ores. *Proceedings of World Gold 1990*, pp. 335 – 363.
- Simeonova, F.P. and Fishbein, L. (2004). Hydrogen cyanide and cyanides: human health aspects. Concise International Chemical Assessment Document 61, World Health Organization, Geneva.
- Smith, H. (2005). *Chapter 5: Process simulation and modelling*, in *Advances in Gold Ore Processing*, 1st ed., Adams, M.D., Elsevier, B.V., Amsterdam, Netherlands, pp. 109 – 121.
- Souren, A. (2000). Living with Cyanide, *The Geochemical News*, Quarterly Newsletter of The Geochemical Society, 105.
- Sun, T.M. and Yen, W.T. (1993). Kinetics of gold chloride adsorption onto activated carbon, *Minerals Engineering*, 6, pp. 17 – 29.
- Süss, H.U., Nimmerfroth, N.F. and Kronis, J.D. (1997). The naked truth on hot peroxide bleaching, *Proceeding of Canadian Pulp and Paper Associate (CPPA) 83rd Annual Meeting*, Montreal, Canada, pp. 129 – 136.
- Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J. (2018a). Adsorption behavior of copper and gold glycinate in alkaline media onto activated carbon. Part 1: Isotherms, *Hydrometallurgy*, 178, pp. 202 – 208.
- Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J. (2018b). Adsorption behavior of copper and gold glycinate in alkaline media onto activated carbon. Part 2: Kinetics, *Hydrometallurgy*, 178, pp. 195 – 201.
- Teir, S., Kotiranta, T., Pakarinen, J. and 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.

- Thomas, K.G. and Cole, A.P. (2005). *Chapter 17: Roasting developments – especially oxygenated roasting* in *Advances in Gold Ore Processing*, 1st ed., Adams, M.D., Elsevier, B.V., Amsterdam, Netherlands, pp. 403 – 432.
- Ubal dini, S., Fornari, P., Massidda, R. and Abbruzzese, C. (1998). An innovative thiourea gold leaching process, *Hydrometallurgy*, 48, pp. 113 – 124.
- Virtanen, H. and Schmachtel, S. (2015). Hydrometallurgical treatment of anode sludge, WO2015/181446 A1, Retrieved on December 3, 2015.
- Wikedzi, A., Arinanda, M.A., Leißner, T., Peuker, U.A. and Mütze, T. (2018). Breakage and liberation characteristics of low grade sulphide gold ore blends, *Minerals Engineering*, 115, pp. 33 – 40.
- Wojnicki, M., Luty-Blocho, M., Socha, R., Mech, K., Pędzich, Z., Fitzner, K. and Rudnik, E. (2015) Kinetic studies of sorption and reduction of gold(III) chloride complex ions on activated carbon Norit ROX 0.8, *Journal of Industrial and Engineering Chemistry*, 29, pp. 289 – 297.
- Xie, F. and Dreisinger, D.B. (2009). Use of ferricyanide for gold and silver cyanidation, *Transactions of Nonferrous Metals Society of China*, 19, pp. 714 – 718.
- Xu, B., Kong, W., Li, Q., Yang, Y., Jiang, T. and Liu, X. (2017). A review of thiosulfate leaching of gold: Focus on thiosulfate consumption and gold recovery from pregnant solution, *Metals*, 7, pp. 222 – 237.
- Yang, H.-Y., Liu, Q., Song, X.-L. and Dong, J.-K. (2013). Research status of carbonaceous matter in carbonaceous gold ores and bio-oxidation pretreatment, *Transactions of Nonferrous Metals Society of China*, 23, pp. 3405 – 3411.
- Yoshimura, A. and Abe, Y. (2017). Method for Recovering Gold from an Ore or a Refining Intermediate Containing Gold, WO2017/170960 A1, Retrieved on October 5, 2017.
- Zammit, C.M., Cook, N., Brugger, J., Ciobanu, C.L. and Reith, F. (2012). The future of biotechnology for gold exploration and processing, *Minerals Engineering*, 32, pp. 35 – 53.
- Zaytsev, P., Shneerson, Y., Fedorov, V., O’Callaghan, J., Haakana, T. and Kaarti, A. (2013). Pokrovskiy pressure oxidation (POX) hub. Proceedings of ALTA 2013, Perth, Australia, pp. 33 – 71.
- Zhou, Q., Barrett, G., Jiang, J. and Choi, Y. (2013). Using surfactants to improve gold recovery of Goldstrike carbonaceous ore, in proceeding of the 52nd Conference of Metallurgists 2013, Montreal, Canada, pp. 1857 – 1865.
- Örgül, S. and Atalay, Ü. (2002). Reaction chemistry of gold leaching in thiourea solution for a Turkish gold ore, *Hydrometallurgy*, 67, pp. 71 – 77.



ISBN 978-952-64-0014-3 (printed)
ISBN 978-952-64-0015-0 (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**