Heap leaching of nickel sulfide ore

Antti Arpalahti
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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 5th of November 2021 at 12.

Aalto University
School of Chemical Engineering
Department of Chemical and Metallurgical Engineering
Hydrometallurgy and Corrosion
Supervising professor
Associate Professor Mari Lundström, Aalto University, Finland

Thesis advisor
Associate Professor Mari Lundström, Aalto University, Finland

Preliminary examiners
Professor David Dixon, University of British Columbia, Canada
Associate Professor Jochen Petersen, University of Cape Town, South Africa

Opponent
Associate Professor Yongxiang Yang, Delft University of Technology, the Netherlands
Heap leaching is a widespread technology for gold and copper production, typically utilized in arid and warm locations. However, the Terrafame (former Talvivaara) operation in Finland is the only operation that utilizes heap leaching for nickel and zinc production, furthermore in a net positive rainfall area with low temperatures. The process relies on high temperature generation within the heap and makes the process quite different compared to most heap leach operations.

The current thesis had three main objectives: α) to gain understanding of the reaction mechanisms and the order of the reactions within the heap leaching operation, to better determine the early signs of sub-standard behavior in the leaching of the target metals; β) to investigate the impact of an increased aeration feed on valuable metal recovery, and γ) to increase understanding of the potential variability of the water balance at the heap leach operation in question today, with the effects of global warming in mind.

It is suggested that the leaching process follows the order: alabandite > pyrrhotite > other minerals. The research results showed that cadmium, cobalt, copper, nickel, and zinc re-precipitate during the early stages of the heap leach process. A very low acid consumption was achieved on production scale (less than 1 kg of acid per tonne of ore) in comparison to previous studies (close to 40 kg of acid per tonne of ore). The amount of temperature generated and acid balance suggested 15% to 20% oxygen efficiency in heap leaching. It was shown that a full oxidation of 10%-w pyrrhotite ore could lead to a 3.6%-w mass increase and 5.7%-V volumetric increase in the heap, which is a unique phenomenon in global heap leaching operations.

The water balance at the site was shown to be heavily dependent on the heat generation. Climate change cases with doubled and tripled CO2 emissions were studied in comparison to a time when the climate was not affected by human activity. The cases showed that the extremes of weather effects are widening. They also showed that it would appear the balance would tend toward the drier side with these climate change scenarios, requiring more fresh water.

Keywords heap leaching, nickel, aeration, heat generation, water balance
Tekijä
Antti Arpalahi

Väitöskirjan nimi
Nikkeli-olivinalmin korkeakoulu

Julkaisija
Kemian teknikko

Yksikkö
Kemian teknikka ja metallurgian laitos

Sarja
Aalto University publication series DOCTORAL DISSERTATIONS 115/2021

Tutkimusala
Materiaalien prosessointi

Käsikirjoituksen pvm
14.01.2021

Väitöspäivä
05.11.2021

Väittelyluvan myöntämispaivä
25.08.2021

Kieli
Englanti

Monografia
Artikkeliväitöskirja
Esseeväitöskirja

Tiivistelmä
Kasaluvontou on yleisesti käytetty tuotantoteknologia kuparin ja kloon valmistuksessa. Kuitenkin
ainoastaan Terrafame (entinen Talvivaara) Suomessa käyttää kasaluvontuteknologiaa nikkelin ja
sinkin valmistuksena. Kasaluvontou on tyypillisesti teknologia jota käytetään kuumilla ja kuivilla
alueilla. Terrafamen kaivoksen sijainti positiivisen nettosadanan alueella ja pohjoisen kymlää
ilmastossa on harvinaista kasaluvontukselle ja koko prosessin toimivuus perustuukin malmin
liuotuksen aikaiselle käytettävässä lämmöntuotannolle.

Tämä väitöskirja sisältää kolme tavoitetta: α) lisätä ymmärrystä reaktiomekanismista ja reaktioiden
järjestystä kasaluvontusoperaatiossa, jotta tuotantometallien liuotusprosessin lopputulosta
pystytään tulkitsemaan kasan aiemman liukenemiskäytäntymisen perusteella; β) tutkia
ilmasyytömmääran vaikutusta metallien liukenemiseen kasaluvontusoperaatiossa; γ) kasvattaa
ymmärrystä kasaluvontusoperaation tusitsee vainetusta sekä tään päivänä että
ilmastonmuutoksen muutokset huomioiden.

Tutkimuksessa löydettiin, että mineraalien liukenemispäristä seuraa kasaluvontuksesta seuraava
järjestystä: alabanditit > pyroottiitit > muut mineraalit, ja että kadmium, koboltti, kupari, nikkel
ja sinkki takaisinsaostuvat kasaluvontusprosessin varhaisessa vaiheessa. Tuotantomittakaavan
liuotuskasolla kyettiin saavuttaamaan erittäin pieni haponkulutus (alle 1 kg hoppaa malmitonnin
kohden) verrattuna edellisiin tutkimuksiin (lähes 40 kg hoppos malmitonnin kohden) ja hapen
hyötysuhteeksi arvioitiin 15-20 % lämmönkehityksen ja hopputasapainon perusteella.

Tutkimuksessa näytettiin, että malmin, jossa on 10 massaprosenttia pyroottiitia, täydellinen
pyroottiitin reaktio kasassa voi arvioidun reaktiomekanismin kautta johtaa 3,6 prosentin massan
kasvun ja 2,5 prosentin tilavuuden kasvun. Tätä ilmiötä ei tiedetä raportoidun aikaisemmin
kasaluvontuksissa.

Vesitaseen käytettiin olevan voimakkaasti riippuvainen kasan lämmöntuotannosta ja sitä kautta
hautumasta. Tutkittiin kaksinkertaista ja kolminkertaista globaalia hiilidioksidipäästöä verratuna
ennen ihmiskunnan vaikutusta päästöihin. Tässä tutkimuksessa havaittiin, että
ilmastonmuutoksen myötä sään vaikutuksen prosessi levenee: kuivasta jaksosta tulee kuivempia
ja märästää märempi. Samalla havaittiin, että keskimääräinen vesitase suuntaa kohti kuivempaa
tutkittujen ilmastonmuutosskenaarioiden myötä.
Acknowledgements

The research work in this thesis was done between 2016 and 2020 at Aalto University and the Terrafame mine. Most of the research was performed at the mine. The work was not funded but done in the author’s leisure time. I wish to thank Terrafame for the opportunity to utilize the production scale heaps for test work that hopefully benefits both the operation and the scientific community.

It was March 2008 when I called Professor Olof Forsén if it would be possible to discuss studying further than Master’s degree. I had studied previously on the department of Chemical Engineering and we had not personally met. Olof was utmost welcoming towards me, considered carefully what studies would benefit my route in understanding Hydrometallurgy and planned my studies accordingly. I would like to thank Olof for all the excellent discussions we had during my studies.

Professor Forsén noted that it would be a benefit for my studies to have a few parts with Professor Erkki Paatero from Lappeenranta University of Technology. Erkki excelled in solvent extraction and the courses with him gave a great understanding on that field of Hydrometallurgy. Erkki was, as Olof was, most welcoming towards me in helping me with my studies. He went as far to help introduce me to a great person in the field of SX, Professor Gordon Ritcey, back in 2008 as we three had a drive from Jyväskylä to Helsinki after a conference. Erkki told me I had a great chance to learn from this international expert, but I... I slept most of that drive. I would like to thank Erkki for all the knowledge he managed to transfer.

In 2015 Professor Mari Lundström took over the Hydrometallurgy and Corrosion professorship at Aalto University. She called me and demanded that I start making my Doctoral Thesis. She gave me the push I needed, and I began planning my articles to come. Mari gave excellent directions on the manuscripts and help by herself and by introducing me to other doctoral candidates. I want to thank her for all the advice, motivation and direction she gave.

I want to thank my family for always supporting me in studying hard. I would like to thank my wife Anni for her support, encouragement and love that were essential to keep me on track.

Kajaani, 19th August 2021
Antti Arpalahi
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<table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>%-w</td>
<td>mass percent</td>
</tr>
<tr>
<td>%-V</td>
<td>volume percent</td>
</tr>
<tr>
<td>DTS</td>
<td>Distributed Temperature Sensing</td>
</tr>
<tr>
<td>FEI</td>
<td>Finnish Environmental Institute</td>
</tr>
<tr>
<td>FNAC</td>
<td>Fives North American Combustion</td>
</tr>
<tr>
<td>IAEA</td>
<td>International Atomic Energy Agency</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductive coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>INE</td>
<td>Instituto Nacionales de Estadisticas, Chile</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>LOM</td>
<td>Life-of-mine</td>
</tr>
<tr>
<td>Me</td>
<td>General two-valent metal cation</td>
</tr>
<tr>
<td>RCP</td>
<td>Representative Concentration Pathway</td>
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List of Publications

This doctoral dissertation contains a summary and the following four publications:


Author’s Contribution

**Publication I:** Heat generation in a production scale sulphide heap leach operation

A.A. defined the research plan, performed the experimental work, and conducted the data analysis. The manuscript was written by A.A. supported by M.L.. The work was carried out under the supervision of M.L..

**Publication II:** The leaching behavior of minerals from a pyrrhotite-rich pentlandite ore during heap leaching

A.A. defined the research plan, performed the experimental work, and conducted the data analysis. The manuscript was written by A.A. supported by M.L.. The work was carried out under the supervision of M.L..

**Publication III:** Dual aeration tests with heap leaching of a pyrrhotite-rich pentlandite ore

A.A. defined the research plan, performed the experimental work, and conducted the data analysis. The manuscript was written by A.A. supported by M.L.. The work was carried out under the supervision of M.L..

**Publication IV:** Water balance of a boreal black-schist heap leach operation

A.A. defined the research plan, performed the experimental work, and conducted the data analysis. The manuscript was written by A.A. supported by M.L.. The work was carried out under the supervision of M.L.
1. Introduction

1.1 Background

Heap leaching was pioneered in the 1950s with the cyanide heap leaching of precious metals (Scheffel, 2002). Today it is a staple technology for gold and copper production around the world (Petersen, 2016). It is not that the ores are more suitable for heap leaching but the accompanied extraction processes, such as solvent extraction for copper and activated carbon adsorption for gold, have been developed to complete the recovery process and make it not only technologically but also economically feasible. However, similar technologies have not yet become available for nickel, and the Terrafame (former Talvivaara) heap process is unique in the world. Currently, it is the sole mine utilizing heap leaching technology for the recovery of nickel and zinc. It is a boreal operation with temperatures that fall to -40 °C in winter and a net positive rainfall, whereas most of the other heap leach operations are located in drier areas of the world where the challenge is to find a source of fresh water (Ghorbani et al., 2015). While the Terrafame nickel heap leaching conditions are unusual, the plant also conducts mining throughout the year, while most heap leach operations that encounter freezing conditions mine only outside the winter period. This is enabled by the high amount of reactive sulfidic raw material in the Terrafame ore, which creates a substantial amount of heat during the leaching reactions.

The Terrafame operation processes one of the largest nickel deposits in Europe. It has an expected lifetime of decades. The weather at the site is likely to be altered during the LOM (life of mine) by the effects of global warming. The Core Writing Team et al. (2014) have defined scenarios for global warming, based on the amount of Watts per square meter of greenhouse gases produced by human activities that will warm the Earth climate by the year 2100. To the knowledge of the author, the effect of global warming on water balances of mines has not been reviewed. Publication IV answers this need, modeling the possible changes to the water balance due to the potential effects of global warming.

Terrafame ore contains pyrrhotite and pyrite as the main sulfide minerals, both varying from 5%-w to 15%-w in the ore. These two minerals are both iron sulfides but differ greatly in their leaching behavior. Pyrrhotite has a much lower electrode potential compared to pyrite. In fact, the difference is of such magnitude that pyrrhotite is reported to have the lowest electrode potential
among the sulfides present in the Terrafame ore, while pyrite has one of the highest (Riekola-Vanhana and Heimala, 1993). This indicates that pyrrhotite is the mineral that reacts first of all the sulfides present in the Terrafame ore while pyrite, if it reacts at all, is one of the last to react. A note has to be added that this view is challenged in Publications II and III, where manganese leaching from alabandite was observed to be faster compared to pyrrhotite.

The Keretti mine in Finland was closed in 1989. The sulfideic mineral left in the mine was considered to have neither economic value nor to have a technologically feasible method for valuable metals (cobalt, copper, nickel, and zinc) extraction. Therefore, bacterial assisted leaching was investigated as an alternative processing option for metals recovery (Ahonen and Tuovinen, 1995). Initially, the microbiological oxidation of ferrous iron was studied (Ahonen and Tuovinen, 1989), followed by investigations about the temperature effect in shake flask tests, at the expected mine temperature of from 4 °C to 37 °C (Ahonen and Tuovinen, 1991). Later the research was continued with column tests (Ahonen and Tuovinen, 1992). Generally, these bacterial leaching tests suggested higher metal extractions at higher temperatures – which should not be a surprise as generally leaching reaction rates double every 10 °C, when not limited by diffusion but rather by the chemical reaction rate. The Keretti orebody investigated in these studies had similar sulfides to the Terrafame ore, albeit a much higher sulfide mineral content in general, with the main sulfide being chalcopyrite. Subsequently, bench-scale column tests were performed and the following observations were made (Ahonen and Tuovinen, 1995): 1) new solid phases formed on surfaces (iron oxides, covellite, and elemental sulfur); 2) sulfuric acid consumption was 43 kg/tonne of ore on average; 3) the lower the pH, the higher the ferric iron concentration and the faster the leaching rates—except for nickel, which was not dependent on ferric concentration; 4) leaching in sterile condition, without inoculation with bacteria, was negligible. The results of the current thesis described in Publication III suggest that the amount of acid needed is significantly lower (below 1 kg/tonne of ore in a similar time period) on large industrial scale, and especially with greater aeration.

Chepushtanova et al. (2012) have examined pyrrhotite leaching in non-oxidative and oxidative conditions. They indicated that the formation of hydrogen sulfide occurs in non-oxidative conditions and a full oxidation of sulfur to sulfate in oxidative conditions. No iron precipitation was made or observed in these studies. Somot and Finch (2010) examined the self-heating of pyrrhotite and came to an interesting hypothesis that with high pyrrhotite content and moisture, hydrogen sulfide gas is formed, and that the hydrogen sulfide reacts with oxygen in air. The gas phase reaction, according to their suggestion, is the phenomenon that causes pyrrhotite to self-heat vigorously. The presence of hydrogen sulfide was verified by placing copper sulfate solution near the gas space. These studies suggest a similar phenomenon: hydrogen sulfide can be formed near the surface of pyrrhotite and/or precipitation of at least copper as sulfide (covellite) can occur near the surface of pyrrhotite. Publications II and III of the current thesis extend this hypothesis further, stating that at least nickel and zinc
can also be precipitated as sulfides when there is a significant amount of pyrrhotite left.

The majority of heap leach operations are operated for cyanide leaching of gold or sulfuric acid leaching of copper oxide ore (Ghorbani et al., 2015). These processes do not require forced aeration (aeration with machinery such as fans/blowers); the open literature has only a limited amount of studies about aeration in heap leaching. The majority of studies related to aeration concern copper sulfide heap leaching. In these, the amount of reactive ore is rather limited—for example should the reacting mineral be covellite, CuS, and the amount of copper 0.5%-w, then the amount of reactive sulfide needing oxidation would be 0.75%-w – a tiny fraction of the ore. For example, Lizama (2001) studied aeration at a 62 500 tonne section of a production heap leach pad with copper ore. The ore had about 1%-w copper, present as chalcocite. He concluded that the rate of forced aeration was shown to improve copper leaching. Schllt (2006) summarized what had been done in the field of heap leaching of copper sulfides using aeration fans. He remarked that this technique had been developed for heap leaching in the mid-1990s, signifying that it is quite recent in the industry, but that the earliest reported tests date back to the beginning of the 20th century. Before the 1990s, test work did show improved leaching of sulfides with forced air utilization; however, sulfide heap leaching processes did not proceed to production due to the technical risks and high costs involved. Schllt (2006) stated that low pressure fans were sufficient as the material is typically permeable for gas flow; installing air lines before the heap is more cost effective than drilling them in later; pushing excessive amounts of air into the heap might prove to have negative effects such as an unwanted high evaporation rate; and the utilization of forced aeration could promote natural convection after the air flow is shut off. Dixon (2000) simulated the effects of forced aeration on the internal heap temperature. He suggested that, with sufficient air feed flowing from the bottom up in the heap, the exiting solution temperature can be cooled as the air becomes saturated with water vapor. This saturated vapor then re-condenses as the air flows upwards in the heap, releasing heat of vaporization energy on its way. He further suggested that this increased aeration-driven vaporization-condensation cycle will (up to a point) increase the average temperature in the heap. Scheffel et al. (2016) noted that while there is a “universal assumption” that forced aeration is always needed when bioleaching is concerned, this has not been scientifically proven. They suggested that raw materials with > 1%-w chalcocite ore grade required forced aeration. In Publication III of this thesis, different levels of forced aeration in production scale heap leaching were studied, finding that additional air feeding accelerated the overall leaching—in other words proving clearly that forced aeration is required in the Terrafame case.

The “bio”-aspect of sulfide heap leaching became a topical study area of its own in the 1990s and certainly during the first decade of the new millennium. As with heap leaching, most of this involved copper ores, the holy grail there being to enable heap leaching of chalcopyrite. Yet despite all the work and effort, no feasible recovery heap leaching process for chalcopyrite ore has been developed. Gericke et al. (2009) for example, presented an overview of the last 25
years of development of bioleaching of minerals. In their view, heap leaching of copper ores was the most important commercial application. The most important example was provided by an Iranian copper operation, Sarcheshmeh, where a pilot was trialed to leach copper from chalcopyrite at an elevated temperature. Success was reported in the article at the time, yet the operation never continued for heap bioleaching of chalcopyrite. Watling (2006) presented another view on the success of bacterial assisted heap leaching, focusing on copper sulfides. The operations of sulfide-containing heap leaches are listed in that article in detail. Are they all biological leaches? What constitutes a “bio”leach? Watling (2006) noted that the commercialization of chalcopyrite heap bioleaching is not necessarily only restricted by technology but also by attitudes. However, no industrial breakthrough has emerged, suggesting that the technology is not quite there, if it ever will be. Watling (2015) continued to discuss bacterial assisted hydrometallurgy, this time focusing on polymetallic ores. Again, a considerable amount of promise in the technology was implied; however, so far the only commercialized process is the Terrafame process investigated in the current thesis.

Lizama et al. (1998) pondered the necessity to inoculate bacteria in a bioleach process. In this paper, it was noted that in gold ore biological pretreatment processes it is a custom to add a prepared bacterial culture to the ore stream, in contrast to copper heap leaching where indigenous microorganisms are relied upon. The paper presented a test involving a zinc mineral and there was no statistical difference between inoculated and uninoculated leaching. In fact, it was suggested that perhaps the studies focused in general too much on comparing inoculated samples with sterilized samples; therefore, the role of indigenous bacteria was forgotten. The current thesis did not test inoculation versus no inoculation but shows the outcomes of productional heap leaching without inoculation. The results of the current study—the phenomenon of substantial heat generation (Publication I) as well as increasing the reaction rate with increasing air-feed (Publication III)—suggest that perhaps the system is not limited by inoculation.

1.2 Objectives and scope

The Terrafame orebody has been studied since it was discovered in the 1970s (Halinen, 2015). Early on, it was found that conventional means of exploiting the orebody, such as froth flotation, did not show promising results. Other means were searched for and bioleaching showed its potential in the 1980s (Puhakka and Tuovinen, 1986). Heap bioleaching was extensively tested in column in the 1990s (Riekkola-Vanhanen and Heimala, 1999) and continued with piloting in 2005 (Halinen, 2015). Later on, the process was scaled up to industrial operational scale, although there were a lot of unknown or only partially understood phenomena. The holistic aim of this thesis is to enhance understanding, and thereafter the processing, of industrial-scale nickel sulfide ore heap leaching.
The specific objectives of this thesis are:

α) To gain an understanding of the reaction mechanisms and order of the reactions within the heap leaching operation, to better determine the early signs of sub-standard behavior in the leaching of the target metals

β) To investigate the impact of increased aeration feed for the valuable metal recoveries in heap leaching

γ) To increase understanding of the potential variability of the water balance at the heap leach operation in question today, taking into account the effects of global warming

The aim of the thesis is to observe the heaps on actual scale and perform the work on them rather than on laboratory scale.

1.3 New scientific contribution and applications

This thesis consists of tests and modeling on a production scale heap leach operation. To the knowledge of the author, such reported work is scarce. Typically, test work for heap leaching is done on column scale, concerning kilograms of the leached material or at best at pilot scale heaps, containing tens of thousands of tonnes of material. The test work consisted of set-ups from 600 000 tonnes up to 6 000 000 tonnes of ore at the heaps.

The test work within the thesis was designed to cover different aspects of the Terrafame ore leaching process. For this, distributed temperature sensing, DTS, was used for the first time (to the best of the author’s knowledge) at a production scale heap. Previously, local heat sensors had been used in different studies—but the DTS cable enabled temperature measurement at one-meter intervals across the heap. In addition to learning about the amount of heat generation, this method of measuring temperature could prove useful in heat-generating heap leaching processes.

The water balance of a functional heap leach operation has not been reported previously as far as the author is aware. In this thesis, not only was the actual water balance recorded but it was modeled with the ore reaction (heat generation from the reactions) in mind, varying the location of the operation from the current boreal to arid desert conditions, and bearing in mind the potential effects of global warming. Such a study has not been conducted previously to the author’s knowledge.

The results also showed clearly for the first time that leaching reactions for a black-schist ore within the heap occur in a specific order. The stage of re-precipitation, which has been suggested before for copper, was found to include several other metals of interest as well, namely nickel, cobalt, zinc, and cadmium. It was shown that leaching occurs first for alabandite, then pyrrhotite,
followed by other minerals. This creates a delay for nickel and zinc leaching. It is very important to understand that such a delay exists as it lasts several months. The thesis proposes that the ultimate nickel and zinc recoveries can be predicted by further studying the manganese and iron behavior in the early stages of leaching. Should this prove correct in the long term, it is also to be expected that similar future predictions can also be made for copper and cobalt. This would also require further work as the leaching of copper and cobalt had hardly started during the observed time period of the heap leaching test work performed in this thesis.

The author suggests that the following findings are original (below the first four findings (i-v) relate to objective $a$, findings v-vi to objective $\beta$, and finding vii to objective $\gamma$):

i) The amount of heat generation at the Terrafame black-schist heap leaching process was investigated for the first time, relating to objective $a$ (Publication I)

ii) The order of dissolution of the metals, and thereby the minerals, was published for the first time in more detail than simply nickel and zinc, relating to objective $a$ (Publication II and III)

iii) It was shown for the first time that re-precipitation of nickel, zinc, cobalt, and cadmium occurs at the black-schist heaps. This relates to objective $a$ (Publication II and III)

iv) A leach heap of high pyrrhotite content will grow in both mass and volume during leaching due to iron re-precipitating in the heap. This relates to objective $a$ (Publication II and III)

v) The acid balance for Terrafame black-schist heap leaching was calculated and from that the oxygen efficiency and the dominating reaction mechanism were revealed. This relates to objectives $a$ and $\beta$ (Publication III)

vi) Different oxidant (air) addition rates were investigated for the first time at full-scale heaps. This relates to objective $\beta$; it was found that the added air accelerated the reaction rate (Publication III)

vii) The water balance of the boreal black-schist heap leaching operation with scenarios of dry climate operation, no heat generation at the heaps, and two potential climate change cases was published and discussed in detail for the first time. This relates to objective $\gamma$ (Publication IV)
The author further suggests that, through findings i) to vii), the overall understanding of the unique heap leach operation as well as the reactions occurring at Terrafame has improved significantly.

1.4 Thesis structure

Figure 1 presents the structure of the thesis with the three main objectives (α-γ). Further, the summary part of the thesis is divided into chapters 1 to 5, with four peer-reviewed and published Publications (I-IV) as attachments. Chapter 1: Introduction, presents the scientific background, objective, findings, and structure of the work. In Chapter 2: Theoretical Background, further describes the field of leaching, heap leaching, and sulfide leaching work carried out prior to the thesis. Chapter 2 further lists earlier work on the water balance of mines and heap leaching operations and describes the scenarios with which it has been agreed to model climate change in the scientific community. Chapter 3: Experimental methods, shows the methodology used in the publications. Chapter 4: Results and discussion, presents the results achieved in the publications and their implication for this field of research. Chapter 5: Conclusions, sums up the thesis work. The thesis publications are one peer-reviewed conference Publication I, and three peer-reviewed journal Publications (II-IV).

![Figure 1. Schematic structure of thesis objectives and publications.](image-url)
2. Theoretical Background

2.1 Leaching

Frias Gomez (2016) gives leaching as the first stage of a hydrometallurgical flow sheet, transferring metals of interest from ores to an aqueous media. He divides leaching into in-situ leaching, dump leaching, heap leaching, vat leaching, stirred tank leaching, autoclave leaching, and bioleaching. This split follows the level of sophistication of equipment from first to last. However, it has to be noted that bioleaching is not strictly speaking a unit process of its own but describes—or aims to describe—the chemistry behind the leaching. For example, bacteria can be added to a stirred tank reactor in which case it is called bioleaching. Alternatively, bacteria can be added to the heap and it is called bioheap leaching. It can be argued that “sophistication” is not the best choice of words as it is quite possible to find a sophisticated in-situ leaching process.

A general comparison of different features in the various types of leaching areas is shown in Table 1. In-situ leaching is, as the Latin name suggests, leaching in place, that is to say the ore is not removed from the ground where it is found but lixiviant is fed directly to the orebody and the enriched solution is collected via underground wells. Production of uranium has utilized in-situ leaching since the 1960s, starting in the Soviet Union, Bulgaria, Czechoslovakia, and the USA. In 2011, almost half of the world’s uranium production was carried out via the in-situ leaching route (IAEA, 2016). Typically, this process is applied for low grade ores (Frias Gomez, 2016). Dump leaching refers to a process where ore is liberated from the mine and stacked on a leach pad, without a comminution process (size alteration such as crushing and grinding). As the particle size is variable, the recovery rate is expected to be poor and the process is typically applied for low grade ores. In addition, aeration via pipelines inside the dump is not feasible due to large particles crushing the pipelines upon impact. Further, as the particle size is variable, truck dumping is used to place the ore on the leach pads. Heap leaching will be discussed in more detail in a separate chapter—suffice to say here that, unlike dump leaching, crushing is applied to the ore, typically to below 25 mm size (Petersen, 2016) before the material is stacked on the leach pad. Unlike in dump leaching, a conveyor-type stacker can be used to place the ore on the leach pad. This allows the material compaction to be limited in comparison to dump leaching. Furthermore, as the particle size is smaller, aeration piping can be implemented, increasing the range of opportunities for more oxidation-demanding types of process, such as sulfide leaching. In vat leaching, ore crushed to below 10 mm size is placed in a basin. The basin is then
filled with leach solution (Petersen, 2016). The finer crushing utilized means more energy and costs of comminution. The basin also requires walls that have a higher construction cost than a simple pad with a bottom structure.

Stirred tank leaching is a process which requires the ore to be ground in addition to crushing. The particle size has to be small enough to allow agitation to keep the material in suspension without excessive wear to the impellers (typically below 100 μm is an acceptable particle size). This translates into more cost in the comminution circuit and, as the vast majority of grinding is wet grinding, the addition of water incurs extra cost in the leaching circuit. However, when water is added this way, the rainfall catchment area is much smaller than in outside leaching pads. The construction cost is typically higher in reactor leaching as reactors cost more than leaching pads per tonne of ore. The control of the process is better in reactor leaching and higher recoveries should be expected in comparison to leaching pads. Autoclave leaching is a type of reactor leaching with added pressure to improve the kinetics and decrease the retention time. Temperatures over 200 °C and pressures over 20 bar have been reached in autoclaves (Frias Gomez, 2016). Adding pressure is an added complexity and the cost of constructing an autoclave is typically high and the maintenance requirement is also very high. It is utilized when atmospheric leaching does not achieve high enough recovery rates. Autoclaves provide another positive feature: as iron is often present in the ore with the valuable metals, it generates a requirement for acid if it co-leaches with the valuable metals. In autoclaves, iron can be effectively precipitated, generating acid, and reducing the overall requirement for acid feed.

<table>
<thead>
<tr>
<th>Table 1. General features in different types of leaching processes</th>
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<tbody>
<tr>
<td><strong>Type of leaching</strong></td>
</tr>
<tr>
<td>In-situ</td>
</tr>
<tr>
<td>Dump</td>
</tr>
<tr>
<td>Heap</td>
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<tr>
<td>Vat</td>
</tr>
<tr>
<td>Reactor</td>
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<tr>
<td>Autoclave</td>
</tr>
</tbody>
</table>

### 2.2 Heap Leaching

Heap leaching consists of crushed material stacked as a heap on top of a solution collection system and irrigation of the heap with a lixiviant with the intention of leaching valuable metals from the solid material stacked on the heap. The simplest possible heap leach structure is presented in Figure 2. It shows a heap stacked on top of a liner with protective layers (under-liner and top-liner) both
below and on top of the fragile liner material (typically plastic such as high density polyethylene, HDPE). In addition, the top-liner consists of drainage gravel and possible other drainage systems such as piping to ensure there is good flow capacity for the solution below the heap itself. A solution distribution system is necessary to deliver the lixiviant to the heap and is generally situated on top of the heap or in the top part of the heap. A solution collection system is needed to collect the solution exiting the heap with the valuable metals in it. Figure 2 does not include a metals recovery plant, which is required as the next stage for removing the valuable metals from the solution exiting the heap.

The technology started to gain ground from the 1950s with early uranium heap leach operations. Today it is used mainly in two applications: cyanide leaching of gold and acidic leaching of copper, both oxidic and sulfidic (Petersen, 2016).

![Solution distribution system](image)

**Figure 2. Simplified heap leach structure.**

There are two general types of irrigation systems utilized in heap leaching: drip irrigation and sprinkler irrigation. In drip irrigation, plastic irrigation pipelines are installed on top of the heap at regular intervals, typically from tens of centimeters up to one-meter distance apart. In sprinkler irrigation, a set of water sprinklers are installed on top of the heap that spray the water in a circular area around them. Petersen and Dixon (2007a) mention a typical heap leaching irrigation rate of 4 to 18 L/m²h while Petersen (2016) gives 5 to 20 L/m²h and Kappes, 2002, gives 7 to 20 L/m²h for the crushed ore irrigation rate. At Terrafame, the design is 5 L/m²h and there are conditions requiring +/-50% alteration to this. The reasons for having a large irrigation rate would be to feed the reactants to the heap faster and to try to maximize contact of the irrigation solution with the particles. Fagan-Endres et al. (2015) studied the change in distribution of liquid in the heap when the flow rate was increased. They came to the conclusion that doubling the flow rate, from 10 to 20 or 20 to 40 L/m²h, had only marginal effects on improving the contact of solution to particles within the heap, but rather the increase in flow increased macro-pore channeling through the heap.

Solution flow inside the heap occurs by two mechanisms: downward flow along the surfaces of the particles, influenced by gravitation, and flows enabled by capillary forces, that further spread the solution laterally in the heap. The solution flows are illustrated in Figure 3. At the top of Figure 3, two arrows indicate two irrigation entry points (droplet points of irrigation) on top of the heap. The flow from both of them moves downwards (by gravity) and laterally by capillary forces. The downward flow is more profound and generates paths
of preferred flow. This creates zones within the heap that are flushed more rapidly and zones that depend on diffusion to move the dissolved metals out of the heap or reagents across the heap. This phenomenon is well described in Petersen and Dixon (2007b) and Petersen (2016) further confirmed small-scale heterogeneous flow inside a column with the help of positron emission topography scanning.

![Diagram of solution flows in a leach heap.](image)

**Figure 3. An illustration of solution flows in a leach heap.**

The dual nature of flow through the heap would suggest that, should there be a change in the irrigation solution, the (potential) impact of this change would be seen in two phases: quickly through the preferred flow paths and more slowly with diffusion changes through the diffusion routes.

Irrigation rate certainly has an optimal range, where there is enough solution to allow flow through the heap and through micro-pores within the heap, while not saturating the heap or causing erosion and ultimately channels in the heap. This rate is heap-specific and dependent on the ore size distribution, the extent of agglomeration, and the mineralogy of the ore.

One key factor in choosing the irrigation system is the water balance of the entire system. Sprinkler irrigation will lead to higher losses from evaporation (2 to 5 percent) compared to drip irrigation (below 1 to 4 percent), when a 10 L/m²h irrigation rate is applied (Kappes, 2002). As most heap leach operations are located in arid climates (Ghorbani et al., 2015), this has led to operations moving toward drip irrigation systems during the last twenty years, to preserve water (Bleiwis, 2012). It is to be noted that while the matter of evaporation losses has been discussed and is a major contributor to water consumption in heap leaching, the overall consumption of water in concentrator processes is much larger, at 0.79 m³ freshwater per tonne of mineral, than in heap leaching, where it was reported to be 0.13 m³ freshwater per tonne of mineral (Brantes and Olivares, 2008).

Heap sizes vary greatly. Typical heights are reported to be from 6 to 10 meters (Petersen, 2016) and 4 to 10 meters (Ghorbani et al., 2015). These figures refer to the lift height of a heap. Mostly the lift height is determined by the maximum height allowed that does not create permeability challenges, as the higher the
lift, the less cost is bound per tonne. At times the lift height is limited by the risk of slope stability (Fallahar et al., 2015). Heap lift designs can be divided into three types: on-off (or dynamic) heap leach, multi-lift pad, and valley fill. In the on-off (or dynamic) heap leach design, the same solution collection system is utilized several times, and the leached heap is removed from the area, followed by a new ore heap being stacked in its place. This is illustrated in Figure 4. There the light heap represents the newest and the dark heap the oldest. Stacking of the new heap and removal of the old heap are both moving towards the north in Figure 4, in the western heap pad. Once the western heap stacking ends in the north, the old heap will have been removed; the removal moves to the eastern heap pad and the removal direction changes towards the south. The heap is continuously being removed and a new heap stacked. The solution collection system is below the heaps in Figure 4 (not shown).

![Figure 4. Simplified on-off (dynamic) heap leach construction scheme, I presenting the western heap stacking with (i) removal and (ii) construction of heap and II the eastern heap.](image)

A multi-lift heap is, as the name implies, stacked in multiple layers. This is illustrated in Figure 5. The principle is to minimize the construction of the solution collection area by constructing a new layer on top of the old one. The irrigation system has to be reconstructed on top of the highest layer with every lift. The benefit of minimized capital expenditure on the solution collection system is challenged by two effects: 1) the permeability of the lower layers could deteriorate as more and more pressure is placed on top of them, which could affect the permeability of the entire heap and 2) every lift is smaller than the one it is constructed on top of, which leads to more frequent heap-to-heap movements with the stacking equipment as the smaller top layers are constructed faster than the bottom layers.
Valley fills are multi-lift heaps where the orebody resides in a mountain/hillside and, rather than preparing a level ground for the heap to be stacked on, a natural valley is covered with the solution collection system and the heap is stacked to fill it. A simple valley fill concept is illustrated in Figure 6. The heap is constructed to fill the valley space (at least partially). This is in fact a special case of a multi-lift heap. Here, the challenge besides permeability is the stability of the heap that is constructed on the slopes.

Methods of stacking a heap include truck stacking and conveyor stacking (Kappes, 2002). This is a matter of definition: an argument could be made that truck stacking forms a dump and conveyor stacking forms a heap. When trucks are used, significant compaction is caused due to the truck roads on top of the heap. These would affect the permeability and are typically treated by cultivating or “rippling” the surface (Kappes, 2002). Conveyor stacker types include radial stackers and horizontal stackers. A radial stacker is at the end of a chain of grasshopper conveyors, mobile conveyor units that move lightly on top of the heap and can be moved flexibly to enable covering the heap area. However, they
are limited by capacity and larger capacity stacking is done with horizontal conveyor stackers, where several track units share the load of the conveyor (Kappes, 2002). These can make several hundreds of meters of heap width at the same time. A conveyor stacker can be utilized to make retreat stacking or forward stacking. Retreat stacking means that the conveyor moves on top of the old layer, stacking the new heap behind it and moving away from the new heap. Forward stacking refers to the method of the conveyor operating from the top of the new heap, feeding material in the slope to create new ground for itself to move onwards. Naturally, retreat stacking causes the least disturbance to the (agglomerated) ore as the drop height is the shortest. Forward stacking is not limited by the height of the stacker but rather by the height of the bench made for it to start the new heap, while retreat stacking is directly limited by the height of the stacking conveyor. The different types of stacking are illustrated in Figure 7.

![Figure 7. Simplified illustrations of the different types of stacking.](image)

### 2.2.1 Heap aeration

Leaching sulfide minerals adds complexity to the heap leaching process. As Scheffel et al. (2016) noted, there is very likely a limit concentration of sulfides needing oxidation in the ore that sets up a requirement for forced oxidation of the heap. Petersen (2016) presented forced aeration applied from the bottom of the heap flowing upwards within the heap. With a well working drainage structure below the heap, the material is not flooded, i.e., void space is available. If air is fed into this layer, it would travel through the drainage void space and out from the heap sides. Instead, air should be fed inside the heap. Shaofeng et al. (2019) studied the effect of forced aeration rates on fracture generation inside the heap. They concluded that the more air was added the more the porosity was increased and postulated that this could improve leaching rates even in heap leach operations not requiring oxidation.

Dixon (2000) modeled air flow through a heap system and suggested another use for aeration: better control of temperature inside the heap. It was postulated that with cold irrigation solution coming from the top of the heap (and heat losses occurring on the top) and solution heating with heat of reaction towards
the bottom of the heap, there is a reverse effect of air heating on the bottom. When the air flowing up from the bottom of the heap comes into contact with the heated solution, part of the solution evaporates, saturating the gas phase with moisture that is then released on the way up when it comes into contact with the cooler solution, in effect transferring heat up the heap. Dixon suggested that, as solutions draw heat downwards and air upwards, there is a possibility to optimize the ratio of air to solution flow in order to optimize the internal heap temperature. In this study it was assumed that the gas in the heap is always saturated with water and that the thermal balance is in equilibrium at all heights within the heap.

2.3 Sulfide minerals

Copper sulfide heap leaching has proved to be a significant method of producing copper. Watling (2006) listed operations that fully and partially produce copper from sulfidic ores via a hydrometallurgical route. She noted that one fifth of the world’s copper was produced using the hydrometallurgical route. She further listed the sulfidic leaching operations that account for 5-7% of the world’s copper production. The sulfidic heap leaches came into production to a larger extent in the 1990s. The main mineral of value in sulfidic heap leaches is chalcocite, Cu₂S. Chalcocite leaching occurs in two stages. There are somewhat contradictory results and statements on the exact stage mechanisms: for example, Petersen and Dixon (2003) give Cu₁.₅S as the intermediate product, Miki et al. (2011) give it as a range of sulfides from Cu₁.₅S to Cu₂S, Niu et al. (2015) give another range of Cu₁.₅S to Cu₂S, and Hashemzadeh et al. (2019) proposed that the intermediate product depends on the conditions. Generally, it is accepted that the first stage in the leaching of Cu₂S is fast, whereas the second stage, i.e., leaching of the remaining copper in the mineral, is slow. In fact, Petersen and Dixon (2003) point out that the first stage reaction is so fast that it consumes all the ferric iron generated in the process and while this stage is occurring, the redox potential stays near the rest potential of chalcocite.

While chalcocite heap leaching is an established production method with tens of operations around the world, the Terrafame type of ore is unique in heap leaching. The vast majority of the earlier work on the Terrafame ore is based on laboratory scale testing. Considering the 2 500 000 tonnes of nickel produced in 2020 (Henckens and Worrrell, 2020), the Terrafame operation represents approx. 1% of the world’s nickel production (approx. 30 000 tonnes). The aim of this Thesis was to study a nickel black-schist ore and provide information for future prospects if a similar deposit would come into focus. It would be valuable then to understand the phenomenon taking place in the heap – the luxury that chalcocite operations have of the earlier work today.

Riekkola-Vanhanen and Heimala (1993) presented the sequence of sulfide mineral electrode potentials in the Terrafame ore. They suggested the order as pyrrhotite < sphalerite < Ni sulfides < chalcopyrite < pyrite. In contrast, Ahonen (1993) gave the rate of sulfide bioleaching in decreasing order from pyrrhotite
> sphalerite > pyrite > pentlandite > chalcopryite. Typically, the sulfide leaching reaction is presented in the form of reaction (1). In reaction (1), “Me” refers to a +2-valency metal cation. For example, reaction (1) can be modified for the sphalerite leaching reaction by replacing “Me” with Zn.

\[ MeS + H_2SO_4 + 0.5O_2(g) \rightarrow MeSO_4(aq) + H_2O + S \]  \hspace{1cm} (1)

Monhemius (1977) warned that it is vital to understand the sulfide precipitation diagrams in sulfide leaching conditions because, if non-oxidizing conditions occur, there may be re-precipitation of secondary sulfides and in particular, copper may re-precipitate back as covellite, CuS. In other words, he was raising the awareness that a combination of reactions (2) and (3) can take place. Maley et al. (2009) noted that this phenomenon occurred at a high pH (>2.3) rather than a low pH. A possible explanation for this could be higher ferric iron solubility at lower pH values: ferric would react with H₂S in preference to Cu, Co, Ni, and Zn.

\[ MeS + H_2SO_4 \rightarrow MeSO_4(aq) + H_2S(g) \]  \hspace{1cm} (2)

\[ H_2S + CuSO_4(aq) \rightarrow H_2SO_4(aq) + CuS(s) \]  \hspace{1cm} (3)

### 2.3.1 Pyrrhotite leaching in heap

Wang (2007) noted that pyrrhotites in nature always occur with other sulfide minerals, including pentlandite, pyrite, and chalcopyrite, and that pyrrhotite is, typically today, an unwanted waste component of the mineral and is separated from the valuable sulfides via flotation. To the best of the author's knowledge, there is no and has never been another pyrrhotite heap leach operation in the world apart from Terrafame. Therefore, it can be assumed that heap leaching of pyrrhotite is quite novel. Leaching of pyrrhotite is not novel, however. Ahonen (1993) noted that pyrrhotite has a low activation energy (25 kJ/mol) in comparison to pyrite (95.5 kJ/mol), for example. He also continued to state that, whereas in pyrite leaching all of the disulfide in the mineral oxidizes to sulfate during leaching, pyrrhotite reacts in several steps, starting with non-oxidative sulfide generation, similarly to reaction (2), followed by elemental sulfur generation, similarly to reaction (1), and finally by oxidation of the formed sulfur to sulfate. It should be noted that Bouffard et al. (2006) disagreed with this, measuring 40% of elemental sulfur generation during pyrite oxidation while the activation energy was 83 kJ/mol. He further confirmed the fears of Monhemius (1977) that copper can precipitate easily in the presence of a mineral reacting in a non-oxidative manner, meaning that secondary covellite can be found to precipitate on the pyrrhotite surface. Figure 8 summarizes the findings in the stages of pyrrhotite leaching. Publications II and III continue from this, suggesting that it is not only copper that re-precipitates on the pyrrhotite surface. Further,
the possibility to avoid stage 2 is discussed and, on the other hand, also the resulting phenomenon of stage 2 is discussed: the growth of the heap volume during the leaching of pyrrhotite.

Ahonen (1993), Mycroft et al. (1995), Mikhlin et al. (2002), Halinen (2005), and Wang (2007) all stated that iron precipitation occurs during pyrrhotite leaching. Goethite and jarosites have been detected. Ahonen (1993) and Halinen (2005) expressed concern about iron precipitates causing permeability problems (both with solution and with gas) during heap leaching.

![Figure 8. Stages of pyrrhotite leaching.](image)

### 2.3.2 Chalcopyrite leaching

As more than two thirds of the world’s copper reserves are found in chalcopyrite (Córdoba et al., 2008), there have been plenty of studies on chalcopyrite leaching. Two dominating reaction paths are generally suggested: reactions to form elemental sulfur or sulfate. Ruiz et al. (2011) noted that the former was common in (atmospheric) sulfate media, also generally resulting in poor recoveries related to the passivation phenomenon. However, the scientific community is not in agreement on the nature of this passivation layer: various sulfide, elemental sulfur, and iron precipitates have been proposed (Li et al., 2013). For example, Khoshkhou et al. (2014) concluded that the layer is made of several components with elemental sulfur and iron oxyhydroxides. A method that would oxidize sulfur further to sulfate (sulfuric acid) would prevent the formation of both of them. Several atmospheric methods have been proposed to tackle passivation: mechanical activation (Li et al., 2017 and Li et al., 2019), utilization of chlorides (Ruiz et al., 2011), utilization of iodine (Winarko et al., 2020), galvanic interaction with pyrite (Nazari et al., 2012), galvanic interaction with carbon black (Nakazawa, 2018), microorganisms (Noguchi and Okibe, 2020), and a combination of galvanic and microbiological methods (Esmailbagi et al., 2018). Dreisinger (2006) noted that one key challenge in the commercialization of these processes is the uniqueness of concentrates and operations and their particular needs and opportunities. For example, if chalcopyrite is leached to form sulfate completely, excess acid could be formed, and this could lead to a neutral-
ization requirement. Excessive neutralization costs could hinder the overall process from being economic. A nearby process that utilizes the generated extra acid would be practical but is not always available.

Regarding heap leaching of chalcopyrite, there are (at least) two routes under investigation to work around the passivation phenomenon: the utilization of chlorides in addition to generally sulfate media, which is gaining interest in Chile (Velásquez-Yévenes et al., 2018), and the utilization of bacterial oxidation (Petersen and Dixon, 2002 and Mokmeli, 2020). Chlorides are suggested to enhance leaching kinetics by 1) allowing the usage of cupric ion as an oxidant and 2) making the morphology of the elemental sulfur layer more porous. Bacteria are suggested to oxidize elemental sulfur, thus reducing the passivation layer from the top of partially leached chalcopyrite. One of the candidates closest to introducing heap leaching of chalcopyrite, the Sarcheshmeh mine in Iran, has run pilots several times during the new millennium and is still today on the verge of being economically viable (Mokmeli, 2020). Despite chalcopyrite being a widely available mineral, motivating the copper industry to develop methods for its processing and heap leaching being one potential route for processing low-grade ores that are not economic or suitable for the conventional flotation- pyrometallurgy process remains a challenge. Chalcopyrite is more noble than many other sulfides and thereby starts to leach after them. The passivation phenomenon of chalcopyrite has not been solved in heap leaching but there are promising rising technologies such as using thiocarbonyl to reduce the passivation layer effect, which is at the point of evaluation of production scale operation (Rebolledo et al., 2019).

### 2.4 Nickel and zinc production

Nickel is essential for modern society mainly for its use in stainless steel. The production of nickel was below 10,000 metric tons per annum before 1900, then reached 100,000 metric tons per annum by the 1930s, one million metric tons per annum by the 1990s and today, in 2020, is close to 2,500,000 metric tons per annum (Henckens and Worrell, 2020). Mudd and Jowitt (2014) estimated the global nickel resources to be 118 million metric tons in sulfides and 178 million metric tons in laterites, totaling 296 million metric tons in the world. Henckens and Worrell (2020) note that the current consumption per capita in the world is on average roughly one fourth of the level in developed countries. This coupled with the fact the world population is estimated to reach 10 billion people, global nickel consumption would rise to 13.5 million metric tons per annum. One of the drivers of the increase in nickel consumption is its use in the Li-ion batteries used in electrical vehicles (Nickel Institute, 2018). Oversimplifying these numbers, there would be only 20–30 years of nickel left in the world. Henckens and Worrell (2020) suggest that, to ensure the availability of nickel for the future, the recycling rate must increase from the current 60% to much higher percentages.

Like nickel, zinc is essential for modern society. It is predominantly used today as a corrosion protection for steel. Sverdrup et al. (2019) estimate zinc resources
at 2676 million tons (not specifying whether metric or archaic tons), current production as 15 million tons per annum, which will peak at 16 million tons per annum during the 2020s. They expect the recycling of zinc to supersede mine production as the dominant source of zinc in the 2040s. Currently, the ratio is 80:20 for mining, and the ratio is forecast to be 2:1 for recycling by the end of the century. Further, they note that nearly all the future zinc ore will be low in grade. One purpose of this thesis is to increase the knowledge and understanding of Terrafame heap leaching, to enable this specific and unique industrial operation to contribute its best for the global demand for zinc as well as for nickel.

### 2.5 Water balance

There are a limited number of articles published on the water balances of heap leach operations. Ghorbani et al. (2015) noted briefly that the majority of heap leach operations are in arid areas of the world. Kauppila et al. (2011) presented a general water balance at a mining operation. There, they described precipitation (rainfall) at the mine, the waste rock areas, and the tailings ponds. The other inlet waters were fresh water for process use and tap water for personnel use. Waters exited the balance via the wastewater treatment process and were discharged into a nearby waterbody. As evaporation was not noted by Kauppila et al. (2011), the precipitation mentioned must refer to net precipitation (rainfall – evaporation).

Brantes and Olivares (2008) presented freshwater water consumption figures in the Chilean mining sector. They noted that the average freshwater consumption decreased for both concentrator plants and heap leach operations. The average freshwater consumption fell from 1.1 m³ to 0.79 m³ per tonne of mineral from 2000 to 2006 in concentrator plants, while in the same time period the decrease in heap leach operations was from 0.3 to 0.13 m³ per tonne of mineral.

Norgate and Lovel (2006) listed the use of water in several different metal production processes with the focus on the Australian mining industry. They noted consumptions of 0.7 m³/tonne of ore in copper concentrator plants followed by a pyro-hydrometallurgical smelting process and 0.5 m³/tonne of ore in heap leaching followed by a solvent extraction – electrowinning process for metal.

Publication IV, for comparison, presented freshwater use of 1 Mm³ per annum for 18 M tonnes per annum of ore mined. This means a freshwater consumption of 0.06 Mm³ per tonne of ore, considerably less than listed in the previous studies. There is a difference, however, to the studies listed, which is the reason for Publication IV in the first place: little has been published on a heap leach operation in a wet area. As Ghorbani et al. (2015) remarked, most heap leach operations lie in arid areas and thereby face the challenge of getting freshwater for processing rather than the discharge of waters. This is also a major difference to what Kauppila et al. (2011) presented as a general mine water balance: in heap leaching the process area is much larger in area than in for example concentrator processes. Therefore, the effect of rain on the process itself is far larger than
in other hydrometallurgical processes. There is another aspect to this increased area: the solution in the heap is richer in metals than the waters at tailings ponds or in the waste rock area. The higher the concentration of metals in water, the higher the cost and difficulty of cleaning them – and rainfall increases the amount of solution in the heap leach circuit, creating a (potential) need for removal of solution from the circuit. The water discharge requirement for the Terrafame operation mentioned in Kauppila et al. (2011) was negligible. This was based on information dating from 2009, when the mining operation (under the previous operator) had just started one year earlier. Eight years later, in an Environmental Impact Assessment, the reported water discharged from the site between the years 2013 to 2016 ranged from 4.8 to 9.6 Mm³ per annum (Terrafame, 2017).

2.6 Global warming

The Intergovernmental Panel on Climate Change (IPCC) used scenarios to link the greenhouse gas emissions that are caused by human behavior with global warming (Core Writing Team, 2014). These scenarios were labeled Representative Concentration Pathways (RCPs) and have a value of Watts per square meter – the radiative force that the greenhouse gases will have by the year 2100. For example, RCP4.5 scenario has 4.5 Watts per square meter radiative force by the year 2100 which corresponds to 2.5 °C global mean temperature rise from calendar year 1870 to 2100. They are the trajectories of CO₂-equivalent greenhouse gas concentrations from today until 2100, but they are numbered not by their concentration but their warming effect. The Core Writing Team (2014) used four scenarios: RCP2.6, RCP4.5, RCP6, and RCP8.5. The annual emission of carbon dioxide alone in RCP8.5 grows from the current 30 Gt CO₂/a to 110 Gt CO₂/a by the year 2100, with the effect of warming the Earth’s atmosphere by approximately 4.5 °C in comparison to the average temperature in the 1870s. In carbon dioxide equivalent concentrations, meaning the total effect of all greenhouse gases represented as a concentration of carbon dioxide that would have the same effect, scenario RCP8.5 more than doubles the amount from today’s value. The scenario parameters are shown in Table 2.

Table 2. Parameters and outcomes of the RCP scenarios (Core Writing Team, 2014)

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Gt CO₂/a by 2100</th>
<th>CO₂-equivalent concentrations by 2100 in ppm</th>
<th>Cumulative Gt CO₂ 1870 to 2100</th>
<th>Global mean surface temperature rise, °C 1870 to 2100</th>
<th>Global mean sea level rise 1995 to 2100, m</th>
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<tbody>
<tr>
<td>Current situation</td>
<td>30 (today)</td>
<td>455 (Rogner et al., 2007)</td>
<td>1800 (1970 to today)</td>
<td>0.7 (1870 to today)</td>
<td>+0.04 (1995 to today)</td>
</tr>
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<td>RCP8.5</td>
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<td>7800</td>
<td>4.5</td>
<td>0.65</td>
</tr>
</tbody>
</table>
The Terrafame orebody has the potential to last until the 2080s (Terrafame, 2020). This means that the effects of global warming may in future alter the weather experienced at the site and with that, the water balance will be altered. Publication IV touched on this topic to observe what the potential effects would be with the current mine set-up, utilizing scenarios RCP4.5 and RCP 8.5.
3. Experimental methods

The theme in this thesis and the four associated publications was to perform the test work and observations on full-scale heaps rather than in a laboratory.

Publication I had two heap sections, each 132 meters long (end-to-end), 350 meters wide (end-to-end), and 8.5 meters high, with 634 000 and 666 000 tonnes of ore, respectively. The ore was stacked with approx. 3.5%-w moisture. The bottom ground angle below the heap sections was approx. 3 degrees. Drainage below the heaps was built with 110 mm outer diameter corrugated drainage pipes every five meters below the heap, drawing water in a downhill direction. The drainage also consisted of 20 cm of coarse gravel (12-32 mm fraction) on top of the drainage pipes, covering all the area under the heap sections. The heap sections were aerated with air pipes in two layers, one 4.5 m from the bottom of the heap and the other one from 1-1.5 m from the bottom of the heap. The air lines had an outer diameter of 110 mm and 5 mm diameter holes every two meters inside the heap sections. The designed aeration level was approx. 0.06 Nm$^3$ air / tonne ore / hour. Irrigation was delivered to the top of the heap sections with section 1 having hoses and drippers at 60 cm intervals and section 2 having hoses and drippers at 30 cm intervals. The irrigation rate was designed to be five liters per square meter per hour during summer and seven liters per square meter per hour during winter. Section 1 of the ore had 7.3%-w pyrrhotite and section 2 17.3%-w pyrrhotite. Pyrite on the other hand was 12.7%-w in section 1 and 3.1%-w in section 2. Pentlandite and sphalerite were similar in both sections, between 0.6% and 7%-w. Alabandite was from 0.4% to 0.5%-w in both sections and chalcopyrite 0.1%-w. The temperatures of irrigation and outlet solution were measured for an approximation of the heat generation within the heap and a Distributed Temperature Sensing (DTS) cable was drawn inside the heap, through both of the sections. This technology has been utilized to measure water, oil, and gas flows in locations where temperature measurement along a distance is of interest (dams, wells, drill holes, etc.). It is based on sending pulses of light into a cable made of optical fiber installed for the distance where temperature measurement is desired. There is a component of backscattered light which changes with temperature, called anti-Stokes Raman backscatter. The scatter can be measured at the point where the pulse of light was sent and a near continuous temperature read from the optical cable (Nuñez-Lopez et al., 2014). The method can achieve a one-meter interval temperature measurement with tens of kilometers of cable length and an accuracy of one Celsius degree of temperature (Ukil et al., 2012). In section 1, a DTS cable was installed above the
lower air line, going across the width of the heap, at an elevation of approximately 2.5 m from the bottom of the heap. In section 2, the DTS cable was installed in three layers: at approximately to 6 m, 4 m, and 2 m from the bottom of the heap – similarly going across the width of the heap. The cables tracked the temperature within the heap every half meter.

Publication II analyzed a similar sized heap section that had 560 000 tonnes of ore. It was 132 m (end-to-end) long, 330 m wide (top-to-top), and 8.5 m high. Fourteen air lines were installed in it across the width of the heap at regular intervals at a height of 4.5 m from the bottom of the heap with, similarly, 32 air lines at a height of 1.5 m from the bottom of heap. Irrigation cells of approximately 40 m in length and 330 m in width were installed on the top of the heap, three cells altogether. The outlet solution was monitored via analysis of the solution coming to two sampling wells, by analyzing the solution with a Thermo Scientific iCAP 6500 Radial View ICP-OES spectrometer. An illustration of the test set-up can be seen in Figure 9. The change in solution concentration across the heap was calculated with a fourteen-day average of outlet solution concentrations minus the week before fourteen-day average concentrations of irrigation solution. The major elements in the ore in the heap in percentage by weight were: Si 17.2, Fe 12.7, S 12.2, Al 4.9, Mg 2, Ca 1.5 and valuable metals Zn 0.46, Ni 0.26, and Cu 0.15, also in %-w.

![Figure 9. Illustration of the heap section analyzed in Publication II, with red dots showing the air lines, green lines the irrigation coils, and sampling wells shown at the bottom (Publication II).](image)

In Publication III, the sample size was increased to Part 1: 3 689 301 and Part 2: 3 546 259 tonnes of ore. The length of Part 1 was 613 m long and Part 2 was 589 m long. Both were 350 m wide (end-to-end) and 9.5 m high. Pipelines for air were installed in both heaps across the 350 m width: in Part 1 mainly to two elevations: 224 lower lines and 208 upper lines. Also, 39 test installations of middle air lines were done in preparation for the Part 2 installations. Part 2 had air lines in three elevations: 218 lower air lines, 203 middle air lines, and 187 upper air lines. The lower air lines for both parts were at one meter from the bottom of the heap, the middle air lines at 3 m, and the upper air lines at 6 m

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when all were installed and at 4.5 m in Part 1, where the tested middle air lines were not installed. Figure 10 presents the installed air line configuration. Part 1 was installed with a low pressure air blowing capacity of 0.05 Nm³ of air per metric ton of ore per hour, all delivered from the uphill side of the heap, whereas Part 2 had approximately 60% extra air, the extra being delivered from the opposite side of the heap and to the middle air lines. Part 1 had four blowers, numbered 1 to 4, and Part 2 five blowers, numbered 5 to 8 and 10. The last blower was numbered 10 to distinguish the different side of the blower (the others blowing east-to-west but number 10 blowing west-to-east).

![Diagram showing air line configuration](image)

**Figure 10.** Air line configuration in Publication III with Part 1 below and Part 2 above, east side on the left and west on the right, with the red dotted lines showing the east-to-west aeration lines, dotted green line showing the west-to-east aeration lines, and the blue circles showing the aeration fans (Publication III).

Finally, Publication IV analyzed the water balance at the operation and ultimately the sample size by heaps that reached close to 100 000 000 tonnes of ore. All the tested and analyzed heaps were part of the productional heaps at Terrafame. The study utilized the actual water balance at the mine site from the calendar years 2017 and 2018. This data was used to first calculate the limits of the water balance with maximum rainfall, 1 000 mm/a, and minimum evaporation, 230 mm/a, and then with minimum rainfall, 500 mm/a, and maximum evaporation, 355 mm/a (FEI, 2019). Next, a set of scenarios were formed to see how the water balance changed in a case where the orebody and similar process would be located in arid conditions with 1.7 mm/a rain (INE, 2017); how the water balance would change in the case of no heat formation from the leaching process, and with two possible climate change scenarios to see how the climate change scenarios would change the water balance at the operation. Representative concentration pathway (RCP) scenarios of 4.5 and 8.5 were selected, signifying the doubling and tripling of CO₂ emissions in the world by the turn of the next century in comparison to the era before the industrial revolution (Rusteenoja, 2013). The catchment area for rainfall was 580 hectares in the Pregnant Leach Solution (PLS) area and 1330 ha in 2018 in the water management area. Rainfall was measured every day at the site using a rainwater container. Ground evaporation was monitored every day from a Finnish Environmental Institute weather observation station (FEI 2019) located nearby. Extra evapo-
ration caused by the elevated temperature of the heap was tracked as the balance figure of the PLS balance, i.e., a suitable value was used for it to explain the unaccounted loss of PLS from the system. Discharge of waters and transfer of waters between the PLS circuit and water circuit were measured using flow meters. The inclusion of water from the metal extraction process connected to the heap leach circuit was also measured using flow meters. Assumptions were made of an increase in moisture in the new ore from 0.5 to 1 % by weight in ore to 10 % by weight in heap in the PLS system.

Publication I tested the usage of the DTS cable for the first time in a heap leach operation, to determine the local variation in temperature inside the heaps during the starting period of heap leaching. We also utilized flow meter information about the solutions and air and solution temperatures to calculate how much energy was transferred by the reaction to the solution and by the air amount and reaction enthalpies to estimate the oxygen efficiency for heating the solution. Publication II utilized flow meter information of solution and air with ICP-OES measurements of dissolved metal concentrations, focusing on Ni, Mn, Fe, and Zn. Publication III used the same methods as in Publications I and II but without DTS cabling. Here, the focus of metal concentrations was Ni, Mn, Fe, Zn, Al, Na, Mg, Cu, Co, and Cd (ICP-OES). Publication IV used flow meter information for the actual balances and combined this with the available information on the local climate change effects to derive a water balance for the system in potential future scenarios.
4. Results and discussion

The entire thesis and the results gained were built on using very large-scale test conditions: parts of the production size heaps at the Terrafame operation. This is exceptional in a scientific context as normally the process is studied mostly before the mining operation has started and then the scale is from bottle-roll tests of some grams to column tests of some kilograms; perhaps at best a pilot test run is held. When the mine is already in operation, the results are not published but kept within the company. As a technology field, heap leaching has the feature of not having much sellable technology such as reactors and their accompanying gear. This naturally leads to the fact that the technology of heap leach aeration is not as established as for example in autoclave design. Aerated heap leaches are also a rarity among all the heap leaches in the world. Hence, the results of the current work addressed the topics of the reaction order of minerals, acid consumption/formation, volumetric changes in the heap, the impact of aeration, and the water balance, under the pre-mentioned unique conditions.

4.1 Order of leaching reactions within heap leaching operation

Objective a of this thesis was to understand the reaction mechanism and the order of the reactions of the minerals within the ore. With this, the aim was to be able to classify better the quality of the heap performance. This objective was especially addressed in Publications II and III. Publication II focused on sulfide minerals and the metals associated with them. It demonstrated clearly how alabandite, MnS, is the fastest sulfide mineral to react, followed by pyrrhotite. Figure 11 shows how manganese extraction starts first (apparent from the first days of sampling) and the quickest, followed by iron. Manganese displayed similar behavior, as was observed in Publication III, during the testing of different air volumetric feed rates – manganese started to leach as soon as the process started, as presented in Figure 12. Manganese leached quickly in both areas without extra air (Wells 1-9 in Figure 12) and with extra air (Wells 10-18 in Figure 12).
Figure 11. Manganese and iron cumulative extraction as a function of irrigation days (modified according to Publication II).

Figure 12. Metric tons of manganese leached by operation time in different tested areas (modified according to Publication III).

As manganese was the first metal cation to come out from the Terrafame heaps, it was the first to indicate how the heap behaved. In other words: with increased insight, one could interpret the latter leaching behavior of nickel based on the early behavior of manganese. This idea is novel, to the best of the author’s knowledge, and can help in developing the understanding of the process and forecasting results. As nickel leaching takes a long time to start (70 to 120 days as described in Publications II and III) and manganese leaching starts significantly sooner (0 to 40 days), there is the potential to understand future nickel recoveries from one to three months in advance, through further studies of manganese and nickel leaching in multiple heaps.

Furthermore, Publication II demonstrated that, during the leaching of these minerals, re-precipitation of nickel, copper, and zinc occurs, similarly as shown for copper in reactions (2) and (3). Publication III further demonstrated that cobalt and cadmium re-precipitate. The possibility of copper (Monhemius, 1977; Maley et al., 2009) and zinc re-precipitation has been suggested before
(Ahonen and Tuovinen, 1995); however, the re-precipitation of nickel, cadmium, and cobalt can be considered as novel findings of the current study. Figure 13a shows how nickel and zinc displayed negative extraction values during the test work of Publication II. Figure 13b shows the same for copper; it is worth noting the longer negative behavior, continuing significantly further than for nickel and zinc. This implies reducing effects in the heap, most likely associated with reducing sulfides such as pyrrhotite and alabandite, that weaken in their reductive strength over time as they are consumed by oxidative leaching. In addition, the nobility of copper sulfide is higher than that for nickel and zinc sulfides, with copper sulfide precipitating more easily and being more difficult to leach. At first, they are strong enough to re-precipitate several valuable—but less noble—metals and later mainly only copper, which is the most noble of the metals to be recovered. This agrees with Monhemius (1977), who suggested that as the sulfide ion amounts decrease, only the most noble sulfides precipitate from solution, copper being not only one of the most noble dissolving metals, but also one of the most noble of the sulfide minerals.

![Figure 13. a) Nickel and zinc and b) copper cumulative extraction curve (modified according to Publication II).](image)

The same conclusion was reached in Publication III for nickel, zinc, and copper in that they re-precipitated in the early days of heap leaching of the Terrafame ore. This is shown in Figures 14 a-c for nickel, zinc, and copper. In addition, Publication III showed that cobalt and cadmium experienced the same re-precipitation phenomenon (Figure 14 d and e).
Figure 14. a) nickel, b) zinc, c) copper, d) cobalt, and e) cadmium leaching as a function of operation days (modified according to Publication III).

It should be noted that the re-precipitation behavior of cobalt, copper and cadmium is similar—these curves are fairly uniform in comparison to nickel and zinc, which clearly start leaching during the observation period of 150 operational days (Publication III). This is fascinating in the sense that one would expect copper and cadmium to exhibit similar behavior, as Monhemius (1977) shows in the sulfide precipitation curves (cadmium sulfide follows copper in nobility). However, cobalt should be similar to nickel, according to the Monhemius (1977) curves of sulfide precipitation. Wang (2007) noted that the leaching rates of metal ions in pyrrhotite decreased from nickel > iron > copper. However, Publications II and III in the current thesis argue that, in the context of heap leaching, the order must be iron > nickel >> cobalt & copper.

4.1.1 Discussion on the reaction mechanism of valuable metal re-precipitation

It is postulated in Publication II, Publication III, and this thesis summary that the mechanism of valuable metal re-precipitation is an exchange reaction, a
combination of reactions (2) and (3) without, possibly, the need for intermediate H$_2$S generation. There are also other possibilities for this phenomenon: reaction via H$_2$S generation, as suggested by Monhemius (1977), or as co-precipitation of the valuable metals to a goethite or jarosite matrix (Dutrizac and Chen, 2004).

As stated in Publications II and III, iron precipitation occurs in the heaps along with acid generation in the early stage of leaching. In these conditions pyrrhotite reacts actively, and under these moderately oxidative leaching conditions elemental sulfur is not likely to react. Theoretically, this could allow the valuable metals to co-precipitate with the formed iron precipitates. Javed (2017) noted that amorphous iron precipitates especially have a tendency to draw valuable metals in them. This phenomenon cannot be completely neglected in the current study. However, it is suggested in Table 3 in Publication II that when the metal precipitation is at its strongest, almost all of the copper is precipitated, even though the inlet (irrigation) concentration is rather low (40-50 mg/L). At the same time half of the nickel and a quarter of the zinc are precipitated, leaving hundreds of milligrams per liter concentrations in the solution. This selectivity for copper suggests a mechanism other than co-precipitation into the jarosite matrix.

Intermediate H$_2$S generation, then again, would follow the order presented by Monhemius (1977), explaining well the precipitation of copper in negligible concentrations. However, the current study also found that zinc and nickel precipitated simultaneously, although zinc precipitation should be preferred during H$_2$S precipitation in the current conditions and nickel should start to precipitate only at very low zinc concentrations. Also, nickel precipitation in the heap even at pH values as low as 2.0 (Publication III, Table 5) is exceptional for H$_2$S precipitation. Therefore, the strongest hypothesis of the author related to the observed precipitation of valuable metals during heap leach operation is that it is an exchange reaction, i.e., a combination of reactions (2) and (3).

4.2 Heat generation in heap leach of the Terrafame ore

Publication I estimated for the first time, as a novel finding for this kind of operation, that air (oxygen) efficiency to heat the solution was between 10% and 14%. This was achieved by calculations of the reaction heat inside the heap, how much oxygen was required, and how much oxygen was fed. The amount of heat transferred to solution in Publication I test work is presented in Figure 15. The oxygen feed amount was 0.06 Nm$^3$/h/metric ton of ore on average and this was calculated in Publication I to form 70 W of heat / metric ton of ore if the oxygen reacted 100% in the heap.
Figure 15. Heating of solution W/metric ton as a function of irrigation days (modified according to Publication I).

It is to be noted that this calculation is indeed oxygen efficiency to heat the solution – it does not contain any other losses of temperature and therefore is lower than the actual overall oxygen efficiency. Dixon (2000) noted that a major portion of the transferred heat goes to moisturizing the air flow (heat of vaporization of water) and the heating of that moisture in the air. This heated air with increased moisture in it moves upwards in the heap and, under the Terrafame conditions, it is suggested to precipitate back in the partially heated zone, where the solution (and heap) temperature is lower. This results in an “evaporation cycle” inside the heap, which allows the gas flow to carry heat upwards but also a dominantly low ambient temperature and irrigation temperature to cool the gas flow subsequently. The phenomenon is illustrated in Figure 16. However, the author postulates that the exiting air temperature is close to the irrigation temperature.

Figure 16. Illustration of the internal temperature zones related to Publication I.
In the current study (Publication I), the exiting air temperature could not be measured. Therefore, its full effect on the thermal balance is an estimate. However, the range of the exiting air temperature is clear: it must be a value between the irrigation temperature and the maximum temperature in the heap. To explain this, the consideration of a 1 m² area of the heap will be used in the following calculation to demonstrate various potential scenarios in which the exiting temperature air can impact on the Terrafame heap operation thermal balance. In the calculation the following values are used: heap height = 8.5 m, bulk density 1.85 tonnes ore / m³, solution flow 5 L/m²/h (Publication I) or alternatively with 1 kg/L density and 5 kg/m²/h solution flow. An air flow of 0.06 Nm³/tonne ore/h with 1.28 kg/Nm³ air density can be calculated as an air flow of 1.2 kg/m²/h. The thermal properties listed in Table 3 were used. In addition, a heat capacity of 4.228 kJ/kg°C for water (Weingärtner et al., 2000) and 1.005 kJ/kg°C for air (Hilsenrath et al., 1955) were used. For the sake of these calculations, it is assumed that the air feed is dry – as the air drawn in during autumn/winter is close to 0 °C, this can be considered to be a close approximation. Table 4 summarizes the results of the calculations conducted. In addition, different components of the thermal balance as a function of exiting air temperature are illustrated in Figure 17.

Table 3. Thermal properties used in air and solution heating and evaporation estimation

<table>
<thead>
<tr>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water vapor kg / kg dry air</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>80</td>
</tr>
</tbody>
</table>
Table 4. Results for thermal balance calculations with varying exit air temperature (according to the system presented in Publication I)

<table>
<thead>
<tr>
<th>Air temperature on exit, °C</th>
<th>Heat to warm dry air 20 °C -&gt; ultimate, kJ/m²/h</th>
<th>kg water vapor/m²/h</th>
<th>Heat of evaporation kJ/m²/h</th>
<th>kg solution flow out/m²/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>-6.1</td>
<td>0.013</td>
<td>32.2</td>
<td>4.99</td>
</tr>
<tr>
<td>20</td>
<td>0.0</td>
<td>0.018</td>
<td>44.3</td>
<td>4.98</td>
</tr>
<tr>
<td>30</td>
<td>12.1</td>
<td>0.033</td>
<td>80.0</td>
<td>4.97</td>
</tr>
<tr>
<td>40</td>
<td>24.3</td>
<td>0.059</td>
<td>142.4</td>
<td>4.94</td>
</tr>
<tr>
<td>60</td>
<td>48.5</td>
<td>0.185</td>
<td>435.6</td>
<td>4.82</td>
</tr>
<tr>
<td>80</td>
<td>72.8</td>
<td>0.666</td>
<td>1536.2</td>
<td>4.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Air temperature on exit, °C</th>
<th>Heat to warm solution 15 -&gt; 40 °C, kJ/m²/h</th>
<th>Evaporation in % of solution flow</th>
<th>Heat to warm moisture in air 15 -&gt; ultimate, kJ/m²/h</th>
<th>Solution warming as % of total energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>527.1</td>
<td>0.26</td>
<td>0</td>
<td>95.3</td>
</tr>
<tr>
<td>20</td>
<td>526.6</td>
<td>0.36</td>
<td>0.4</td>
<td>92.2</td>
</tr>
<tr>
<td>30</td>
<td>525.0</td>
<td>0.66</td>
<td>2.1</td>
<td>84.8</td>
</tr>
<tr>
<td>40</td>
<td>522.2</td>
<td>1.18</td>
<td>6.3</td>
<td>75.1</td>
</tr>
<tr>
<td>60</td>
<td>509.0</td>
<td>3.70</td>
<td>35.2</td>
<td>49.5</td>
</tr>
<tr>
<td>80</td>
<td>458.2</td>
<td>13.31</td>
<td>182.9</td>
<td>20.4</td>
</tr>
</tbody>
</table>

Figure 17. Energy in kJ/m²/h heap transferred to solution and air, with moisturizing air to saturated humidity, as a function of exiting air temperature (according to the system presented in Publication I)

It can be seen in Figure 17 that if the exiting air temperature in the heap is 40 °C or below, over 75% of the heat is transferred to the solution. In such a case, the calculated oxygen efficiency based on heat transferred to the solution would represent at least 75% of the total heat generated. It is also shown in Figure 17 that with the exiting air temperature increasing up to 80 °C (saturated with water vapor), the energy associated with that air would be higher than the energy associated for the irrigation solution to warm up to a temperature of 40 °C. This suggests that either (i) the air flow would not be saturated with vapor in the heap, (ii) the air flow would not reach 80 °C temperature, or (iii) the air flow would leave the heap at a significantly higher temperature than the irrigation
solution temperature. In Publication I the gas-space temperature in the sampling wells (which were closed between sampling times) equals the exiting solution temperature of 40 °C. It should be noted that this gas space can be physically sensed as much warmer compared to the heap top, where air exits the heap. Furthermore, much more evident “steaming” behavior is visibly present in the open ponds (solution) than on top of the heaps. This all suggests that the exiting air temperature from the heap is well below 40 °C, concluding that (iii) is not probable. Measurements of the internal temperature showed 80 °C in the heap, indicating that (ii) is not probable. The author concludes therefore that (i) is the most probable explanation: the air does not reach saturation moisture content at 80 °C in the heap.

This evaporation can be further considered with Publication IV in mind. There, the annual evaporation caused by the high-temperature heaps and solution ponds (labeled “extra evaporation” in Publication IV) was experienced to be from 3 300 000 m³/a (2017) to 4 370 000 m³/a (2018). The average irrigation at Terrafame was 8000 (2017) and 9700 m³/h (2018) during the same years. Taking into account the 25 °C temperature decrease at the ponds (exit of heap solution back to irrigation), using 30 °C latent heat of 2429.6 kJ/kg (Weingärtner et al., 2000) and estimating that all the lost heat at the ponds leads to evaporation would mean 3 000 000 m³ evaporation with the 8000 m³/h flow (in 2017) and 3 700 000 m³ evaporation with the 9700 m³/h flow (in 2018). This accounts for 93% (in 2017) and 85% (in 2018) of the experienced evaporation, which means that the remaining content of approx. 250 000 m³ (2017) and 660 000 m³ (2018) would have evaporated at the heaps. This consequently represents 0.35% (2017) and 0.77% (2018) of irrigation, suggesting an exiting air temperature of 20 °C to 35 °C, as shown in Table 4. The calculations and observations above suggest that measuring the temperature change across the heap to the solution can be finally considered as a reasonable representation of the total heat generated in the actual heap operation, representing approx. 80-90% of the total heat generation.

The reaction heats calculated per reacted oxygen in Publication I are shown to differ from those calculated in Petersen and Dixon (2002). Petersen and Dixon (2002) observed that the reactions generated 100 kJ energy for every electron mol that reacts, and therefore the heat of reaction per reacted oxygen is the same for several different sulfides as well as for elemental sulfur. The enthalpy calculations have been redone here for the thesis. The enthalpy values used for the calculations are shown in Table 5. It is to be noted that the value used for pyrrhotite differs quite significantly from the one used in Publication I, as it would appear that the value used there was erroneous. The value used for alabandite also differs from the source used in Publication I.
Using these values, similar calculations were made to those by Petersen and Dixon (2002), and the results are shown in Table 6. Table 6 shows how the heat of reaction for pyrrhotite and alabandite per reacted oxygen differs from those of chalcopyrite, pyrite, and elemental sulfur.

**Table 6. Reaction enthalpies recalculated for pyrrhotite and alabandite and compared with Petersen and Dixon (2002)**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>DHF, kJ/mol in Petersen and Dixon (2002)</th>
<th>kJ/mol transferred</th>
<th>kJ/g O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₅S₈ + 3.5 O₂ + 7 H₂SO₄ → 7 FeSO₄ + 8 S + 7 H₂O</td>
<td>-1888</td>
<td>-16.9</td>
<td>-135</td>
</tr>
<tr>
<td>MnS + 0.5 O₂ + H₂SO₄ → MnSO₄ + S + H₂O</td>
<td>-292</td>
<td>-18.3</td>
<td>-146</td>
</tr>
<tr>
<td>FeSO₄ + 0.25 O₂ + H₂SO₄ → FeO₂(OH) + H₂SO₄</td>
<td>-41</td>
<td>-5.2</td>
<td>-41</td>
</tr>
<tr>
<td>CuFe₅S₈ + 1.25 O₂ + 2.5 H₂SO₄ → CuSO₄ + 0.5 Fe₅(SO₄)₂ + 2 S + 2.5 H₂O</td>
<td>-524</td>
<td>-508</td>
<td>-13.1</td>
</tr>
<tr>
<td>CuFe₂S₄ + 4.25 O₂ + 0.5 H₂SO₄ → CuSO₄ + 0.5 Fe₂(SO₄)₃ + 0.5 H₂O</td>
<td>-1771</td>
<td>-1755</td>
<td>-13.0</td>
</tr>
<tr>
<td>FeS₂ + 1.25 O₂ + 1.5 H₂SO₄ → 0.5 Fe₂(SO₄)₃ + 2 S + 1.5 H₂O</td>
<td>-299</td>
<td>-306</td>
<td>-12.5</td>
</tr>
<tr>
<td>FeS₂ + 3.75 O₂ + 0.5 H₂O → 0.5 Fe₅(SO₄)₂ + 0.5 H₂SO₄</td>
<td>-1546</td>
<td>-1505</td>
<td>-12.9</td>
</tr>
<tr>
<td>S + 1.5 O₂ + H₂O → H₂SO₄</td>
<td>-623</td>
<td>-624</td>
<td>-13.0</td>
</tr>
</tbody>
</table>

Using the new values recalculated for Table 6 (and assuming the same reaction combination as in Publication I), it can be suggested that with 10% of alabandite reaction and 90% pyrrhotite reaction combined with a continuation to goethite precipitation, the average reaction heat is -13.5 kJ/g of reacted O₂. This corresponds with the oxygen flow of 16.1 g O₂/tonne ore/h (0.06 Nm³/tonne ore/h with air feed 0.077 kg air/tonne ore/h and with 21% oxygen in air). This suggests that using the assumed reactions, 217.7 kJ/tonne ore/h heat is generated, or approximately 60 W/tonne ore (vs. 70 W/tonne ore in Publication I). This is assuming 100% of oxygen reacting.

Earlier in this chapter, it was estimated that the heat transfer to solution represents approximately 85% of the total energy created. 7 W and 10 W were measured in Publication I as being transferred to solution, which corresponds to 8 W...
and 12 W of total energy creation. This suggests that, in the current study, oxygen efficiency varies from 14% to 20%.

4.3 Reagent need and impact of additional air feed

In Publication III, the total mass (and especially acid) balance revealed that the air (oxygen) efficiency overall was from 15% to 20%. This is an important finding as if any party would design a similar type of heap leaching operation, this would provide a proven and novel value for the determination of oxygen efficiency, therefore supporting the proper design of the aeration system for the heap. However, this calculation had to be arrived with estimations on the reaction rate of pyrrhotite at the end of the 150-day observation period. The observed iron recovery (reporting to solution) was below 7% in all areas. However, as mentioned in Publication III, this cannot be the total. The acid balance suggested that more elemental sulfur reacted than would be generated by the 7% pyrrhotite reaction. For this reason, an estimation was made that pyrrhotite could have reacted up to the same reaction extent as that measured for manganese (alabandite), of which the recoveries were around 35% in most of the observed areas. Reaction (4) explains why the estimate is necessary should a major part of the reaction continue via this path; iron does not report to solution from this path.

\[ Fe_7S_8 + 3.5 H_2O + 5.25O_2(g) \rightarrow 7 FeOOH + 8S \]  \hspace{1cm} (4)

Publication III shows that both manganese and iron were still leaching at the end of the 150-day observation period – the leaching of pyrrhotite is certainly not 100% but it could, in theory, be higher than estimated in Publication III. Consequently, this would result in higher oxygen efficiencies. A critical evaluation of the different pyrrhotite reaction rates is presented in Table 7. The author postulates that the extent of the pyrrhotite reaction is close to 35% as, with this value, the calculated oxygen efficiency matches the one calculated for the heat balance in Publication I and the heat balance in Publication I matches the estimation of evaporation in Publication IV.

<table>
<thead>
<tr>
<th>Pyrrhotite reaction extent, %</th>
<th>Oxygen efficiency, %</th>
<th>Formed elemental sulfur reacted to sulfate, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>21.9</td>
<td>15.9</td>
</tr>
<tr>
<td>50</td>
<td>29.3</td>
<td>11</td>
</tr>
<tr>
<td>65</td>
<td>36.7</td>
<td>8.4</td>
</tr>
<tr>
<td>80</td>
<td>44.1</td>
<td>6.8</td>
</tr>
<tr>
<td>95</td>
<td>51.4</td>
<td>5.7</td>
</tr>
</tbody>
</table>
An estimation was made in Publication II of the acid and air requirement for the mineral leaching reactions, considering two stages: 1) leaching of alabandite, pyrrhotite, pentlandite, and sphalerite, generating elemental sulfur and 2) leaching of chalcopyrite and pyrite, generating sulfate. Here the calculation has been redone with stage 2 converting all of the elemental sulfur to sulfate. Consequently, chalcopyrite and pyrite are calculated to completely form sulfate in this evaluation, presented in Table 8.

Table 8. Calculated reagent demand in two stages: elemental sulfur generation and total oxidation (modified from Publication II)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>% in ore</th>
<th>Elemental sulfur formed</th>
<th>Air demand Nm³/tonne ore</th>
<th>Acid demand, kg/tonne ore</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stage 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alabandite</td>
<td>0.47</td>
<td>0.17</td>
<td>3</td>
<td>5.3</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>0.76</td>
<td>0.25</td>
<td>4.9</td>
<td>8.7</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>5.81</td>
<td>2.3</td>
<td>34.7</td>
<td>61.6</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>0.68</td>
<td>0.23</td>
<td>3.9</td>
<td>6.9</td>
</tr>
<tr>
<td>Sum of above</td>
<td></td>
<td>2.95</td>
<td>46.4</td>
<td>82.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stage 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elemental sulfur reacting further</td>
<td>2.95</td>
<td>0</td>
<td>152.3</td>
<td>-90.2</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>0.16</td>
<td>0</td>
<td>3.7</td>
<td>0</td>
</tr>
<tr>
<td>Pyrite</td>
<td>18.40</td>
<td>0</td>
<td>592.4</td>
<td>-150.4</td>
</tr>
<tr>
<td>Total oxidation</td>
<td></td>
<td>0</td>
<td>794.8</td>
<td>-158.2</td>
</tr>
</tbody>
</table>

Table 8 shows how the early Stage 1 of leaching requires acid. Publications II and III show how the redox potential in the heap remains low (between 380 and 440 mV vs. Ag/AgCl). At these redox levels, the author postulates that iron precipitation is much more likely than further elemental sulfur oxidation. Stage 2 is shown for theoretical consideration of all the sulfides being converted to sulfates – in that case there would be an excess of acid. However, it is unrealistic that all of the formed elemental sulfur and all of the chalcopyrite and pyrite react. They would require 17 times the air compared to Stage 1 in Table 8 and would bring mainly iron to solution. Iron in solution is of low value and require a cleaning process. It would be more economical to turn off the air supply.

In Publications II and III, it was also observed that the vast majority of the acid needed for the reactions in the heap was generated in the heap. This result differs from earlier studies (Halinen, 2015), yet there is a good reason for this: these observations were made at the actual production scale heaps. Acid in the feed solution is consumed as the solution flows down the heap. If the heap is short, as in a laboratory column, some of the feed acid might reach the bottom. If the heap is tall, as in a full-scale heap, the acid is consumed at the top part of the heap and the rest behaves similarly as if no acid came with the feed. Halinen (2015) had an acid consumption of 38 kg sulfuric acid/tonne ore in 140 days; whereas it was stated in Publication II that the acid consumption was 4.3 kg sulfuric acid/tonne ore and in Publication III from 0.3 to 0.9 kg sulfuric acid/tonne ore.
acid/tonne ore in 150 days. If we consider a mining rate of 18 million tonnes of ore per annum, assuming the cost would continue on a similar scale annualized (e.g., 140 days to 365 days) and assuming that sulfuric acid costs 60 euros per tonne, Halinen (2015) would expect a cost of 107 million euros per annum, whereas the cost would be only 11 million euros per annum according to Publication II and below 2 million euros according to Publication III. If we assume a price of 10 000 euros per tonne of nickel, 10 700 tonnes of nickel would have to be produced to pay for the acid alone, estimated by laboratory test work such as that carried out by Halinen (2015). This means that almost one quarter of the nickel in the ore (0.26%-w Ni) would pay for the acid cost, while the figure would be 2.4% according to Publication II and 0.37% according to Publication III. This very low acid consumption is vital for the operation and a novel finding in the research of this ore.

Further, while it has been noted that, if Publication II is correct and the dominating reaction route is pyrrhotite transformation to goethite, there is a significant change in the heap mass and volume during the reaction of the ore. Table 9 lists the densities and molar masses required for the estimation of an example mass and volumetric change.

Table 9. Molecular masses and densities of pyrrhotite, goethite, quartz, and elemental sulfur

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Density (specific gravity)</th>
<th>Molar mass (g/mol)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>4.28</td>
<td>88.8475</td>
<td>Washburn, 2003b</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>4.6</td>
<td>647.4</td>
<td>Washburn, 2003b</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.651</td>
<td>60.06</td>
<td>Washburn, 2003a</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.0023</td>
<td>32.066</td>
<td>Yaws, 2012a&amp;2012b</td>
</tr>
</tbody>
</table>

In a material with 10%-w pyrrhotite, considering that 1 mol of pyrrhotite weighs 647.4 grams, there is 5826.6 grams of other material. By reaction (6), 878.5 grams of material is formed with 100% transformation, meaning a total mass change from 6474 grams to 6705.1 grams, or an increase of 3.6%-w. The heap grows during leaching. This is unique in the world, and a novel finding of this work. When thinking about leaching, one would expect that part of the solid is removed to solution. To estimate the volumetric change of the ore during leaching, let us consider for the sake of simplicity that the other mass in the ore is of the density of quartz. Then, using the data in Table 9 and considering pyrrhotite to extend fully to 100% transformation to goethite, the change of volume is from 2338.6 cm³ of unreacted material to 2471.3 cm³ after transformation, or an increase of 5.7%-V, i.e., the volumetric growth is even larger than the growth of the mass. The heap swells during leaching, also novel in the world of heap leaching.

Objective β of this thesis was to investigate the impact of increasing the feed of air to the system. Publication III showed that an increase in the air feed increased the leaching kinetics in the heap. This can be seen from Figure 14: nickel and zinc started to leach in the extra aerated areas while their leaching remained very low in the normally aerated areas, in other words, leaching had not yet
started. In figures: zinc leaching improved by 1309% while nickel leaching improved by 1932% with 60% higher aeration in 150 days. The same effect can be seen in iron, manganese, and magnesium as well: more of these metals leached into the solution during the observation period in the area where additional air was being fed. In figures: iron leaching increased by 142%, manganese by 14%, and magnesium by 171%. It was further seen that acid generation started more vigorously in the extra aerated part of the heap. This can be seen from the acid consumption figures: the production of acid reached a level where no extra acid was needed in the extra aerated part of the heap, shown in Figure 18, where Wells 1 to 9 represent the normally aerated heap and Wells 10 to 18 the extra aerated heap.

![Graph showing acid consumption as a function of operation days](image)

**Figure 18. Acid consumption as a function of operation days (modified according to Publication III)**

It was further shown by the leaching reaction calculation in Publication III that as extra air was added, there was a rise in the efficiency of air in percentage terms or at least it remained the same. However, the temperature of the exiting solution in Publication III was not as high as with lower aeration. This could be an indication of the phenomenon described by Dixon (2000), that a higher air feed increases evaporation and consequently cools the exiting solution flow.

### 4.3.1 Low aeration efficiency and increase of reaction with feed

The current thesis states that the oxygen efficiency observed was close to 20% and by increasing the oxygen feed (by approximately 60%) more reactions would occur, with the observed oxygen efficiency remaining at 20%. Petersen (2010) indicated that, especially in high saline conditions (and at high altitudes), the rate of oxygen mass transfer from gas to liquid should be the limiting factor of the process. The oxidative reaction could be limited by the reaction rate itself, the mass transport of the reactant (oxygen) to the solution phase, or the delivery of the oxygen to the gas space (i.e., oxygen depletion in the gas space). If the reaction itself is limiting the system, the delivery of extra oxygen would not change the situation as the solution would be saturated with oxygen. On the other hand, if oxygen delivery is the limiting factor, one would expect the oxygen
to be depleted from the gas space. This cannot be the case, as both of the two separate ways calculated for oxygen efficiency result in a similar value of approx. 20%. If mass transfer from gas to liquid is the limiting factor, it should not be affected directly by the flow of oxygen to the system.

In Publication III it was noted that with the same evaporation rate (i.e., the same amount of thermal energy drawn from the solution to moisturize the air flow), the higher air flow would lead to a lower partial pressure of water vapor in the air and hence a somewhat higher oxygen partial pressure. Petersen (2010) gave the following equation (5) for oxygen gas-liquid mass transfer in rapid reaction systems:

\[ R_{\text{O}_2, \text{ads}} \approx 0.9 \times k_L a \times C^* \]  

(5)

where \( R_{\text{O}_2, \text{ads}} \) is the rate of oxygen gas-liquid mass transfer, \( k_L a \) is the mass transfer coefficient, and \( C^* \) the maximum concentration of oxygen in solution (i.e., equilibrium concentration). Further, \( C^* \) was given as a function of oxygen partial pressure (6), which is limited by the pressure of water vapor:

\[ C^* = p_{\text{O}_2} \times k \]  

(6)

where \( p_{\text{O}_2} \) is the partial pressure of oxygen and \( k \) is the partition coefficient that decreases with increasing temperature. Hence, if the same thermal energy (the same amount of evaporation of water) occurs for a larger air flow, the flow will have a smaller water vapor content, thus higher oxygen partial pressure. If more air flow cools the heap further (by more evaporation), this will lower the temperature, which also decreases the water vapor pressure in air, increasing the oxygen partial pressure (in addition to increasing the partition coefficient \( k \)).

One potential explanation for the increased reaction rate with an increase in air flow relates to the distance of the air pipes from one another. It is possible that the baseline design (Part 1, no extra aeration) in Publication III was not optimal, leading to heterogeneous performance inside the heap, and consequently distant areas from the air pipes having limited access to air. This would result in an air flow more directly upwards in the heap than desired. The air pipe amount in this baseline was 471 pipes in a 613-m long heap; hence the average pipe interval was 1.3 meters. In the extra aerated Part 2 of the heap, there were 608 pipes installed in a 589-m long heap, making the average pipe-to-pipe interval 1.0 meters. If air flow preferentially moves upwards in the heap, this would leave a significantly larger area of less contact between the air pipes when the distance between them is longer.

Another potential explanation for the improved performance could be a better temperature profile in the heap, enhancing the reaction rate. This theory was simulated by Dixon (2000). The air flow cools the hot solution at the bottom of the heap and leads to precipitation of moisture on the top part of the heap, releasing energy there and heating the upper part of the heap. A higher average temperature inside the heap could also enhance the reaction kinetics.
4.4 Water balance at the Terrafame operation

Objective of this thesis was to understand better the water balance of the heap leach system and the associated mine site. Specifically, this is topical bearing in mind global warming and potential fluctuations in temperatures and precipitation (i.e., amount of rainfall). Publication IV added this new dimension in the consideration of this hydrometallurgical process: the vast fields of heap leaching bring another dimension to the water balance: either bringing water into the system in net positive rainfall areas or wasting water due to evaporation in net negative rainfall areas. The climate change scenarios analyzed were doubled (RCP, Representative Concentration Pathway, 4.5) and tripled (RCP 8.5) CO₂ emissions at the turn of the next century in comparison to the era before the Industrial Revolution, with their effect on temperature and estimated effect on rainfall. The publication pointed out that, with climate change, the direction would be towards a drier balance at the Terrafame mine. These results are summarized in Table 10. It can be observed that during the wettest conditions, i.e., maximum rain and minimum evaporation, the discharge of water would increase by 0.5 Mm³/yr. in both of the climate change cases in comparison to the set Base case based on the balance of the calendar year 2018. On the other hand, during the driest conditions, i.e., minimum rain and maximum evaporation, the raw water demand on the system would increase by 1.8 to 3.2 Mm³/a in the environmental change cases RCP4.5 and RCP8.5, respectively.

It was also shown in Publication IV that the heat generated in the heap leaching process is quite important in respect of the water balance as well—should the heat generation be negligible, the discharge of water would increase by 4.3 Mm³/a during a year similar to the calendar year 2018, or nearly tripling the discharge of water. While this result is fairly obvious, it has not been reported before and implies that a normal copper oxide type heap leach operation is not to be recommended in a net positive water balance area such as Finland, due to the fact that the water balance would prove to be extremely difficult.

Further, it was shown in Publication IV that a similar heat generating heap leach operation would be technically challenging to include in an dry climate location similar to the Chilean Antofagasta mountains, due to the very high requirement for fresh water it would set for the process.
Table 10. Usage and discharge of water in the analyzed scenarios (Publication IV)

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Fresh water usage, m3/yr.</th>
<th>Discharge of water, m3/yr.</th>
<th>Effect of metals plant on the PLS balance, m3/yr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case 2017</td>
<td>1,000,000</td>
<td>5,240,000</td>
<td>400,000</td>
</tr>
<tr>
<td>Base case 2018</td>
<td>1,000,000</td>
<td>2,510,000</td>
<td>1,020,000</td>
</tr>
<tr>
<td>Base case max. rain, min. evaporation</td>
<td>1,000,000</td>
<td>8,977,000</td>
<td>1,020,000</td>
</tr>
<tr>
<td>Base case min. rain, max. evaporation</td>
<td>3,960,500</td>
<td>0</td>
<td>1,020,000</td>
</tr>
<tr>
<td>Antofagasta case</td>
<td>8,460,000</td>
<td>0</td>
<td>1,020,000</td>
</tr>
<tr>
<td>Non-heat generation case</td>
<td>1,000,000</td>
<td>6,853,000</td>
<td>-704,000</td>
</tr>
<tr>
<td>RCP4.5 case: max. rain, min. evaporation</td>
<td>1,000,000</td>
<td>9,405,562</td>
<td>1,020,000</td>
</tr>
<tr>
<td>RCP8.5 case: max. rain, min. evaporation</td>
<td>1,000,000</td>
<td>9,430,902</td>
<td>1,020,000</td>
</tr>
<tr>
<td>RCP4.5 case: min. rain, max. evaporation</td>
<td>5,790,329</td>
<td>0</td>
<td>1,020,000</td>
</tr>
<tr>
<td>RCP8.5 case: min. rain, max. evaporation</td>
<td>7,245,999</td>
<td>0</td>
<td>1,020,000</td>
</tr>
</tbody>
</table>

4.5 Sources of error in the research

This thesis was entirely based on test work and scenarios at an industrial scale heap leach operation. The heaps in the different studies were 300 to 400 m wide, 8.5 to 9.5 m tall and varied from tens of meters to hundreds of meters in length. The sampling points, where solution samples were taken (Publications I-III), were from 66 m of heap length. Thus, the amount of material that one sample represents is quite large, in the range of 66 m x 350 m x 9 m or approximately 210 000 m³. Air lines were installed in two and three layers in the heap, a few meters apart one from another. In order to analyze the results, the material reaction was assumed to be homogeneous. This is a clear source of error in the research as some degree of heterogeneity must have existed in this large volume. Samples were also collected at intervals, twice per week for the above-mentioned sampling points. There could have been changes between the sampling that was not observed, bringing a source of error to this research. It was also assumed there was no migration of solution from one area to the next via the drainage layer. This migration cannot be completely negated and adds error to the results.

In Publication I, a simplification was made so that the calculated energy was the energy transferred purely to solution. There are also other potential sources for heat losses: the heat used to heat air and the heat of vaporization of water to saturate the air with moisture. These were not measured in Publication I and therefore the estimated oxygen efficiency (to heat the solution) is only partial, and slightly too low compared to total oxygen efficiency. The calculations had potential sources of error and were therefore recalculated for section 4.2 of the summary part of this thesis.

In Publication III, an estimation was made about the reaction extent of pyrrhotite in order to give a range of oxygen utilization and, with that, the efficiency. The extent of manganese leaching was used as a maximum for this value, as it should react before pyrrhotite. However, if the extent of pyrrhotite leaching was known more accurately, it would more clearly determine the oxygen efficiency and the reaction of the formed elemental sulfur further to sulfate.

In Publication IV, a large area of operation (1330 ha for the external site and 580 ha for the leaching heaps) was observed and modeled. Potential error
comes from using one source of rainfall measurement and one weather station for ground evaporation estimation. Assumptions had to be made that there was no leakage from the leaching heaps and that the ditch system surrounding the external site (around the heaps) kept water outside the external site from entering the area.

### 4.6 Recommendations for future research

- The aeration amount was tested in Publication III with two rates: 0.05 Nm$^3$/tonne ore/h and 0.081 Nm$^3$/tonne ore/h. It was shown that increased aeration benefited the leaching while maintaining oxygen efficiency. Thus, it would be worth continuing to increase aeration even further, looking for the point of air feed rate where feeding no longer accelerates the reaction.
- The mechanism by which increased aeration helped the process should investigated with heterogeneous conditions inside the heap due to the interval of pipelines inside the heap. Narrowing the gap between the pipelines could be investigated. If increased performance is due to the smaller distance between air pipes, there could be the potential to achieve the same results with less air and higher air efficiency. This theory could also be confirmed by excavations at the heaps. Better understanding of air distribution within the heap could also enlighten why the air flow did not reach saturation with water vapor in the study related to this Thesis.
- Temperature generation was measured using one condition of air feed rate and irrigation, as described in Publication I. There is the potential to learn about the heat generation and overall chemistry inside the heap by continuing this research at different aeration and irrigation rates. In addition, only the heat transferred to the solution was measured for the energy amount. Methods could be developed to track the relative humidity entering and exiting the heap with aeration, and the temperatures of air in different locations of the heap. This would allow the building of a more accurate description of the heat balance.
- The heap size was not varied in the research of this thesis. There is the potential to find further improvements by testing the optimal heap height and width.
- The observation period in Publications II and III was kept at 150 days to learn about the early part of leaching. There is a clear potential to expand upon this by continuing the observation until the valuable metals stop leaching. It is to be noted that copper and cobalt did not leach significantly during the observation period of test work within this thesis. By increasing the retention time, their individual behavior could be analyzed more deeply. In addition, as the extent of pyrrhotite leaching had to be estimated, a prolonged study could better confirm the estimated oxygen efficiency.
• The mechanism of valuable metal precipitation in the heap during the early part of leaching should be confirmed by solids sampling. It would be worthwhile studying whether this precipitated metal re-leaches easily or if it poses difficulties for the overall recovery. The possibility of valuable metal co-precipitation in iron precipitates should be verified.

• The particle size distribution was fixed in the research of this thesis, p80, at approx. 8 mm in Publications I to III. This particle size distribution could be varied, to ascertain the optimal size for heap leaching of this particular ore.

• In this research it is proposed that, through continuing research, a way to estimate nickel recovery in advance is to observe the process of manganese recovery, which clearly occurs before that of nickel. This needs confirmation and is a potential avenue for future research.

• In this research the quality of agglomeration was not addressed. In future research, it would be worth investigating agglomeration optimization.

• Publication IV reported that evaporation generated by the Terrafame heap was higher than naturally achieved with the ambient temperature at the whole operation level. It would be valuable to research the evaporation on a smaller scale and find ways to influence the amount of evaporation from the heaps.
5. Conclusions

This thesis presented the governing reaction mechanism at the Terrafame black-schist heap leach operation and the implications of this reaction. It shows that oxygen is a much more important variable in this leaching than acid, and further that, by investigating the effect of different air feed rates, the valuable metal recovery could be enhanced. In fact, acid feed was found to be substantially lower in comparison to earlier laboratory scale studies. For example, Publication III reported 0.3 to 0.9 kg/tonne in 150 days while Halinen, 2015, reported 38 kg/tonne in 140 days.

Oxygen addition was shown to improve the leaching of nickel and zinc, recoveries of which improved by 1932% and 1309%, respectively, with 60% higher aeration in 150 days. At the same time the leaching of impurities: iron, manganese and magnesium, increased by 142%, 14%, and 171%, respectively. Oxygen efficiency was reported to be 15% to 20% in Publication III, which is rarely reported altogether in publications, adding scientific significance to the thesis.

Pyrrhotite is the most important reactive mineral in the Terrafame ore and it reacts by transforming into goethite and similar ferric precipitates. The heap expands during leaching and re-precipitates valuable metals during the early stages of leaching. It was shown that 10%-w pyrrhotite in the ore can lead to an overall heap mass increase of 3.6%-w and a volumetric increase of 5.7%-V. This expanding behavior of the heap is unique in the world of heap leaching. It was also shown that not only can copper and zinc exhibit re-precipitation in the presence of pyrrhotite, but also nickel, cobalt, and cadmium behave in this way.

In addition to notable re-precipitation occurring at an early stage of the heap leaching process, there is a clear order in which the reactions occur. Manganese reports early to the solution as the process is started, followed by iron—indicating that alabandite, MnS, is the most reactive sulfide within the ore, followed by pyrrhotite. As there is such a clear order in which the minerals leach, a galvanic series of sulfides of a sort, this implies that, with further detailed study, results from early stage manganese leaching and iron leaching can be used to predict future nickel and zinc recoveries. This can be widely beneficial with the very long delay period currently observed for nickel and zinc in mind—it has been normal to wait for months to determine the future performance of a particular heap. In the future, this method of using earlier leaching metals to predict the outcome of later leaching metals can be expanded to include forecasting of copper and cobalt recoveries.

Water balance will have a greater variation as a result of climate change and will tend to change toward a drier climate in mining operations. It was shown
that the discharge need for purified waters in the wettest years will increase somewhat (+0.5 Mm³ to 9.0 Mm³ or by 6%) but the need for fresh water will increase significantly in the driest years (+3.2 Mm³ to 4.0 Mm³ or by 80%). Furthermore, the necessity of heat generation at the heaps in terms of the water balance of the operation was shown by scenario analysis: the discharge amount of purified water from the site would nearly triple during climatically average rainfall-evaporation years. Finally, the significance of the location to the water balance was analyzed and shown that in an arid climate, the need for fresh water would be over eight times higher.
References


Yaws, C.L. (2012b). Yaws’ Critical Property Data for Engineers and Chemists, Table 223.