

Matti Lampinen

DEVELOPMENT OF HYDROMETALLURGICAL REACTOR LEACHING FOR RECOVERY OF ZINC AND GOLD

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ABSTRACT

Matti Lampinen

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Hydrometallurgical methods offer promising techniques for resolving the challenge of producing metals essential to modern life in an environmentally and economically sustainable manner. Leaching has a central role in most hydrometallurgical processes. Hence, leaching performance has a great impact on the performance of the hydrometallurgical process as a whole. Reactor leaching is an approach that enables leaching to be carried out with good control and relatively short leaching time. The main drawback of reactor leaching is the high cost. The challenge thus becomes to develop leaching processes that improve the process economics and at the same time fulfil technical and environmental requirements. There is potential to meet this challenge through continued development of existing reactor leaching technologies, but demand for breakthrough technologies also exists.

Hydrometallurgical reactor leaching is a multiphase reaction system, and research and development of reactor leaching faces many of the difficulties typically found when investigating such systems. There are a large number of physical and chemical phenomena, only the most relevant of which can be taken into consideration and under study. The starting point of development should be a comprehensive understanding of the process solution and solid raw material behavior. This can be achieved by mastering the thermodynamics and kinetics of the processes involved using experimental methods and rigorous modeling and simulation approaches. Thereafter, reactor concepts can be investigated and reactors designed based on the mass and heat transfer aspects, flow dynamics and the desired capacity.

The current work examines two hydrometallurgical reactor leaching processes used for metal recovery: thiosulfate leaching for gold recovery and direct leaching for zinc recovery. The leaching processes studied are at different levels of technological development. Thiosulfate leaching can be considered a breakthrough technology that may initiate an era of cyanide-free gold production. Direct leaching processes have several industrial applications and they have been proven to meet the requirements set for the metals producing industry. Therefore, it is

evident that direct leaching processes will play a significant role in zinc production also in the future and development of these processes is still ongoing.

In this work, new experimental data are presented that improve understanding of chemical and physical phenomena related to the two reactor leaching processes studied. The ammoniacal thiosulfate leaching experiments of pressure oxidized gold concentrate show that gold can be effectively leached with thiosulfate as a lixiviant using low reagent concentrations in the leaching stage and pressure oxidation as a pretreatment method. This approach enables low reagent consumption and stabilizes the process solution, which facilitates the following recovery stage and makes re-use of the leaching solution possible. The experiments performed in this work provide new data on the leaching of gold with thiosulfate as a lixiviant and bring new insights into the leaching chemistry. New experimental results are also presented for direct leaching of zinc concentrate in conditions close to those of industrial leaching processes. The results from experiments of direct leaching of zinc concentrate show that the solution composition has a remarkable effect on the leaching kinetics, which clearly demonstrates that it is important to have experimental data for the leaching kinetics at the conditions of industrial leaching process.

A modeling approach for leaching processes is presented, which brings new understanding to process development. The most significant contribution of the modeling approach in this work can be found in the quantitative modeling of the solid raw material, with inclusion of particle size distribution, determination of the role of internal diffusion in the kinetics, and application of sophisticated mathematical methods (MCMC methods) to study the reliability of the established models and model parameters. The presented modeling approach offers a way to discriminate and study the phenomena behind the leaching process closely and with high reliability. The simulation approach developed for direct atmospheric leaching of zinc concentrates allows the role of different phenomena in the progress of the leaching to be evaluated. The simulation approach developed furthermore offers an effective tool for evaluation of leaching processes and downstream operations and thus aids attempts to increase the throughput of hydrometallurgical plants.

Keywords: Process development, Reactor leaching, Hydrometallurgy, Modeling, Parameter estimation, Simulation

TIIVISTELMÄ

Matti Lampinen

Hydrometallurgisen reaktoriliuotuksen kehittäminen sinkin ja kullan talteenotossa

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Nykyaikaiselle elämälle välttämättömiä metalleja on mahdollista tuottaa hydrometallurgisilla prosesseilla ympäristön ja talouden kannalta kestäväällä tavalla. Useimmissa hydrometallurgisissa prosesseissa liuotuksella on keskeinen rooli. Näin ollen liuotuksella on suuri vaikutus koko hydrometallurgisen prosessin tehokkuuteen. Liuotus voidaan toteuttaa suhteellisen lyhyellä liuotusajalla sekä hallita hyvin reaktoriliuotuksen avulla. Reaktoriliuotuksen merkittävin haittapuoli on korkeat kustannukset, mikä asettaa haasteen kehittää reaktoriliuotusprosesseja, jotka parantavat metallien tuotannon taloudellisuutta ja samanaikaisesti täyttävät tekniset sekä ympäristönsuojelun vaatimukset. Nykyisiä teknologioita kehittämällä voidaan vastata metallien talteenottoon liittyviin kasvaviin haasteisiin, mutta läpimurtoteknologioille on myös tarve.

Hydrometallurgiset reaktoriliuotusprosessit ovat monifaasisia reaktiosysteemejä ja niiden tutkimukseen sekä kehitykseen liittyy haasteita, jotka ovat tyypillisiä tällaisille systeemeille. Fysikaalisten ja kemiallisten ilmiöiden määrä on suuri, joten ainoastaan tärkeimpiä ilmiöitä voidaan ottaa tarkasteluun ja tutkia. Prosessiliuoksen ja kiintoaineen käyttäytymisen kokonaisvaltainen ymmärtäminen tulisi olla kehitystyön lähtökohta. Tähän lähtökohtaan voidaan päästä hallitsemalla prosessin termodynamiikka ja kinetiikka sekä kokeellisilla menetelmillä että perusteellisen mallintamisen ja simuloinnin avulla. Tämän jälkeen reaktorin rakennetta voidaan tutkia ja reaktori voidaan suunnitella halutulle kapasiteetille sekä esim. aineen- ja lämmönsiirto, virtausdynamiikka jne. voidaan ratkaista.

Tässä väitöskirjassa tutkittiin kahta reaktoriliuotusprosessia, joita käytetään metallien talteenotossa: kullan talteenotossa käytettävää tiosulfaattiliuotusta ja sinkin talteenotossa käytettävää suoraliuotusta. Tutkittavat reaktoriliuotusprosessit ovat teknologian kehityksen eri vaiheessa. Tiosulfaattiliuotusta voidaan pitää läpimurtoteknologiana, joka mahdollisesti aloittaa syanidi-vapaiden teknologioiden aikakauden. Suoraliuotusprosesseilla on monia teollisia sovelluksia ja ne ovat osoittaneet täyttävän vaatimukset, joita metallienjalostusteollisuudelle on

asetettu. On siis syytä odottaa, että suoraliuotusprosessit ovat merkittävässä roolissa sinkin talteenotossa myös tulevaisuudessa, ja että näiden prosessien kehitys tulee jatkumaan.

Tässä väitöskirjassa esitetään uutta kokeellista dataa kahteen tutkittavaan reaktoriliuotusprosessiin liittyen, mikä parantaa näiden prosessien kemiallisten ja fysikaalisten ilmiöiden ymmärrystä. Painehapatetun kultarikasteen ammoniakaaliset tiosulfaattiliuotuskokeet osoittavat, että kulta voidaan tehokkaasti liuottaa tiosulfaattiliuoksessa käyttäen alhaista reagenssikonsentraatiota liuotusvaiheessa ja painehapatusta esikäsitelymenetelmänä. Tämä lähestymistapa mahdollistaa alhaisen reagenssikulutuksen ja stabiloi prosessiliuosta, mikä on hyödyllistä liuotusta seuraavalla talteenottovaiheelle ja mahdollistaa prosessiliuoksen uudelleen käytön. Tässä työssä suoritettavat kokeet tarjoavat uutta dataa kulta liuotukseen tiosulfaattipohjaisella liuottimella ja antavat uuden näkökulman liuotuksen kemiaan. Työssä esitetään myös uusia kokeellisia tuloksia sinkkirikasteen suoraliuotukselle olosuhteissa, jotka ovat lähellä teollista sovellusta liuotusprosessista. Sinkkirikasteen suoraliuotuskokeet osoittavat, että liuoksen koostumuksella on merkittävä vaikutus liuotuksen kinetiikkaan. Tämä selvästi osoittaa, että on tärkeää olla kokeellista dataa liuotuksen kinetiikasta olosuhteissa, jotka vastaavat teollista sovellusta.

Liuotusprosessien mallintamiseen esitetään uusi metodologia, joka tuo uutta tietoa prosessikehitykseen. Kyseisessä väitöskirjassa esitetyn metodologian merkittävin panos olemassa olevaan tietoon on löydettävissä kiintoaineen kvantitatiivisesta mallintamisesta, joka sisältää partikkelikokojakauman sekä sisäisen diffuusiovastuksen roolin määrittämisen kinetiikassa, ja luodun mallin sekä mallin parametrien luotettavuuden tutkimisesta matemaattisilla menetelmillä (MCMC menetit). Esitetyn metodologian avulla on mahdollista erottaa ja tutkia liuotusprosessin takana olevia ilmiöitä tarkasti ja hyvällä luotettavuudella. Ilmanpaineessa suoritettavalle sinkkirikasteen suoraliuotukselle kehitetty simulointimalli mahdollistaa prosessissa vaikuttavien ilmiöiden roolien estimoinnin liuotuksen edistyessä. Lisäksi kehitetty simulointimalli on tehokas työkalu liuotusvaiheen sekä jatkokäsittelyn vaiheiden arvioitiin ja täten auttaa pyrkimyksissä lisätä hydrometallurgisen tuotannon tehokkuutta.

Avainsanat: Prosessikehitys, Reaktoriliuotus, Hydrometallurgia, Mallintaminen, Parametrien estimointi, Simulointi

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“You can’t stop the waves, but you can learn to surf”

- Jon Kabat-Zinn

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LIST OF PUBLICATIONS

This thesis is based on the following papers, which are referred to in the text by the Roman numerals **I-IV**

- I** Lampinen, M., Laari, A., Turunen, I., Ammoniacal thiosulfate leaching of pressure oxidized sulfide gold concentrate with low reagent consumption, 2015. *Hydrometallurgy* 151, 1–9.
- II** Lampinen, M., Laari, A., Turunen, I., Kinetic model for direct leaching of zinc sulfide concentrates at high slurry and solute concentration, 2015. *Hydrometallurgy* 153, 160–169.
- III** Lampinen, M., Laari, A., Turunen, I., Koiranen, T., Determination of the role of intrinsic surface reactions and internal diffusion resistances in direct leaching of sphalerite by mechanistic modeling, 2016. *Hydrometallurgy*, Submitted.
- IV** Lampinen, M., Laari, A., Turunen, I., Simulation of direct leaching of zinc concentrate in a non-ideally mixed CSTR, 2010. *The Canadian Journal of Chemical Engineering* 88, 625–632.

AUTHOR'S CONTRIBUTION

The author has been the primary contributor in all publications. The author has done all of the experiments and analyses for papers I and II. The author has done most of the design of the experimental work and interpretation of the data for papers I and II. In papers II, III and IV, the author has done most of the modeling and simulation. The author has done most of the writing of the manuscripts of papers I-IV. In addition to the publications listed above, the author has presented related work at scientific conferences and in other scientific forums.

Related publications

Lampinen, M., Laari, A., Turunen, I., Simulation of direct leaching of zinc concentrate in a CSTR, 8th World Congress of Chemical Engineering, August 23-27, 2009, Montreal, Canada.

Grenman, H., Bernas, H., Wärnå, J., Murzin, D., Salmi, T., Lampinen, M., Laari, A., Turunen, I., Model comparison and discrimination in solid-liquid reactions: leaching of zinc with ferric iron, 8th World Congress of Chemical Engineering, August 23-27, 2009, Montreal, Canada.

Related conference presentations

Lampinen, M., Laari, A., Turunen, I., Kinetics of direct leaching of zinc concentrate, Topical issues of subsoil usage, April 22-24, 2009, St. Petersburg, Russia. Oral presentation.

Lampinen, M., Turunen, I., Thiosulfate leaching system for gold production from primary and secondary sources, 1st International Conference on Minerals in Circular Economy, November 26-27, 2014, Espoo, Finland. Oral presentation.

Other publications

Herney-Ramirez, J., Lampinen, M., Vicente, M., A., Costa, C., A., Madeira, L., M., Experimental design to optimize the oxidation of orange II dye solution using a clay-based Fenton-like catalyst, 2008, *Industrial & Engineering Chemistry Research* 47 (2), 284–294.

Nomenclature

A_i	inner surface area of particle (reactive area), dm^2
A_o	outer surface area of reacting particle, dm^2
$c_{\text{Fe}^{3+}}$	concentration of Fe^{3+} in liquid, $\text{mol Fe}^{3+}/\text{dmL}^3$
$c_{\text{Fe}^{3+},s}$	concentration of Fe^{3+} at the reactive surface, $\text{mol Fe}^{3+}/\text{dmL}^3$
$c_{\text{H}_2\text{SO}_4}$	concentration of H_2SO_4 in liquid, $\text{mol H}_2\text{SO}_4/\text{dmL}^3$
D_e	effective diffusivity in particles, m^2/min
$D_{e,mean}$	effective diffusivity in particles at mean temperature, m^2/min
E_a	activation energy, kJ/mol
k	reaction rate constant
k_0	pre-exponential factor
$k_{l,mean}$	reaction rate constant at mean temperature, $\text{mol}^{-0.34}/\text{m}^{-2.01} \text{ min}$
n_1	reaction order for Fe^{3+} , -
n_2	reaction order for H_2SO_4 , -
r_i	radius of the reacting surface, dm
r_o	radius of the particle outer surface, dm
r_s	leaching reaction rate without diffusion limitations, $\text{mol dm}^2/\text{min}$
r_{SD}	leaching rate including diffusion limitations, $\text{mol dm}^2/\text{min}$
α	conversion, -

Abbreviations

AAS	Atomic absorption spectroscopy
ICP	Inductively coupled plasma
PSD	Particle size distribution
RLE	Roasting-leaching-electrolysis
SCM	Shrinking core model
SEM	Scanning electron microscopy
XRD	X-ray diffraction

1 INTRODUCTION

The metals producing industry faces formidable challenges in the modern globalized world, in particular, the need to use natural resources in a sustainable and ecologically acceptable way while simultaneously meeting economic goals in volatile markets. Utilization of low-grade ores, more complex raw materials, scarcity of water, demands for greater energy efficiency, tailings and water management, and a need to use less harmful chemicals can be considered the main challenges confronting future metals production. There is potential to overcome some of these challenges with continued development of current technologies, but a need for breakthrough technologies also exists. Clearly, the demands placed on the metals producing industry, now and in the immediate future, set new requirements for process development in the field.

Hydrometallurgical methods offer promising techniques for resolving the challenge of producing metals essential to modern life in an environmentally and economically sustainable manner. Compared with pyrometallurgical processes, hydrometallurgical processes offer relatively low capital costs, reduced environmental impact (e.g. no hazardous gases/dusts) and high metal recovery rates, as well as suitability for small-scale applications. These attributes make hydrometallurgical processes potential alternatives for the production of metals from primary and secondary sources. However, metal recovery through hydrometallurgical routes produces significant amounts of waste water and process residues, which are stored at mine sites or industrial sites. In most cases, hydrometallurgical wastes are classed as hazardous (Knuutila, 2015). Pyro- and hydrometallurgical processes have their pros and cons, hence it can be argued that best outcomes can be achieved by intelligent integration of both hydrometallurgical and pyrometallurgical processes. Leaching processes play an important role in the hydrometallurgical industry, where leaching operations are carried out on a large scale. The leaching stage is a key operation in raw materials processing and, as a result, the efficiency of the leaching has a great effect on the technical and economic success of hydrometallurgical operations (Crundwell, 2013).

The current work examines two hydrometallurgical reactor leaching processes used for metal recovery: thiosulfate leaching for gold recovery and direct leaching for zinc recovery. The leaching processes studied are at different levels of technological development. Direct leaching processes for zinc recovery have been used on an industrial scale since the 1980s (Ozberk et al., 1995), but research is still active to find processes and approaches that are more efficient. Increased investment in recent years in atmospheric direct leaching of zinc concentrates provides evidence that the process can meet the criteria set for metal recovery. Thiosulfate leaching is at a less advanced stage, although thiosulfate leaching systems have been extensively researched and first industrial applications, in the production of gold, started in 2014 (Choi et al, 2013). Thiosulfate leaching can be considered a breakthrough technology that may start an era of cyanide-free gold production. In addition to thiosulfate, chloride appears to be a promising lixiviant to replace cyanide (Aylmore, 2005; Lundström et al., 2015). Consequently, industrial applications of thiosulfate and/or chloride based leaching processes can be expected in the near future.

The two processes studied are of importance since they are representative of the developmental direction of industrial leaching, i.e., processes with reduced environmental impact, improved safety, and lower energy consumption. In practice, this means the use of less harmful reagents and less extreme operating conditions (lower concentrations, temperatures, pressures etc.). Consequently, longer residence times and larger reactors are often required, which poses a challenge for development in the field. The behavior of process solutions and raw materials in non-ideal conditions needs to be mastered in order to achieve techno-economical goals set for metals recovery. New, more in-depth sight is needed, which can be achieved by the use of experimental methods coupled with sophisticated modeling and simulation approaches. In this work, leaching experiments are carried out to improve understanding of the leaching behavior of the studied processes. Novel modeling procedures are developed by applying mechanistic numerical modeling and parameter estimation using sophisticated mathematical methods. Furthermore, a new simulation approach is presented, that applies non-steady mass balances to evaluate the overall performance of a non-ideally mixed leaching reactor.

2. AIM OF THE STUDY

This study focuses on process development of two reactor leaching process through the generation of new experimental data and the development of a novel modeling and simulation approach. The processes studied are thiosulfate leaching for gold recovery and direct atmospheric leaching for zinc recovery. Knowledge of the physico-chemical phenomena related to the leaching process is essential in the development of reactor leaching. The aim of the research is to develop understanding of the phenomena underlying the studied leaching processes in such a way that scientifically justified and reliable premises for process development exist.

Gold recovery with thiosulfate leaching

In order for thiosulfate leaching to become a commercially viable process, the following major issues need to be resolved: (1) how to master the complex leaching chemistry; (2) how to reduce reagent consumption; and (3) how to handle difficulties posed by the recovery of metals after leaching. These issues are studied in the current work, where the focus is on understanding and mastering the phenomena behind the process. It became clear during this thesis work that although a lot of experimental research has already been published, an experimental approach remains the best way to continue research work.

Zinc recovery with atmospheric direct leaching

Direct leaching has been used on an industrial scale for recovery of zinc from zinc sulfides for decades. The major challenges in atmospheric direct leaching processes are the slow kinetics and oxygen consumption. During work on this thesis, it became clear that although a lot of research has been conducted, there are still many aspects that have not been solved and many questions on which the scientific community has yet to agree. In particular, major effort is required on development of suitable kinetic modeling procedures. Although defects in traditional modeling

approaches (e.g. the shrinking core model (SCM)) are well recognized, such models are still often used. For instance, the importance of describing the raw material with particle size distribution (PSD) is widely agreed, but PSD is often neglected, and the importance of conducting leaching experiment also in conditions found in industrial leaching processes is also well documented, but often bypassed. Furthermore, the existence of internal diffusion resistance during leaching processes is widely reported. However, a lack of suitable analytical techniques and comprehensive modeling approaches has made it difficult to determine the precise role of internal diffusion resistance in the course of leaching. Finally, in many modeling approaches surprisingly little attention is paid to the reliability of the established kinetic parameters.

More in-depth understanding of phenomena behind the direct leaching process can be achieved by using a more thorough modeling approach, with using already published data, to develop more advanced and reliable models. In addition, new experimental data are needed to improve model reliability. A simulation model is needed, especially for the development of direct atmospheric leaching of zinc concentrates, that helps to understand the interaction between the different phenomena involved and takes into account fluctuating process conditions, (e.g. non-uniform pressure and concentration profiles) and other non-idealities (e.g. in mixing) in leaching reactors. Hence, the aim of the current work was: (1) to develop an improved modeling approach that brings more in-depth understanding of the phenomena behind the leaching process and improves the reliability of the modeling by use of sophisticated mathematical methods in parameter estimation; (2) to generate new experimental data in conditions close to those of industrial applications; (3) to develop simulation models for development of the studied process.

3. OUTLINE

This work consists of a literature part and an applied part, which includes experimental, modeling and simulation sections. The literature part gives background information on hydrometallurgy, leaching and reactor leaching, and presents the development history of the processes studied. In addition, requirements for development of hydrometallurgical leaching reactors are discussed including features of importance for development of modeling and simulation procedures.

The experimental part describes the experimental design, the experiments conducted and the analyses done. The aim of the experimental work related to thiosulfate leaching was to achieve ≥ 90 % conversion while minimizing reagent consumption and to study the phenomena behind the process. For direct leaching of zinc concentrate the aim of the experimental work was to study leaching kinetics at conditions corresponding to those of an industrial atmospheric reactor. The goal of the modeling of direct leaching of zinc concentrates was to develop a more thorough modeling approach that can bring new understanding and better reliability to process development. The modeling part of the work covers development of the models together with evaluation of their performance and the reliability of the model parameters. The objective of the simulation study was to construct a simulation model for atmospheric direct leaching that can be used for reactor development in the sense that it helps to understand the role of different physico-chemical phenomena and the effects of different parameters on the leaching process.

4. NEW RESULTS

The following findings are believed to be original:

Ammoniacal thiosulfate leaching of gold concentrate

i) Oxidative pre-treatment of sulfide containing gold ores/concentrates followed by ammoniacal thiosulfate leaching with low reagent concentrations offers a way to overcome problems hitherto identified in the leaching stage and facilitate the following recovery stage. Copper concentration is critical in the leaching stage, since the experimental results show that increased copper concentration can lead to precipitation of the leached gold.

Direct leaching of zinc sulfide concentrate

ii) The experimental results from direct leaching of zinc concentrate show that the solution composition, especially the sulfate concentration, has an effect on the leaching kinetics, which clearly demonstrates that it is important to have experimental data for the leaching kinetics at the conditions of industrial application.

iii) The modeling approach presented in the current work improves kinetic analysis of leaching by introducing rate equations that include internal diffusion resistances and surface reactions, which are solved numerically, and by inclusion of particle size distribution. Furthermore, the current work demonstrates how sophisticated mathematical methods (MCMC methods) can be applied in kinetic analysis to thoroughly analyze the reliability of the rate equations established. It is argued that the presented modeling approach brings new understanding and improved reliability to process development.

iv) A comprehensive simulation model for reactor leaching composed of non-steady state mass balance equations was developed in the current work. The reactor model takes into account the effects of non-ideal mixing, surface reactions between zinc in the solids and ferric ions in the liquid phase, oxidation of ferrous ions back to ferric ions, gas-liquid mass transfer of oxygen, decrease of particle size as the reaction proceeds, and the effect of hydrostatic pressure on the process performance. The developed simulation model provides improved premises for effective process development in the sense that it enables evaluation of the relative importance of different phenomena and allows consideration of the effects of process variables on a larger scale.

5. HYDROMETALLURGY

Hydrometallurgy, as can be inferred from the word, consists of methods and techniques used for extracting metals from raw materials in an aqueous medium (Habashi, 1999). The discovery of aqua regia by the Arab alchemist Jabir Ibn Hayyan (720 – 830 AD) may be considered as the milestone marking the beginning of hydrometallurgy (Habashi, 2005). So-called modern hydrometallurgy can be traced to the end of the nineteenth century, when two major techniques were discovered: the cyanidation process for gold and silver and the Bauer process for bauxite (Habashi, 1999). Cyanidation is currently the prevailing technique in gold recovery and is applied, for example, in the Kittilä mine, Finland, the largest operating gold mine in Europe.

The history of industrial production of metals through hydrometallurgical process routes is not as long as that of pyrometallurgy, but the importance of hydrometallurgy in metals production has increased steadily in recent years. Furthermore, hydrometallurgical and pyrometallurgical processes are nowadays also used together. Additionally, hydrometallurgical processes have a strong role in smelters. Hydrometallurgy generally involves two distinct steps (Habashi, 1999):

- Selective dissolution of the metal values from a raw material – a process known as leaching
- Selective recovery of the metal values from the solution - an operation that involves precipitation.

Routes for metal recovery are presented in Fig. 1.

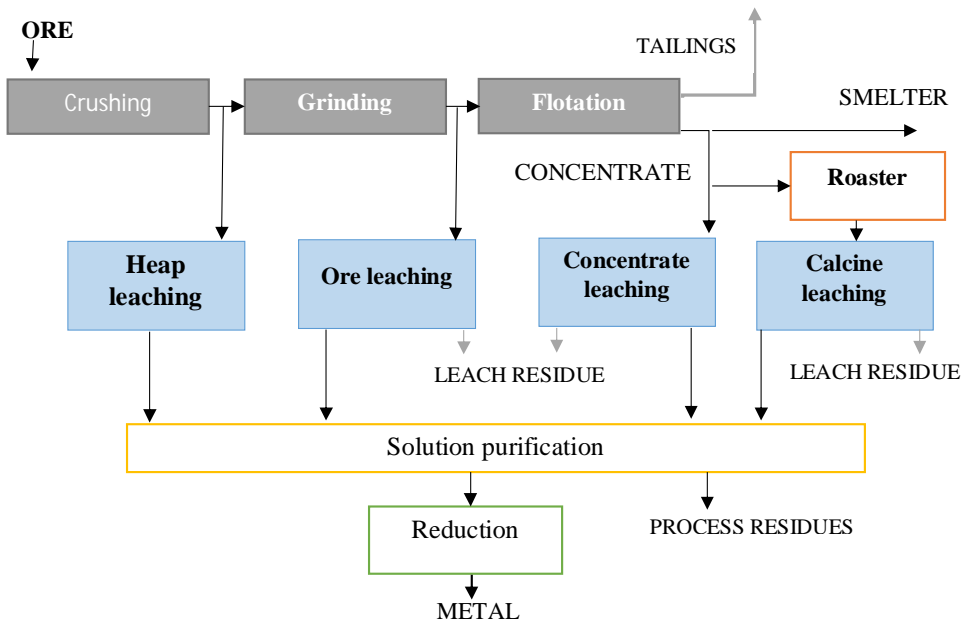


Fig 1. Routes for metal production.

5.1 Leaching

Leaching is the process in hydrometallurgy where the metals from a raw material (e.g. ore, concentrate or recycled material) are converted into dissolved form by means of a solvent. In this respect, either one of two purposes can be achieved (Habashi, 1999):

- Opening of raw materials to solubilize the metal values.
- Leaching of soluble constituents (usually gangue minerals) to gain raw material in a more concentrated pure form.

As can be seen from Fig. 1, the leaching stage is only one of the processing phases in metals recovery. Commonly, leaching reagents include water, acids (H_2SO_4 , HCl , etc.), bases ($NaOH$,

NH_4OH , $\text{Ca}(\text{OH})_2$, CaO , $\text{Mg}(\text{OH})_2$, salt solutions and combinations thereof. Leaching processes typically include also oxidizing agents (O_2 , Fe^{3+} , Cu^{2+} , H_2O_2 , Cl_2 , HClO , NaClO) or reducing agents (Fe^{2+} , SO_2). Elevated temperatures and/or pressure are frequently used in leaching, since the equilibrium and kinetics of leaching are often favored by more aggressive conditions than normal temperature and pressure (NTP). Methods used for hydrometallurgical leaching processes include in-situ leaching (leachate is pumped into the ore deposit), dump ore leaching (leaching without crushing), heap leaching, vat leaching, reactor leaching, and autoclave leaching (leaching at high temperature and pressure). The composition of the raw material mainly determines the selection of the leaching method used. Raw materials with low metal content are usually processed with methods that have lower costs but also lower efficiency, and higher grade raw materials are usually processed with more effective but more expensive methods, as presented in Fig. 2.

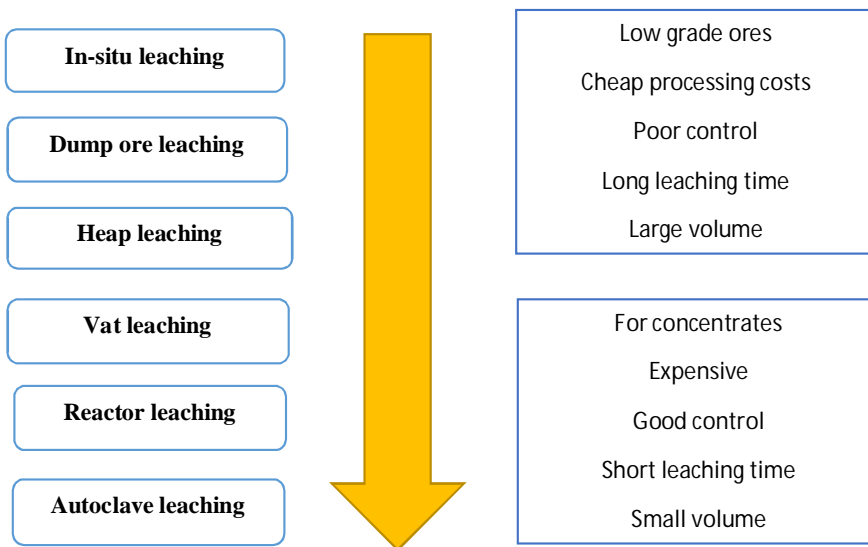


Fig. 2. Leaching methods.

Bioreaching, also known as minerals bio-oxidation, has been widely employed commercially for heap and dump bioreaching of secondary copper sulfide ores and sulfidic-refractory gold concentrates (Brierley, 2010). The Talvivaara mine in Sotkamo, Finland, (operated currently by Terrafame) produces nickel, zinc, copper and cobalt through a bioreaching process (Riekkola-Vanhanen, 2010). Technical and commercial challenges, such as slow kinetics and difficult process control, remain for bioreaching of primary sulfides and complex ores (Brierley, 2010). In bioreaching, bacteria oxidize Fe^{2+} to Fe^{3+} , which then oxidizes the minerals (Rohwerder, 2003). Bioreaching is slower than chemical leaching but does not require pure gaseous oxygen, which is a prerequisite of many chemical leaching processes. In bioreaching air can be used instead of pure oxygen, since air is required for bacteria respiration. This is a beneficial feature since oxygen consumption can be a determinant factor in the economics of chemical leaching processes such as direct leaching to treat zinc sulfides (de Souza et al., 2007). The possibility of integrating bioreaching with chemical leaching has been studied (de Souza et al., 2007) in efforts to find cost-effective processes to treat zinc sulfide.

Attempts have been made to improve the performance of conventional leaching processes using, for example, microwave (Al-Harashseh and Kingsman, 2004; Kingsman and Rowson, 1998) and ultrasound treatments (Grénman et al., 2007; Luque-Carcia and Luque, 2003; Narayana et al., 1997) but no industrial scale applications have been reported for these approaches. In recent years, there has been renewed interest in ultrasound (Zhang et al., 2016; Wang et al., 2013) and microwave (Suoranta et al., 2015) assisted leaching for the processing of waste material and by-products.

5.2 Mechanism of leaching

The leaching of a solid in an aqueous phase depends primarily on the nature of the solid raw material whether it is ionic, covalent, or metallic (Habashi, 1999). Since bonding in solids is intermediate between these cases, a variety of leaching mechanisms can be identified. These mechanisms may be physical, chemical, electrochemical, reduction or electrolytic. When considering leaching from a purely chemical point of view, leaching reactions can be redox,

acid/alkaline or complexing. (Ballester et al., 2007). Commercial processes are mostly redox, and 90 % of them are oxidizing processes utilizing reagents such as oxygen, ferric ion, chlorine etc. (Ballester et al., 2007). In these cases, the mechanism involved is electrochemical, since electronic transfer through the solid mineral and between this solid and the leaching reactant is necessary for the reaction to take place (Ballester et al., 2007). The reaction mechanism of leaching can be very complex, comprising several often unknown elementary steps. Moreover, the structure of the solid material and structural changes therein can be difficult to ascertain. Thus, several leaching mechanisms can be involved in leaching reactions, e.g., in direct leaching of sphalerite it has been presented (Dutrizac, 2006) that acid has a role in the course of the leaching, although the leaching proceeds mainly through redox reactions. The leaching rate of a solid raw material, such as sphalerite, depends on the processes taking place at the solid-solution phase boundary. These processes are complex and can include formation of complexes, transfer of charged species, and adsorption of ions at the solid surface. The leaching processes are usually classified on the basis of the rate-determining step, for example, chemical reaction, charge transfer, or mass transport.

5.2.1 Electrochemical mechanism of leaching

The electrochemical mechanism is considered the most important leaching mechanism in the leaching of minerals, such as sulfides (Ballester et al., 2007). Direct leaching of zinc sulfides (Fig. 3) has been described with an electrochemical mechanism (Crundwell, 2013; Verbaan and Crundwell, 1986), and it is widely presented (Nicol, 1993; Senanayake, 2004) that oxidation of gold is electrochemical in nature, and thus the kinetics can be modelled using the corrosion theory of metals. An important fact to consider in electrochemical processes is that the kinetics depends on the electronic transfer between the anodic and cathodic sites on the mineral (Ballester et al., 2007). Thus, any action capable of modifying the electronic conductivity can positively affect the kinetics of the process.

Zinc is mainly recovered from sulfides, and in most cases sulfides are semiconductor solids that can be leached in the presence of an oxidant (e.g. oxygen) dissolved in water (Ballester et al., 2007). The main features of the electrochemical mechanism of dissolution are illustrated for direct leaching of zinc in Eqs. (1)-(3). The dissolution of sphalerite in ferric sulfate or ferric chloride solutions occurs according to the reaction in Eq. (1). (Crundwell, 2013)



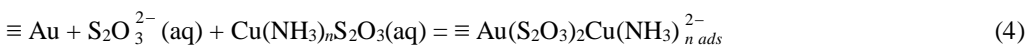
The half-reaction for the dissolution of the mineral is irreversible and given by Eq. (2).



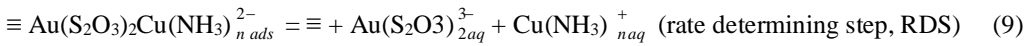
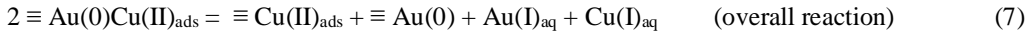
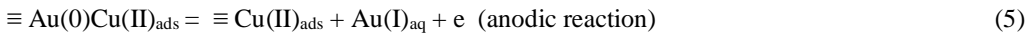
The half-reaction for the reduction of the oxidant might be reversible and the half reaction is given by Eq. (3).



Senanayake (2004) proposed a surface reaction mechanism for gold leaching in a thiosulfate lixiviant with Cu^{2+} by combining electrochemical rate equations with the well-known adsorption theory. The equilibrium that represents the adsorption of $\text{S}_2\text{O}_3^{2-}$ and the mixed complex $\text{Cu}(\text{NH}_3)_n\text{S}_2\text{O}_3$ onto the gold surface to form $\equiv \text{Au}(\text{S}_2\text{O}_3)_2\text{Cu}(\text{NH}_3)_{n \text{ ads}}^{2-}$ (\equiv presents surface complex) is presented in Eq. (4).

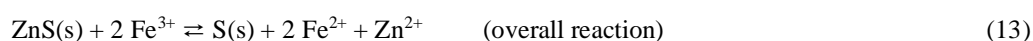


Due to its redox nature, the surface reaction for the oxidation of gold by Cu(II) can be represented by simultaneous oxidation $\text{Au}(0) \rightarrow \text{Au}(\text{I}) + e$ and reduction $\text{Cu}(\text{II}) + e \rightarrow \text{Cu}(\text{I})$. For the sake of simplicity, $\equiv \text{Au}(\text{S}_2\text{O}_3)_2\text{Cu}(\text{NH}_3)_{n\text{ ads}}^{2-}$ can be represented by $\equiv \text{Au}(0)\text{Cu}(\text{II})_{\text{ads}}$ and the electrode reactions by Eqs. (5) and (6). Thus, the overall redox reaction is described by Eq. (9), i.e., the simplified version of the sum of Eqs. (5) and (6), and represents the apparent surface reaction which, according to Senanayake (2004), is also the rate determining step (RDS).



5.2.2 Chemical mechanism of leaching

A chemical mechanism is also used to describe various leaching processes, e.g. direct leaching of zinc sulfides has been widely described (Dutrizac, 2006; Göknan, 2009; Salmi et al., 2010; Souza et al., 2007) with a chemical mechanism. According to chemical mechanism, the mineral leaches through chemical species in solution with oxidizing character. Salmi et al., (2010) proposed a stepwise surface reaction mechanism for the reaction between ZnS and ferric ions. The ferric ion forms a surface complex (I_1) with zinc sulfide, the complex reacts further with another ferric ion, forming a surface intermediate (I_2) that releases ferrous ions, and elemental sulfur is formed. Elemental sulfur is immediately removed from the surface, the shrinking particle model can thus be applied to describe the leaching kinetics. The reaction mechanism can be written as:



In cases where the reaction proceeds by chemical mechanism, the crystalline solid raw material may be partly ionic and partly covalent or mainly covalent (Habashi, 1999). The first type of solid covers a variety of compounds: oxides, hydroxides, sulfides, sulfates, some halides and carbonates; while the second type is mainly found with silica and silicates. These are insoluble in water but may be solubilized in the presence of certain reagents (Habashi, 1999).

5.3 Reactor leaching

As presented in Fig. 2, the features that distinguishing reactor leaching from other methods are use of concentrated raw materials, good control, short leaching time, small volume, and high costs. Due to the high costs, high recovery rates are required. In reactor leaching, finely ground raw material is generally added to the leaching solution and a slurry is formed. Extensive crushing and grinding is necessary when the metal values are of fine grain size and disseminated in the host raw material. The slurry has to be mixed continuously to prevent the solid raw material from settling and to terminate the leaching in the shortest possible time.

The equipment that is be used in reactor leaching varies greatly. Agitation can be carried out pneumatically or mechanically. Pneumatic agitation uses compressed air, whereas mechanical agitation uses motor-driven impellers. Agitation of slurries by pneumatic means is generally carried out using airlift reactors, also known as Pachuca tanks. Pachuca tanks used to used by the alumina industry for precipitation in the Bayer process (Shaw, 1982). Over time, Pachuca systems have become increasingly expensive because of the cost of the cone bottom tanks,

compressors, and piping required to meet increased processing rates and larger equipment capacities (Altman et al., 2002). The high energy consumption for the level of agitation produced is another major drawback of Pachuca tanks. The alumina industry first began to study the design of mechanical agitation systems in the 1960s, and the mechanical draft tube circulator was the result of this research work (Altman et al., 2002). The concept has spread to a number of other industries and processes, including gold leaching (Shaw, 1982).

Draft tube circulators are applied in atmospheric direct leaching of zinc concentrates. As can be seen from Fig. 4, the draft tube circulator is a tank that contains a draft tube inside it. Typically, the draft tube diameter is 20-40 % of the tank diameter. When leaching is conducted at atmospheric pressure large reactors are usually required, e.g., the Outotec Zinc Concentrate Direct Leaching process (DL) reactor in the zinc plant in Kokkola, Finland, has a volume of about 900 m³ and a height of 20 m (Svens, 2012).

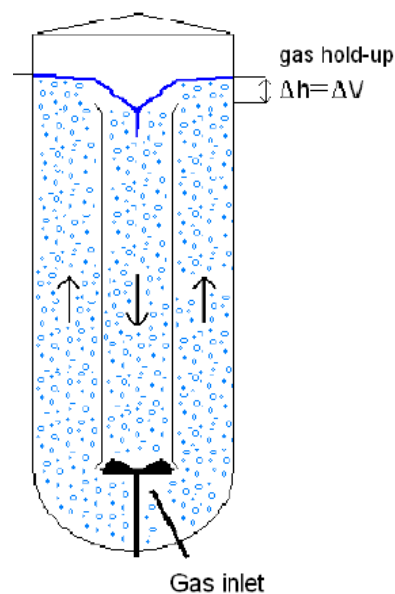


Fig. 4. Draft tube circulator (Kaskiala, 2005).

Autoclave leaching is the most commonly used term for describing leaching carried out at high pressure. A division between high pressure (autoclave) and atmospheric (reactor) leaching is justified since the equipment and related challenges are notably different. When leaching is carried out at high pressure and temperature, the leaching itself is not much of a problem compared to the technical issues related to the autoclaves. The problems associated with pressure leaching are mainly found in the operation and maintenance of the autoclaves (Takala, 1999; Babu et al., 2002; Svens, 2012). A typical horizontal, multi-compartment autoclave with mechanical agitation is shown in Fig. 5.

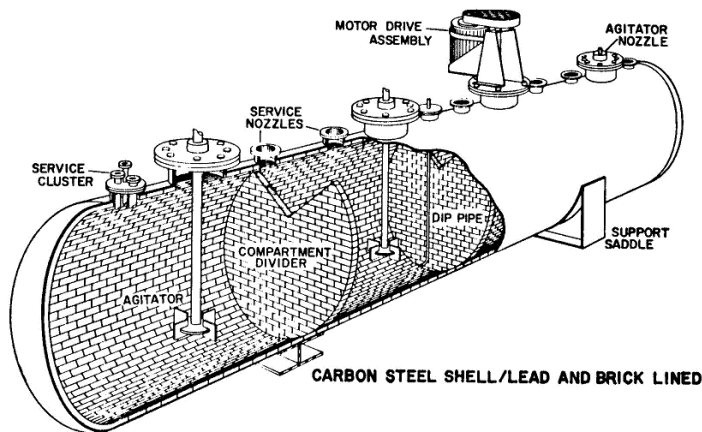


Fig. 5. Horizontal multi-compartment autoclave. (Veltman and Weir, 1981)

6. DEVELOPMENT HISTORY OF THE LEACHING PROCESSES STUDIED

The metals producing industry can be considered as highly complex since a large number of different processes are in operation in metals production globally. This is a challenge for process development in the field, as the benefit of development work should serve the whole process chain and not merely one unit process. Furthermore, metals recovery processes increasingly include recycling of streams. Consequently, the time required for development activities is relatively long, especially for breakthrough technologies, where research work stretching over a decade or more is often required. For example, direct leaching of zinc concentrates is usually integrated into a recovery plant using conventional technology (Fig. 6). Feed to the direct leaching unit, where oxygen is used as the oxidant, consists of zinc concentrate, slurry from the conversion process, and acid from the electrolysis (Fig. 6). This complexity complicates development efforts, and a holistic view of any changes made to the process is required, as improvement of one process parameter might increase recovery but result in an overall reduction in economic profitability.

6.1 Direct leaching for zinc recovery

Zinc is an important base metal and is required in many applications, mainly in the metallurgical industry. Sixty percent of zinc production in 2013 was used for galvanizing steel (International Zinc Association). Zinc is mainly recovered from primary sulfide concentrates. The primary route for production of zinc from its sulfides comprises roasting, leaching and electrolysis, i.e., the RLE process (Fig. 6). The RLE process accounts for some 85 % of primary zinc production (de Souza et al., 2007).

The RLE process was devised to treat zinc sulfide concentrates, and it includes a zinc sulfide roasting step to produce ZnO and SO₂. The calcine (ZnO) is sent to leaching, followed by purification and electrolysis steps, where the zinc is produced. The SO₂ is converted to sulfuric acid, an important by-product. However, the connection between zinc production and sulfuric acid production can cause problems when possible expansion of a zinc plant is considered.

Sulfuric acid markets, as well as fertilizer markets, are saturated in many areas, leading to problems monetizing the sulfuric acid produced, and the economic feasibility of the roasting-acid plant section of a zinc plant following any possible expansion can be called into question (Svens, 2012). Fugitive SO_2 from the roasting step causes air pollution, which is a challenge from the environmental point of view. The economic and ecological impacts of the RLE process have led to a search for alternative techniques that directly leach zinc from concentrate without a roasting step. Direct leaching of zinc concentrates is usually integrated into an existing RLE process in order to increase zinc production capacity without increasing sulfuric acid production, e.g. the Boliden Kokkola Oy zinc plant started direct leaching in 1998 (Fig. 6).

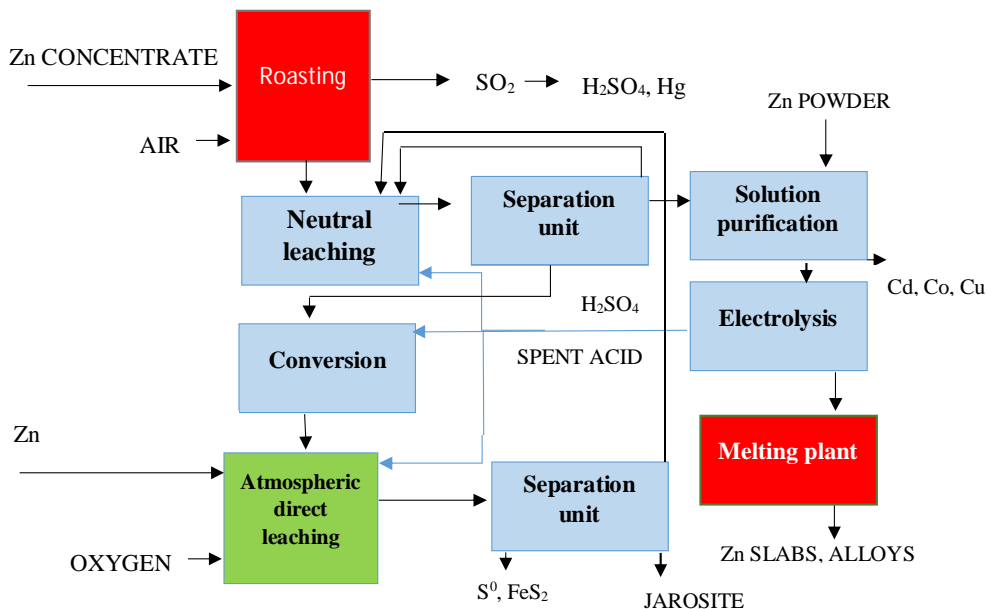


Fig. 6. Block diagram for zinc production of the Boliden Kokkola Oy plant after commencing use of a direct leaching process in 1998.

Methods for commercialized direct leaching of zinc can be divided into two categories, namely, processes under atmospheric pressure and processes under elevated pressure. Oxidation pressure

leaching of base metal sulfides using continuous autoclaves was first successfully applied commercially in the early 1950's (Ozberk et al., 1995). The horizontal, multi compartment autoclave was developed at that time and continues to be the preferred equipment for pressure leaching processes. In the 1970s, interest grew in the zinc pressure leach process, which enables avoidance of sulfur dioxide emissions when processing zinc sulfide concentrates. Large-scale piloting took place towards the end of the decade, and the first commercial plant was started up in 1981 (Ozberk et al., 1995). In the 1990s, with euphoria surrounding high zinc prices, a number of new integrated processes were implemented for the extraction of zinc from various mineral resources (Filippou, 2004). In 1994, Korea Zinc adopted Union Minière atmospheric direct leaching of zinc sulfide concentrates to expand the capacity of the Onsan plant in South Korea, and in 1998, Outokumpu expanded the Kokkola plant in Finland using a proprietary process for the atmospheric leaching of zinc sulfide concentrates. Nowadays, direct atmospheric leaching and pressure leaching both have many industrial applications (Haakana et al., 2008; Ozberk et al., 1995; Takala, 1999). Industrial applications of zinc pressure leach processes are listed in Table 1.

Table 1. Sherrit zinc pressure leach process implementations (Svens, 2012)

Location	Start-up year	Capacity, t/a Zn	Process description
Xining, Qinghai, China	2011?	100 000	Two stage counter-current
Shaoguang, Guangdong, China	2009	84 000	Two stage counter-current
Balkhash, Kazakhstan	2003 closed 2008	100 000	Two stage counter-current, recovery of S ⁰
Flin Flon, Manitoba, Canada	1993	90 000 (now 115 000)	Two stage counter-current, recovery of S ⁰ (not in operation)
Timmins, Ontario, Canada	1983 closed 2010	20 000 - 25 000	Single stage
Trail, B.C., Canada	1981	30 000 (now 75 000)	Single stage, recovery of S ⁰ by melting and filtration

As presented earlier, problems associated with pressure leaching are mainly found in the operation and maintenance of the autoclaves (Takala, 1999; Babu et al., 2002; Svens, 2012). Due to significant erosion and scaling the autoclaves need a lot of maintenance (Svens, 2012).

Atmospheric leaching, on the other hand, suffers only minor scaling, erosion and corrosion, and thus has minor maintenance requirements (Svens, 2012; Takala, 1999). Autoclave operations also involve more complicated process control (temperature, molten sulfur, heating, scaling problems, and leaching additives). Atmospheric leaching is hence considered an option to address many of the problems found in industrial pressure leaching processes. Two proven technologies are available for atmospheric leaching: the Outotec zinc concentrate direct leaching process (DL) and the Albion process.

First laboratory tests in the development of DL were performed at the Outotec (former Outokumpu) Research Center (ORC) in Pori, Finland, with several zinc concentrates used at the Kokkola zinc plant (Svens, 2012). Following these laboratory tests, initial piloting was carried out in 1991 with a 10 m high pilot reactor, and piloting was later continued at the Kokkola zinc plant with a 20 m high pilot reactor. The results from the Kokkola pilot tests were used for first economic calculations comparing pressure leaching and atmospheric leaching. Following this economic assessment, expansion of the operations of the Kokkola plant with the DL process was started in 1996 (completed in 1998) by integrating atmospheric leaching reactors (Fig. 3) of about 900 m³ and similar height as the large pilot reactor into existing operations.

DL has been implemented on an industrial scale in several different locations (Table 2), and in recent years, a number of companies have announced investments in DL. Boliden is investing in DL to increase the capacity of the Odda zinc plant in Norway from 170 000 to 200 000 t Zn/a (Outotec.com). Equipment delivery will take place in 2015 and 2016. The Peñoles Group is expanding the annual zinc production capacity of the Met-Mex Peñoles zinc production facilities in Torreon, Mexico, by 100 000 t (Outotec.com). Equipment delivery will take place between 2015 and 2017.

Table 2. Industrial implementations of the Outotec atmospheric leach process (Svens, 2012).

Location	Start-up year	Capacity, t/a Zn
Zhuzhou, China	2009	130 000 (incl. 30 000 from neutral leach residue)
Odda, Norway	2004	50 000
Kokkola, Finland	2001	50 000
Kokkola, Finland	1998	50 000
*****	*****	*****
Onsan, R.O. Korea/Umicore (Outotec)	1997	260 000

The Albion process was developed in 1994 by Glencore, and three Albion process plants are currently in operation (Albionprocess.com). Two of the plants treat a zinc sulfide concentrate and the third plant treats a refractory gold/silver concentrate. A fourth plant, for the treatment of refractory gold, is under construction in Armenia. The two plants that treat a zinc sulfide concentrate are located in Spain (4 000 t/a zinc metal) and Germany (18 000 t/a zinc metal). The Albion process is a combination of ultrafine grinding and oxidative leaching at atmospheric pressure. To produce the finely ground concentrate required for the Albion process, a new grinding technology, IsaMill, was developed.

de Souza et al. (2007) present that the economics of direct leaching processes are determined mainly by the oxygen consumption, as oxygen is a relatively expensive raw material. Furthermore, the elemental sulfur produced during ZnS oxidation by Fe(III) is not easily commercialized, due to its generally high impurities content. The problematic aspects of handling of the residue of direct leaching have caused concerns, and it has been presented (Li et al., 2014) that there is an urgent need to develop a cost-effective technology for proper treatment of such residue and for recovery of the elemental sulfur. Nevertheless, direct leaching processes are considered more environmentally friendly than the RLE process because sulfur dioxide is not produced, and furthermore, the capital costs are lower.

Pressurized direct leaching systems are operated at temperatures above 120 °C and at pressures up to 1600 kPa (Ozberk et al., 1995; Svens, 2012). Atmospheric leaching on the other hand is carried out near the boiling point of the solutions used (~100 °C) (Filippou, 2004; Svens, 2012).

The high oxygen pressure in the former leaching process enables fast concentrate dissolution, 90 min being the usual residence time. The direct atmospheric leaching process requires around 24 h for leaching, and larger reactors are therefore needed (Takala, 1999). Consequently, research work related to process development of atmospheric direct leaching reactors has tended to focus on improving the kinetics (Dutrizac, 2006; Salmi et al., 2010; Verbaan and Crundwell, 1986) and decreasing the oxygen consumption of the process (de Souza et al., 2007; Kaskiala, 2005).

Direct leaching processes can meet the requirements set for the metals producing industry, especially atmospheric direct leaching, so it is evident that direct leaching processes will play a significant role in zinc production also in the future. Increased investments (Outotec.com; Albionprocess.com) in these technologies in recent years and active research (Talonen, 2015; Xu et al., 2013; Zhihong, 2015) provide further evidence of the potentially promising future of direct leaching. However, direct leaching residues contain sulfur components and hazardous metals, which poses a significant disposal challenge (Li et al., 2014). Hence, development of a sustainable solution for direct leaching residues, so that sustainable operations can be assured, is a matter of urgency.

6.2 Thiosulphate leaching system for gold recovery

For the past century, hydrometallurgical recovery of gold from ores and concentrates has largely involved the use of cyanide as a lixiviant. However, the metals industry is under increasing pressure to reconsider the use of cyanide. Factors driving the move away from cyanide include a series of accidents involving cyanide contaminated tailings, which have worsened an already negative public perception of mining activities, the inability of cyanide solutions to effectively leach carbonaceous or complex ores, which has promoted interest in non-cyanide practices from the economical point of view, and increasingly stringent environmental legislation.

Many alternatives to cyanide have been presented, such as thiosulfate, halides, thiourea and thiocyanate (Hilson and Monhemius, 2006). Thiosulfate is considered the most promising

alternative, and there is already one example of industrial-scale use of thiosulfate for gold recovery (Choi et al., 2013). When the thiosulphate process is compared with conventional cyanidation, the thiosulphate process has the advantages of greater efficiency and versatility, as well as significantly lower environmental impact (Kerley, 1981; Wan et al., 1993). Thiosulphate liquors are also less prone to contamination by unwanted metal ions (Grosse et al., 2003) and hence can be used with a wide array of raw materials from primary and secondary sources. Furthermore, the liquors have good recycling potential.

The development history of thiosulfate leaching can be traced back to the 1900s when the recovery of precious metals using thiosulfate was first proposed (White, 1900). Early research tended to concentrate on leaching at high temperatures and pressures to prevent a copper sulfide and sulfur layer from forming on the gold particles and thus preventing their leaching (Aylmore and Muir, 2001). However, high reagent consumption tended to make the process uneconomical, and the focus is nowadays on using mild conditions (atmospheric pressure, low temperature and reagent concentrations). Many papers have been published and many patents have been filed in the area of thiosulphate leaching, but widespread commercialization of thiosulphate processes has not yet been achieved. The main reasons for this lack of acceptance in industry are that the solution chemistry is not understood adequately, thiosulphate-based processes have high reagent consumption, and recovery of gold after the leaching stage is challenging. The industrial context is, however, becoming more favorable; public concern regarding the use of cyanide is driving research and development in the direction of cyanide-free recovery of gold and the industrial application (Fig. 7) of thiosulfate-based processes possesses many of the features that are increasingly demanded of the metals producing industry, e.g. reagent recycling, environmental friendliness and safety. These requirements, together with problems encountered in the use of thiosulfate as a lixiviant, set a challenge for development of the leaching process, as leaching has a central role in hydrometallurgical recovery of metals.

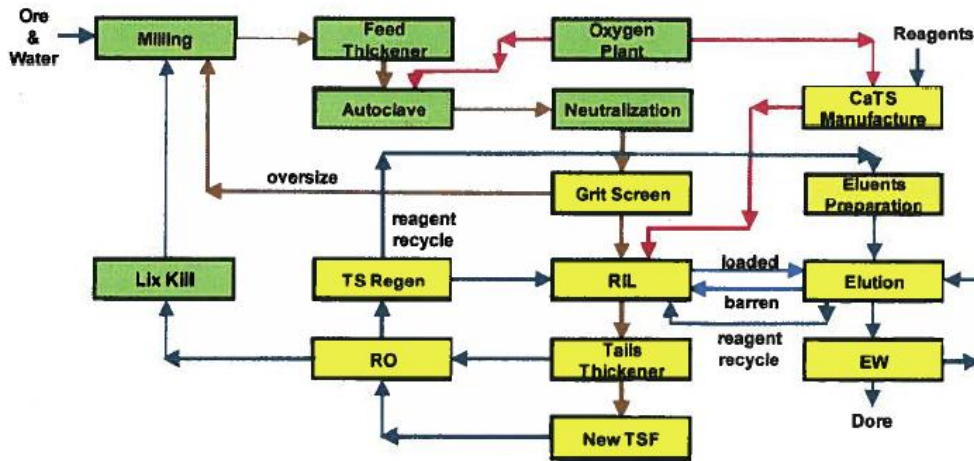


Fig. 7. Simplified flow sheet of Barrick's pressure oxidation and thiosulfate leaching processing plant. CaTS = calcium thiosulfate, RO = reverse osmosis, RIL = resin-in-leach, TS Regen = thiosulfate regeneration, EW= electrowinning. (Choi et al., 2013)

7. DEVELOPMENT OF HYDROMETALLURGICAL REACTOR LEACHING

Hydrometallurgical reactor leaching is a multiphase reaction system, and research and development of reactor leaching faces many of the challenges typically found with such reaction systems. A large number of physical and chemical phenomena are involved, only the most relevant of which can be taken into consideration and studied. Challenges are also posed by the raw material, as the composition of the ores and concentrates (i.e. the mineralogy of the ore and quality of the gangue materials) is always unique and quality can vary considerably. Consequently, although the method may be the same, every recovery plant has a unique process with different parameters and operating conditions. It is evident that implementing a new reactor leaching process or developing an already existing process requires in-depth knowledge of all the steps involved, and the phenomena behind the process should be well known and scientifically justified so that scaling up to industrial scale can be done effectively and reliably. Consequently, development of industrial reactor leaching has to be based on a detailed understanding of the thermodynamics and kinetics of the chemical reactions involved. Once this is achieved, mass and

heat transfer considerations can be assessed and aspects such as flow dynamics and capacity considered.

The industrial and societal context means that the metals producing industry is under pressure to find processes with reduced environmental impact, improved safety and lower energy consumption. In practice, this means the use of less harmful reagents, less drastic conditions (lower concentrations, temperatures and pressures, etc.) and recycling of waters and chemicals. Clearly, the thermodynamics and kinetics become more complex and, for example, solution chemistry and speciation of the process solution need to be handled for the process chain as a whole, including recycling of streams.

In leaching reactor development, it is important to examine operations at the plant scale and not just at the unit level. Thus, upstream as well as downstream processes and possible recycling of solutions need to be considered. In view of the complexity of the task, the use of sophisticated modeling and simulation tools is a valid approach for analysis of the important phenomena behind the leaching process, their interactions and relative importance. An outline of the development process for hydrometallurgical reactor leaching is presented in Fig. 8. The different parts of process development presented in Fig. 8 are discussed in the following chapters.

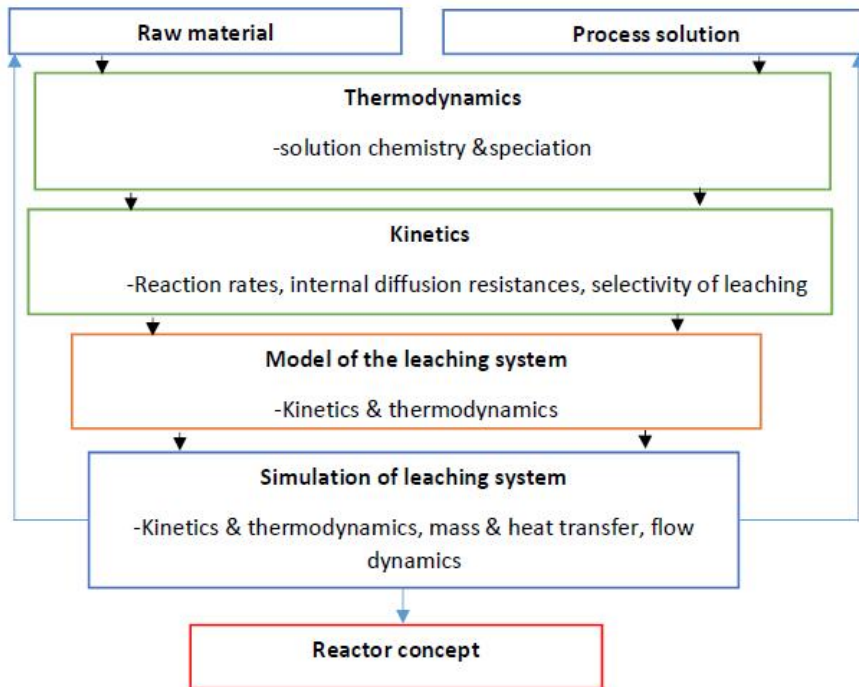


Fig. 8. Process development of hydrometallurgical reactor leaching.

7.1 Raw material

Knowledge of the composition and structure of the raw material used in the leaching stage is important because the mineralogy and morphology of the raw material has a significant effect on the efficiency and effectiveness of the leaching process. Moreover, the composition and structure of the leach residue is also important for the overall performance of the hydrometallurgical operations. The leach residues require proper handling so that sustainable operations can be achieved, hence it is important that remaining leach residue can be treated cost-effectively. Knuutila (2015) underlined that the mineralogy of the ore is the key factor for process selection. For direct leaching of zinc concentrates, it has been shown (Crundwell 1988a, b; Palencia-Perez and Dutrizac, 1991) that higher iron content in the sphalerite increases the leaching rate. Pre-

treatment stages, e.g., pressure oxidation or fine grinding, before leaching can have a significant influence on the leaching process. An important aspect in the first commercial application of thiosulfate leaching is pre-treatment in an autoclave (Braul, 2013). There is evidence that the gold form can change in the autoclave, with elemental gold potentially being changed to an ionic form such as a gold chloride salt (Braul, 2013). An important aspect of the Albion process is the combination of ultrafine grinding and oxidative leaching at atmospheric pressure. It has been presented (Albionprocess.com) that ultrafine grinding of a mineral to a particle size of 80 % passing 10-12 μm will prevent passivation of the raw material, as the raw material will disintegrate prior to the passivating layer becoming thick enough to passivate the raw material. Ore type is often the main driver in development of novel processes for hydrometallurgical processing, e.g. the first industrial application of a thiosulfate-based process for gold production was developed for sulfidic highly preg-robbing ores, which are difficult to treat with traditional cyanidation (Choi et al., 2013). Ore type can also be the driver for development of processes that are already operating, e.g. development of a zinc pressure leach process to recover gallium and germanium (Zhihong, 2015).

7.2 Thermodynamics

The first step in process development of reactor leaching is gaining a detailed understanding of the thermodynamics, since the thermodynamics predicts whether a reaction is possible or not. Most often, three types of thermodynamic equilibria should be considered in hydrometallurgical reactor leaching: solid-liquid equilibria, vapor-liquid equilibria and aqueous speciation equilibria. The Eh-pH diagram (Fig. 9) shows that to leach ZnS the conditions in the solution must be acidic and the potential of the standard hydrogen electrode must be positive (Takala, 1999).

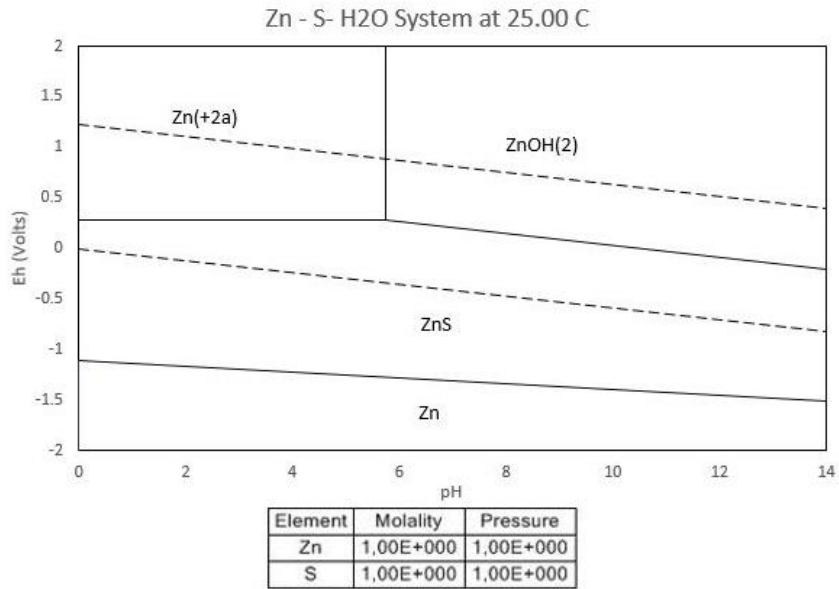


Fig. 9. Eh-pH-diagram of ZnS-Zn²⁺-equilibrium. Constructed using HSC Software (2015).

Oxygen is often used as an oxidant in hydrometallurgical reactor leaching. Hence, vapor-liquid equilibria of oxygen, its solubility phenomena and mass transfer are of importance:

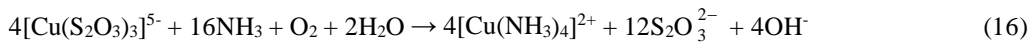
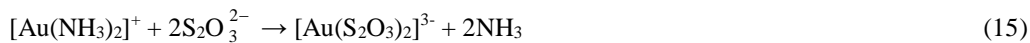
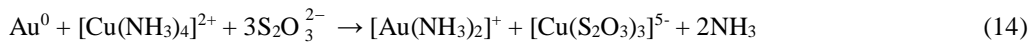


The sulfide concentrates used in zinc production usually contain small amounts of other non-zinc sulfides (Fe, Cu, Cd, Pb), which can also be leached from the concentrate. Hence, the composition of the process solution is highly complex and contains both zinc sulfates and components such as iron(II)sulfates, iron(III)sulfates, iron(II) and iron(III) complexes, sulfides, elemental sulfur and aqueous sulfuric acid. Aqueous speciation equilibria define the solution chemistry and speciation of process solution. It is evident that hydrometallurgical leaching processes are complex aqueous systems. The behavior of complex aqueous processing systems is

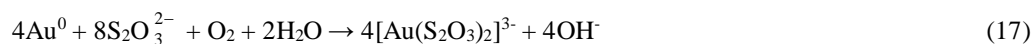
challenging to understand and predict. Understanding the behavior of the process solution is important from the process development point of view since it makes it possible to analyze, design, optimize and control the conditions of the leaching process. Chemical modeling of complex aqueous processing systems has undergone tremendous development in recent years, and modeling is becoming increasingly important in the development of hydrometallurgical processes (Liu and Papangelakis, 2005a). The chemistry of process solutions in direct leaching of zinc concentrates has been studied (Kobylin et al., 2007; Liu and Papangelakis, 2005b) as a part of efforts to develop the process.

7.2.1 Thermodynamics in gold recovery with thiosulfate leaching

Cyanidation is considered a robust technique for gold extraction, while the main challenge with thiosulfate leaching is its complex chemistry, which has been difficult to master. Unlike cyanide, thiosulfate is metastable and tends to undergo chemical decomposition under improper leach conditions. The system's stability can be affected by numerous factors. The solution chemistry and the gold leaching reactions are closely linked in thiosulfate leaching, and hence from a process development point of view, the thermodynamic studies should be coupled with kinetic studies. Thiosulfate leaching has been widely studied and solution chemistry aspects have been presented in a number of reviews (Aylmore and Muir, 2001; Grosse et al., 2003). The complicated chemistry of the thiosulfate leaching system is due to the simultaneous presence of complexing ligands (ammonia and thiosulfate), the stability of thiosulfate in solution, and the Cu(II)-Cu(I) redox couple. The reactions that describe the leaching behavior of gold in an ammoniacal thiosulfate system are shown below (Eqs. (14) – (17)) (Grosse et al., 2003):



The net reaction:



Important steps in the development have been the results of solution chemistry and speciation studies, e.g., work that revealed the involvement of $\text{S}_2\text{O}_3^{2-}$ in the gold dissolution mechanism in gold extraction with $\text{Cu(II)-NH}_3\text{-S}_2\text{O}_3^{2-}$ (Perera and Senanayake, 2004) and the extra stability of the $\text{Au(I)-S}_2\text{O}_3^{2-}\text{-SO}_3^{2-}$ system (Perera et al., 2005). These studies indicate the importance of solution chemistry research to development of thiosulfate leaching. The former fundamental study is important for understanding of the leaching behavior, while the latter is important for the discovery of an efficient elution process (Breuer et al., 2012; Muslim, 2015). Perera et al. (2005) studied an $\text{Au(I)-S}_2\text{O}_3^{2-}\text{-SO}_3^{2-}$ system using hydrodynamic voltammetry, gold potentiometry, UV-Vis spectrophotometry and Raman spectroscopy and presented a speciation diagram of the $\text{Au(I)-S}_2\text{O}_3^{2-}\text{-SO}_3^{2-}$ system (Fig. 10).

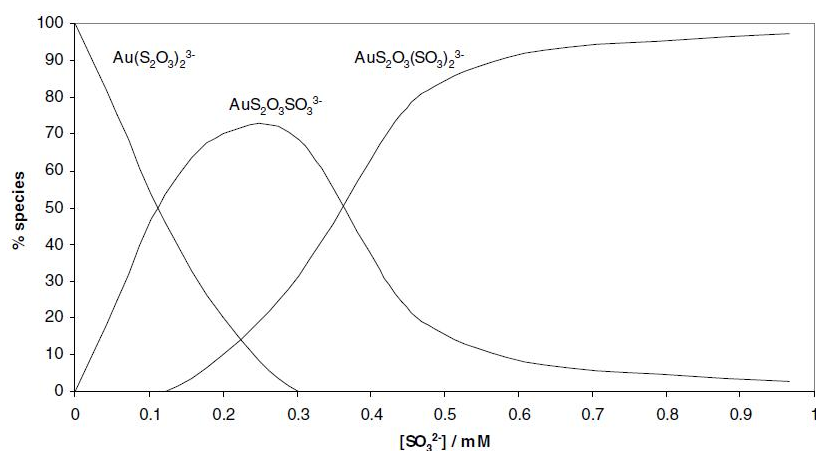


Fig. 10. Speciation diagram of the $\text{Au(I)-S}_2\text{O}_3^{2-}\text{-SO}_3^{2-}$ system at $[\text{Au(I)}] = 0.23 \text{ mM}$. (Perera et al., 2005).

7.3 Kinetics

Once thermodynamically favorable conditions have been found, kinetic studies are required, since kinetics determine the possibility of the reaction to occur in finite time and in a time frame acceptable for commercial application. The major factors governing the rates of chemical reactions are the concentrations or activities of the reacting species, temperature, pressure and mass and heat transfer limitations. Reaction rates are usually studied in laboratory reactors, because well-controlled reaction conditions can be obtained at a small scale (constant temperature and pressure, gradient free conditions, rapid mass and heat transfer) and for economic reasons. Commonly, the laboratory experiments are carried out in batch, semi-batch or continuous reactors. The progress of the leaching reaction is often monitored by determining the product concentration in the liquid phase and/or observing the changes of the solid phase. Various analytical techniques are available for determining the product concentrations in the liquid phase, such as atomic absorption spectrometry (AAS), inductively coupled plasma (ICP), liquid chromatography and titrimetry. Methods for observing changes in the solid phase include X-ray diffraction (XRD), scanning electron microscopy (SEM) and laser diffraction.

Only a few parameters, for example temperature, pressure, and pH, can be reliably determined in-situ. Hence, kinetic studies rely greatly on sampling. Modern analytical techniques allow precise analyses of liquid samples, and representative liquid samples can be obtained rather easily. However, analyzing the structure and structural changes (e.g. product layer formation) of the solids remains challenging. Representative sampling of solids can be challenging since the solids in the sample treatment are usually dried prior to analysis, which is not representative of the actual leaching process, where the solid is immersed in a liquid. Analytical methods exist for determining the overall surface area of solids, e.g. mercury porosimetry and gas physisorption, but they are not very precise for low surface areas and furthermore they are rather time-consuming (Diamond, 2000; León y León, 1998; Sing et al., 1985). Hence, determining the actual reactive surface area, which would be an optimum parameter for kinetic studies, remains a major challenge. This creates difficulties for determining the kinetics of leaching processes, because the influence of particle size distribution and change in the morphology of the solids in

the course of the leaching are crucial factors. Moreover, the behavior of the raw material can be highly unpredictable, as mean particle size might increase in some cases and decrease in others (Crundwell et al., 2013). Hence, development of analytical techniques together with modeling and simulation procedures are needed in order to overcome these difficulties.

7.4 Simulation of leaching system

As presented above, there are a large number of physical and chemical phenomena in hydrometallurgical leaching systems, and only the most relevant of them can be taken into consideration and under study. Hence, there is a need to identify the process parameters that affect the process as a whole and to target process development resources at these parameters. Simulation of the leaching system can contribute significantly to these efforts by identifying important process parameters. Furthermore, simulation of leaching systems offers effective tools to design the experimental work related to process development, since the effect on the process of changes in the identified parameters can be evaluated by simulation. Consequently, the time required for experimental work is reduced and the costs of process development decrease notably, as experimental work is typically the most time consuming and expensive part of process development. Simulations can contribute significantly to process control and optimization in such a way that the effect of changes in the processing plant can be anticipated and optimization can be carried out more thoroughly. As a consequence, improved safety and cost-effectiveness can be achieved.

8. EXPERIMENTAL WORK

A detailed description of the experimental design and experimental work is given in Publications II and III.

8.1 Thiosulfate leaching of pressure oxidized sulfide gold concentrate

Experimental data were obtained by from a 1.1 dm³ batch reactor (d = 8.4). Pressure oxidized gold concentrate received from a gold mine was used in the leaching experiments. All the solid samples (gold concentrate received from a gold mine and leaching residues) were analyzed by a commercial analytical laboratory (Labtium). Metal concentrations in the liquid samples were analyzed by atomic absorption spectroscopy (Thermo Scientific iCE 3000 Series AA spectrophotometer). The thiosulfate concentration in the liquid samples was analyzed by ion chromatography (Thermo Scientific DIONEX ICS-1100 Ion Chromatography System). An IonPac AS22 analytical column and IonPac AG22 guard column were used for the analyses.

8.2 Direct leaching of zinc sulfide concentrate

Leaching experiments of the zinc sulfide concentrate were carried out as batch experiments in a 1.1 dm³ autoclave reactor. Metal concentrations of the solutions samples were analyzed with atomic absorption spectroscopy (Thermo Scientific iCE 3000 Series AA spectrophotometer). Ferrous ion concentrations and sulfuric acid concentrations were analyzed by titration with potassium dichromate and by iodometric titration with sodium thiosulfate, respectively.

9. MODELING

Mathematical modeling of leaching systems is usually used to interpret experimental results and to gain insight into the reaction mechanism. In principle mathematical models used in hydrometallurgy are divided into mechanistic models and empirical models. Mechanistic models are based on physico-chemical fundamentals, while empirical models are built by inferring relationships between variables directly from the available data. Empirical models are used in many cases (Herney-Ramirez et al., 2008; Salmimies et al., 2013), especially when the number of phenomenon involved is vast and/or the phenomena cannot be modeled exactly. However, mechanistic modeling is preferred, because the cause-effect relationship are more apparent, which aids effective and reliable process development.

The leaching kinetics of a solid raw material depends on the processes taking place at the solid-liquid boundary. These processes are complex and can involve chemical reactions and mass transfer. The leaching reactions can occur at the surface of the solid, in the film around the solid, or in the liquid bulk phase. A number of models (Dickinson and Heal, 1999; Órfão and Martins, 2002; Levenspiel, 1999) for dissolution reactions have been developed, of which the major models for non-catalytic solid-liquid reactions are the shrinking core, shrinking particle, homogeneous and grain models. The shrinking core model (SCM) is widely used to model fluid-solid reactions and also to model leaching of metals from raw materials (Gbor and Jia, 2004). Commonly, conclusions regarding particle shapes and reaction mechanisms are based on comparing different models to the experimental data and evaluating which model gives the best fit. If a shrinking sphere mechanism is assumed, $1-(1-\alpha)^{1/3}$ (where α is conversion, Levenspiel (1999)) is plotted as a function of time for the experimental data, and if the plot gives a linear correlation, the assumption is considered to be correct. Analogously, $1-3(1-\alpha)^{2/3}+2(1-\alpha)$ is plotted for the data if a shrinking core is assumed. Typically, it is assumed that the morphology of the solid raw material is uniform and has some ideal, non-porous shape, e.g. sphere or slab. Model parameters such as activation energy (E_a) and pre-exponential factor (k_0) can also be obtained by fitting the model to experimental data. This methodology is widely used but is not unproblematic. Discrimination of the models can be challenging and several models may fit the experimental data (Pecina et al., 2008; Espiari et al., 2006; Grénman et al., 2011; Markus et al.,

2004), especially in cases of non-ideal behavior, more complex kinetics (e.g. several rate limiting step changes in time) and when considerable scattering in the experimental data exists.

As discussed earlier, requirements set for the metals producing industry make development of hydrometallurgical processes difficult. Behavior of the process solution and raw material in non-ideal conditions (e.g. non-identical concentrations of components through the reactor, non-monosized particle feed and non-ideal mixing) need to be comprehended in order to achieve the techno-economical goals set for metals production. Hence, more rigorous modeling is needed in terms of describing the behavior of process solution and solid raw material, and to guarantee the reliability of the modeling.

Different steps can determine the leaching rate, such as mass transfer, chemical reaction or charge transfer. The ultimate goal in kinetics studies of leaching is to understand what controls the rate of the leaching, so that the process can be manipulated and controlled. However, this is not always a straightforward task as the rate determining step in hydrometallurgical leaching is always dependent on the reaction conditions and the raw material. In the case of direct leaching of zinc sulfide concentrates, there is not complete agreement on the rate determining step; some authors state that the leaching rate is controlled by the chemical (Dutrizac, 2006; Göknan, 2009; Markus et al., 2004; Pecina et al., 2008; Salmi et al., 2010) or electrochemical reaction (Verbaan and Crundwell, 1986), while others propose (da Silva, 2004; Lochmann and Pedlík, 1995; Weisener et al., 2004; Souza et al., 2007) that mass transfer through the product layer controls the overall rate. Usually, the overall kinetics is controlled by several rate limiting steps and, hence, experimental studies together with modeling and simulation are required to achieve effective process development.

9.1 Quantification of raw material

The structural properties of the solid particles influence significantly the progress of the reaction, thus quantification of the solid particles is of importance. Quantification of the reactive surface area is a key goal when modeling solid particles dispersed in a liquid because the reaction rate depends on the reactive surface area. This makes the modeling task complicated, as quantification of the reactive surface area is not straightforward, e.g. the total surface area is not always equal to the reactive surface area. In hydrometallurgical applications, the solid particles are often heterogeneous, comprising several compounds, and extreme conditions might sometimes lead to changes in the solid particles, e.g. a possible change of elemental gold to an ionic form in the autoclave (Braul, 2013).

The reactive surface is in most cases difficult to quantify, especially in situ, hence for modeling purposes, assumptions need to be made regarding solid particle behavior. Commonly, the total surface area is determined and the change in the surface area is correlated to reactant conversion. Particle characterization should be carefully considered in the modeling task, otherwise inaccurate conclusions can be drawn, e.g. erroneous shift in the control regime resulting from neglect of PSD was quantified by Gbor and Jia (2004), who also pointed out that in most cases PSD of the solid material is disregarded. Furthermore, it has been noted (Crundwell et al., 2013) that surprisingly little work has been published on the effect of PSD on leaching reactor performance. Clearly, particle size distribution should be implemented in modeling, but it is also important to consider the surface morphology of the particles. In some cases (Souza et al., 2007) particles might be porous, and for that reason, particle size might play only a minor role in the leaching process, while the importance of pore diffusion is pronounced. Kinetic modeling together with particle characterization analysis offers the best approach to study the role of solid particles in reactor leaching.

9.2 Process solution

When considering the modeling of particulate leaching reactors it has been presented (Crundwell and Bryson, 1992) that in order to produce a reliable leaching reactor model, it is important to have experimental data for the kinetics of the leaching at the conditions of the industrial process. In practice, this means non-ideal particles, concentrated solutions, and non-uniform concentration profiles in the solution. Leaching conditions thus change depending on the position in the reactor and time from the start of the reaction. Changing concentrations of the solution should be taken into account in process development. However, kinetic studies are most often conducted in dilute suspensions to guarantee that concentrations stay constant. Fugleberg (2012) presented results (Fig. 11) from a pilot study that demonstrate the evolution of concentrations of sulfuric acid, iron and zinc. Zinc leaching rate has been presented (Dutrizac, 2006) to decrease with increasing initial concentrations of $ZnSO_4$, $MgSO_4$ or $FeSO_4$ in the ferric sulfate leaching solution, which emphasizes the importance of controlling the sulfate concentration of the leaching solution and maintaining the dissolved iron in a fully oxidized form in commercial applications.

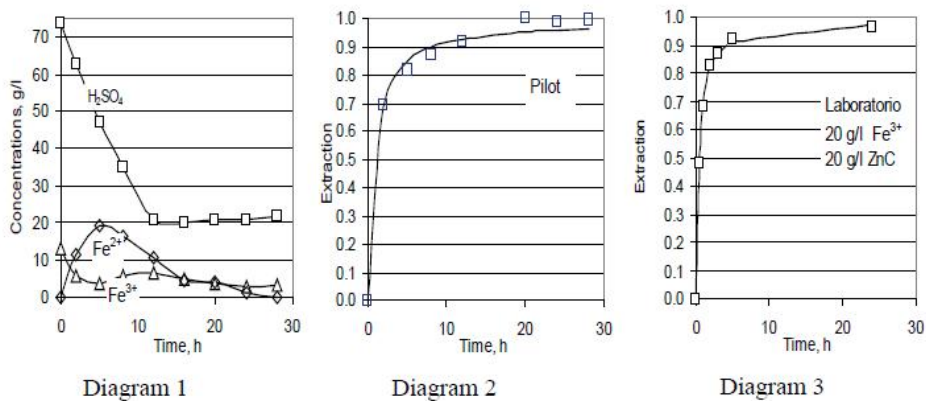


Fig. 11. Behavior of sulfuric acid and iron (Diagram 1) and zinc extraction during a batch pilot run of direct leaching of zinc sulfide concentrate (Diagram 2). Zinc extraction of a laboratory test is shown in Diagram 3. The lines in Diagrams 2 and 3 are obtained with the Avrami model. (Fugleberg, 2012)

The importance of understanding the process solution is emphasized in gold recovery with thiosulfate leaching. Mastering the fluctuating solution conditions is a key factor in process development of gold recovery with thiosulfate leaching (Jeffrey et al., 2003; Senanayake, 2005; Wan, 1997). Thus, modeling the solution chemistry and speciation is of great importance.

9.3 Parameter estimation

Established leaching models are usually complicated and include several experimental parameters. Parameter estimates are often uncertain, since they are estimated from incomplete and noisy measurements. The reliability of the parameters is very important, as this reliability is reflected in the reliability of the modeling, and ultimately, the reliability of the process simulation. Hence, the reliability of the model parameters should be studied carefully, for which purpose advanced mathematical methods and statistical analysis offer effective tools. The main task of statistical analysis of mathematical models is quantification of uncertainty. Traditionally, in nonlinear model fitting, point estimates for the parameters are obtained, e.g. by solving a least squares optimization problem. The result of the statistical analysis is typically given in a Gaussian form (as a covariance matrix). Nowadays, use of a Bayesian framework for model fitting has become a popular approach for dealing with uncertainty in parameter estimation (Solonen, 2011). In Bayesian model fitting, the parameters are considered as random variables, and the target for estimation is the distribution of the parameters rather than a point estimate. In the Bayesian approach, both the data and the prior knowledge of the parameters are modeled statistically, which gives a solid basis for the uncertainty analysis. Markov Chain Monte Carlo (MCMC) sampling methods, in particular, have made it possible to solve many nonlinear parameter estimation problems in a fully statistical manner, without performing, for example, Gaussian approximations (Solonen, 2011). In MCMC, the parameter distribution is approximated by producing a set of random samples from the parameter. Thus, the answer to a given parameter estimation problem is given as a ‘chain’ of parameters instead of a single estimate (Solonen, 2011).

When the applicability of the model is assessed, the range of operating conditions, the fit of the model (e.g. coefficient of determination) and the reliability of the model parameters should be carefully considered. A high degree of explanation together with well identified parameters can usually be achieved if the experimental data are from a narrow range (small changes in concentrations, temperatures etc.), but the applicability of the model may be limited to this narrow range. Though interpretation of the leaching results is mainly based on determining kinetic parameters and the necessity for accurate kinetic parameters in process models has been stressed (Baldwin and Demopoulos, 1998), surprisingly little attention is paid to the reliability of the parameters, even though sophisticated mathematical methods for assessment of reliability are widely available.

10. SIMULATION

When models for the phenomena behind the process have been established, operation of the whole process should be considered, which can be done by process simulation. When considering reactor leaching on the industrial scale, the overall reaction rate is often limited by external and internal mass transfer and heat transfer. Hence, reliable process development, design and scale-up requires a reactor model that can be used to simulate the effects of the different factors involved (e.g. mass transfer and heat transfer, temperature, pressure, particle size etc.) with high enough accuracy for the studied case. The simplest procedure to model ideal perfectly mixed reactors is to perform mass balance calculations that assume that the temperature and concentration of all components is uniform throughout the reactor and also at the outlet of the reactor. This type of study is usually considered to be adequate in the initial phase of modeling and simulation studies (Nikkhah, 1998), although it neglects the effect of particle size distribution and residence time distribution on the reactor performance. When considering reactors with non-ideal behavior, as in the case of hydrometallurgical reactor leaching, the residence time and particle size distributions need to be considered to guarantee desirable accuracy. Several models exist for estimating the performance of reactor leaching (Fogler, 1999). The population balance method (Papangelakis and Demopoulos, 1992b; Crundwell et al., 2013; Baldwin et al., 1995; Rubisov and Papangelakis, 2000) and segregated flow model (Papangelakis

et al., 1990; Papangelakis and Demopoulos, 1992a, 1992b; Crundwell et al., 2013) have been used to predict the performance of reactor leaching with non-ideal characteristics. Both approaches are actually population balances (Crundwell 1994, 2005), with the first corresponding to the maximum-mixedness assumption (Zwietering, 1959) and the second to the segregated-flow mixing assumption (Zwietering, 1959). Based on a view that conditions in reactor leaching are more likely to be described by maximum-mixedness, the population balance is considered to be the preferable approach (Crundwell et al., 2013). The overall mass balance approach is a simple technique that allows easy calculation, and approximate outcome, while the population balance method is more rigorous but is complex and difficult to apply, especially with multistage reactor leaching (Dorfling et al., 2013).

As metals producing industry processes are moving in the direction of the use of less drastic conditions, atmospheric conditions together with lower concentrations and increased circulation of the process solutions need to be applied in reactor leaching. It is clear that larger scale reactors are needed to reach desired production rates, which in turn means that ideal mixing cannot be assumed. The overall rate of leaching stage can be limited by gas diffusion into the aqueous phase in moderately agitated stirred tank reactors (Adams and Mathew, 1981). Ferrous oxidation by dissolved oxygen has been presented (Dreisinger and Peters, 1987) controlling the overall rate of direct pressure leaching of zinc in the early stages of the process, and clearly, the lack of poorly soluble oxygen in the solution is accentuated at atmospheric conditions. Hence, simulation models are needed, that take into account non-ideal mixing, non-uniform concentration and pressure profiles, non-ideal raw material, multiple reactions and rate limiting steps, and that are able to use detailed descriptions of gas-liquid mass transfer (e.g. in the case of atmospheric direct leaching of zinc concentrates, where tall reactors are used).

11. RESULTS AND DISCUSSION

11.1 Experimental results

In this work the ammoniacal thiosulfate leaching experiments (Publication I) on pressure oxidized gold concentrate received from a gold mine show that leaching can be mastered using low reagent concentrations. The copper concentration of the solution is critical, since increased copper concentrations can lead to precipitation of leached gold (Publication I, Fig. 8). The highest gold extraction (89 %) was achieved in 6 h with the following leaching solution: 0.2 mol S_2O_3/L , 0.2 mol NH_3/L , 0.1 g Cu/L ; and with the following conditions: solids, 30 m-%; pressure, 1 atm; continuous aeration; and temperature, 30 °C. Measured thiosulphate and copper concentrations after 6 hours of leaching were 0.19 M and 0.08 g/L, respectively. Measured pH varied between 9.8 – 10, oxidation potential between 199 – 215 mV, and concentration of dissolved oxygen in the slurry between 5.0 – 6.3 mg/L.

The results from the direct leaching experiments of zinc concentrate (Publication II) show that temperature, pressure, particle size of the concentrate, and the iron and sulfate concentration of the slurry are the key parameters that have substantial effect on the leaching. The results further show that the temperature has a great impact (Publication II, Fig. 2) on the zinc concentrate leaching rate and solution composition, and that the sulfate concentration (Publication II, Fig. 5), in particular, has an important effect on the leaching kinetics.

11.2 Modeling results

In Publication III, a numerical mechanistic model based on the SCM approach is described and fitted to data described by Souza et al., (2007). The model solves numerically, from the mass balance, the concentration of ferric ion at the reacting surface for the direct leaching of zinc sulfides. At the reacting surface, the mass balance for ferric ion can be written as:

$$2k_1 c_{Fe^{3+},s}^{n_1} c_{H_2SO_4}^{n_2} A_i - D_e A_o \frac{r_i (c_{Fe^{3+}} - c_{Fe^{3+},s})}{(r_o - r_i) r_o} = 0 \quad (18)$$

The reliability of the model parameters is studied with MCMC methods. Application of the model presented in Publication III allows construction of simulated curves that describe the actual leaching rate (r_{SD}) over the leaching rate (r_S) without diffusion limitations (leaching agent concentration at the surface equals the bulk leaching agent concentration):

$$\frac{r_{SD}}{r_S} = \frac{k_1 c_{Fe^{3+},s}^{n_1} c_{H_2SO_4}^{n_2}}{k_1 c_{Fe^{3+}}^{n_1} c_{H_2SO_4}^{n_2}} = \left(\frac{c_{Fe^{3+},s}}{c_{Fe^{3+}}} \right)^{n_1} \quad (19)$$

Results in Publication III show that the presented modeling approach allows to the different rate limiting steps to be distinguished, and it is possible to determine whether the leaching is under chemical, diffusion or mixed control. This is an important feature as it is the interaction of these rate controlling steps controlling the apparent leaching kinetics that is most often determined in kinetic studies. Hence, it can be argued that the presented modeling approach gives more thorough and in-depth insight into the leaching kinetics. If the ratio presented in Fig. 12 is close to unity, the leaching is mainly controlled by the intrinsic surface reaction. If, on the other hand, the ratio is low ($\ll 1$), this indicates that the overall leaching rate is limited by diffusion of the leaching reagents or leaching products. Between these two cases, the leaching rate is affected by both the reaction and diffusion. The modeling results show that the leaching process is mainly under diffusion control, thought to be due to pore diffusion and formation of an elemental sulfur product layer. With low sulfuric acid concentrations the rate controlling step was found to change from mainly intrinsic surface reaction control to mixed control as the leaching proceeds. The rate was determined to be proportional to sulfuric acid concentration to the power of 1.3, showing that sulfuric acid has a crucial influence on the leaching kinetics. Thus, the results further indicate that the reaction between sphalerite and the ferric ion goes through a state where sulfuric acid participates as an intermediate.

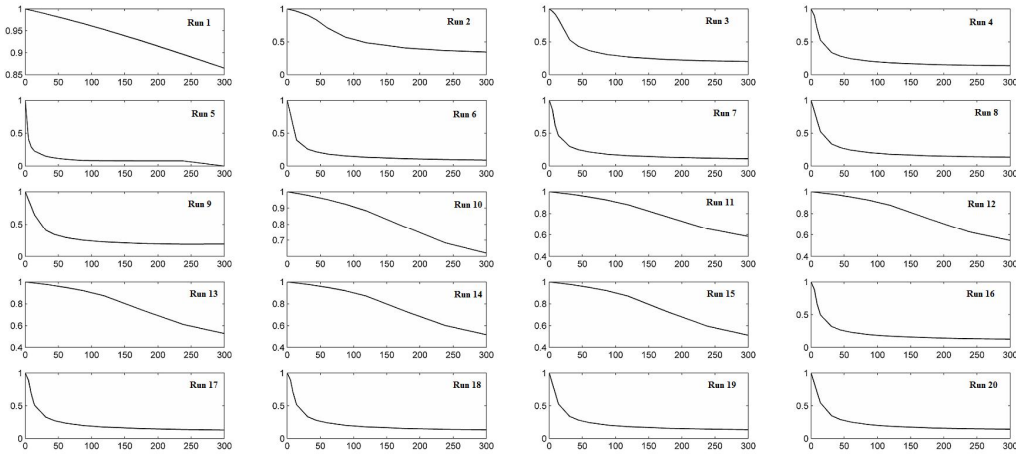


Fig. 12. Effect of internal diffusion on the leaching system. The ratio (r_{SD}/r_S) of the actual leaching rate (r_{SD}) over the leaching rate (r_S) without diffusion limitations on the y-axis and time (min) on the x-axis.

In Publication IV, the same modeling approach is used as in Publication III, and a MCMC method is employed to analyze the reliability of the model parameters, which allows the rate determining steps to be studied more closely. Data used for the model fitting is presented by Dutrizac (2006). The results presented in Publication IV are in agreement with the results presented by Dutrizac (2006). Dutrizac (2006) proposed that the apparent activation energy for leaching is 44 kJ/mol and concluded that the relatively high activation energy indicates that the rate is chemically controlled. Additional rotating disk experiments by Dutrizac (2006) support this conclusion. Dutrizac (2006) proposed a reaction order of 0.34 at 100 °C and 0.39 at 75 °C for ferric ion concentration. In Publication IV, 39 kJ/mol is proposed for the activation energy of the intrinsic surface reaction and a reaction order of 0.34 for the ferric ion surface concentration. The value determined in Publication IV for the internal diffusion coefficient was relatively large ($4.98 \times 10^{-5} \text{ m}^2/\text{min}$) and the MCMC analysis clearly showed that the parameter was not well determined. Based on the results from the modeling, it was concluded in Publication IV that the rate is undoubtedly chemically controlled. The MCMC analysis showed cross-correlation between parameters n_1 and $k_{1,\text{mean}}$, which lowers the reliability of these two parameters. Simulated curves (the actual leaching rate over the leaching rate without diffusion limitations)

were constructed in the work, and they gave a value of 1 for all the experiments, meaning that leaching agent concentration at the surface equals the bulk leaching agent concentration. Hence, the simulated curves support the conclusion that the leaching rate is chemically controlled, and thus the activation energy determined for the intrinsic surface reaction (39 kJ/mol) is comparable to the apparent activation energy (44 kJ/mol) determined by Dutrizac (2006). Additionally, the proposed reaction order of 0.34 for ferric ion surface concentration is comparable to the reaction order of 0.34 at 100 °C and 0.39 at 75 °C for ferric ion concentration determined by Dutrizac (2006). Consequently, it can be claimed that the model predictions are plausible and the modeling approach gives more in-depth understanding of parameter reliability by showing the cross-correlation between parameters n_1 and $k_{1,\text{mean}}$.

As discussed above, when assessing the applicability of a model, the range of operating conditions, the fit of the model (coefficient of determination) and the reliability of the model parameters should be carefully considered. These issues are discussed in Publication II, where models developed for simple solutions were applied to a more complex solution having a composition close to that found in industrial applications. The mechanistic model developed by Salmi et al. (2010) for leaching of zinc with ferric ions could not describe the leaching process with an acceptable level of accuracy, and, hence, an alternative model had to be developed, which was presented in Publication III. Although the coefficient of determination of the model presented by Salmi et al. (2010) was reasonable (91.37 %), notable uncertainty in the parameter values was discovered. This can be seen from the results of the MCMC analysis shown in Fig. 13, which illustrates two-dimensional posterior distributions for the parameters. Each dot in the figure represents a sample in the Markov chain. The density of the dots represents probability. The contour lines in the figures represent 50 % and 90 % probability regions. Fig. 13 shows in graphical form the identifiability and cross-correlation between the parameters. In the ideal case, the dots are tightly centered in a circular form around the most probable point. The 1-dimensional projections on the axis show a sharp peak in the probability. This is not the case for the parameters in Fig. 13, thus indicating uncertainty and cross-correlation in the parameters. This finding emphasizes the importance of rigorous parameter estimation and analysis in model development.

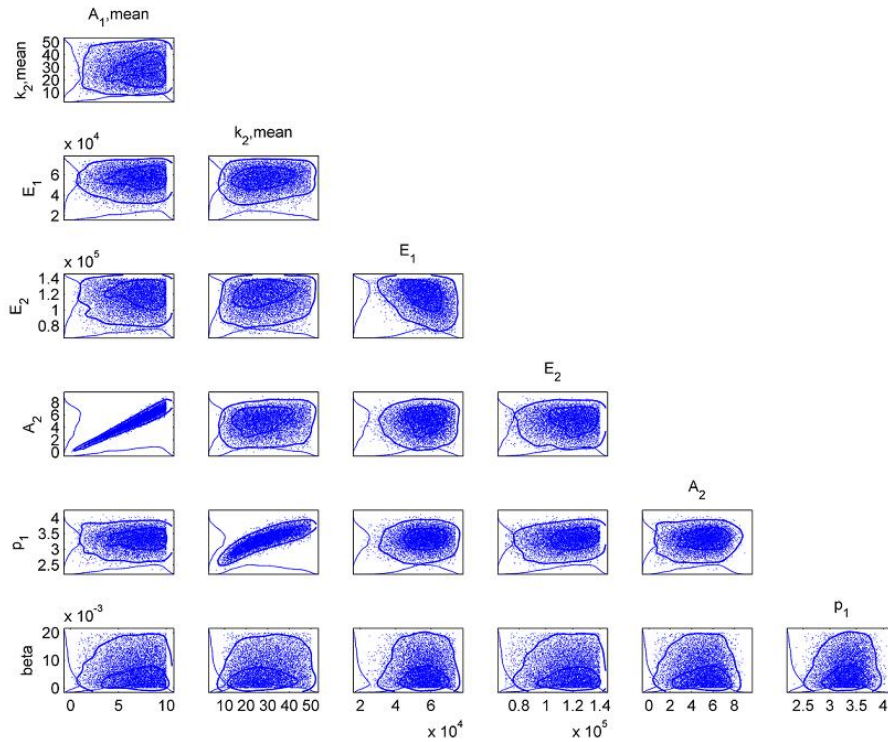


Fig. 13. Results from MCMC-analysis showing two dimensional posterior probability distributions. The parameters are defined in Publication II.

Some uncertainty and cross-correlation was observed also in the model presented by Rönholm et al., (1999) used to describe the kinetics of the oxidation of Fe^{2+} to Fe^{3+} in Publication III (Fig. 9, Publication III). Uncertainty and cross-correlation in the result was attributed to the more complex process solution used in Publication III than in the work by Rönholm et al. (1999).

As presented earlier, one of the most crucial factors in the modeling is the influence of particle size distribution and change in morphology of the solids during leaching. Publication II presents a model that includes particle size distribution and demonstrates its use for interpretation of the results of leaching experiments. Population balances were used when the dissolution rate of zinc was calculated. The concentrate particles were divided into six classes. The dissolution rate for

each class was calculated using an average particle size and the portion of particles in the class. Finally, all classes were summed to obtain the overall leaching rate of the zinc. The dissolution rate of zinc can be described by the following equation.

$$-\frac{dc_{zn}}{dt} = \sum_{N=1}^6 r_2 A_{i,N} n_N P_N \quad (20)$$

Changing process solution concentrations can have an effect on the leaching process. The model presented in Publication II is numerical and allows the changing sulfuric acid and ferric ion concentrations determined in the leaching experiments to be taken into account, thus incorporating the effects of changing process solution conditions.

The results presented in Publications II, III and IV show that the presented modeling approach together with MCMC analysis can give more detailed information on model performance in terms of separation of the different mechanisms involved (surface reaction, diffusion, mixed control), in-depth insight into parameter reliability, and description of the changing properties of the solid raw material (PSD, pore diffusion, product layer formation), thus promoting more efficient development of reactor leaching.

11.3 Simulation results

In Publication IV, a pseudo-homogeneous simulation model for direct leaching of zinc concentrates is developed that allows evaluation of how concentration and process variable changes are distributed along the height of a tall industrial reactor. This is an important feature from the process development, design and optimization point of view. Leaching results gained from laboratory scale batch tests might be significantly different from those observed in industrial scale reactors. Hence, scale-up from laboratory scale to larger scale requires effective and reliable simulations so that the performance of the leaching stage can be evaluated and the downstream operations can be accurately determined. A particularly important feature of the

developed model is that it allows the oxidation-reduction cycle of the iron and behavior of oxygen (e.g. molar flow, gas velocity) to be simulated, as they can control the overall kinetics in the course of the leaching. Furthermore, oxygen consumption is important for the economics of reactor leaching, especially in the case of direct leaching of zinc concentrates. The performance of the developed simulation model can be improved by conducting kinetic studies in the way presented in Publication II. This approach improves the simulation, since the kinetic model takes into account non-uniform concentration profiles, conditions close to industrial applications and particle size distribution. Hence, the simulation model is an effective tool for evaluation of leaching processes and downstream operations, and thus it can contribute to efforts to increase the throughput of hydrometallurgical operations.

12. CONCLUSIONS

This thesis work studied development of hydrometallurgical reactor leaching. Such development requires comprehensive understanding of the process solution and solid raw material behavior by mastering the thermodynamics and kinetics of the processes. This kind of a comprehensive understanding can be achieved by experimental methods and by the use of rigorous modeling and simulation approaches. The two reactor leaching processes investigated were thiosulfate leaching for gold recovery and atmospheric direct leaching for zinc recovery.

In this work, new experimental data were presented that increase understanding of phenomena related to the two reactor leaching processes studied. The ammoniacal thiosulfate leaching experiments of pressure oxidized gold concentrate show that gold can be effectively leached with thiosulfate as a lixiviant using low reagent concentrations in the leaching stage and pressure oxidation as a pretreatment method. This approach enables low reagent consumption and facilitates the following recovery stage, and the stability of the process solution, which makes re-use of the leaching solution possible. The experiments performed in this work provide new data on the leaching of gold with thiosulfate as a lixiviant and brings new insights into the leaching chemistry. New experimental results are presented for direct leaching of zinc concentrate in conditions close to found in industrial leaching processes. The results from the experiments of direct leaching of zinc concentrate show that the solution composition has an effect on the leaching kinetics, which clearly demonstrates that it is important to have experimental data for the kinetics of the leaching at the conditions of the industrial leaching process.

A modeling approach is presented, that brings new understanding to process development. The most significant contribution of the modeling approach used in this work can be found in the quantitative modeling of the solid raw material, with inclusion of particle size distribution, determination of the role of internal diffusion in the kinetic studies, and the application of sophisticated mathematical methods (MCMC methods) to study the reliability of the established model. The presented modeling approach offers a way to discriminate and study the phenomena

behind the leaching process in detail and with high reliability. The simulation approach developed for direct atmospheric leaching of zinc concentrates enables evaluation of the role of various phenomena in the course of the leaching. The simulation approach is a useful tool for development, analysis, design, optimization and control of such complex leaching processes.

Development of novel technologies together with development and optimization over the whole process chain of already existing technologies are aspect of the metals producing industry's efforts to respond to economic and environmental concerns of modern society. Such development can only be achieved by improving understating of the phenomena driving metal recovery processes. In the case of hydrometallurgical reactor leaching, which is characterized by considerable complexity, sophisticated mathematical modeling and simulation procedures need to be applied alongside experimental procedures. Sophisticated modeling procedures need to be adopted in kinetic and thermodynamic studies in the field to ensure rigorous and reliable models, which in tum are the foundation of simulation work. Understanding of the behavior of the raw material and process solution and utilization of reliable models in simulation work provide good premises for the development of not only the leaching stage but also downstream processes.

Development of advanced analytical techniques, for example, X-ray micro computed tomography (XMT or Micro-CT), can provide improved characterization of the solid raw material, as the nature of particles becomes more visible, and this information can be used to improve modeling precision and reliability. The actual shapes of the particles and the real distributions of the mineral grains can be used in the modeling rather than assumptions such as ideal shapes of particles (e.g. spherical particles) and uniformly distributed mineral grains. Chemical modeling development allows the behavior of process solutions in hydrometallurgical processes to be described more accurately. Improved understanding of the solid raw material and process solution give greater sight into the leaching process, thus allowing more thorough and reliable models to be constructed. As a consequence, more rigorous simulation of hydrometallurgical processes becomes possible, thus providing better premises for process development, analysis, design and control. However, the amount of data to be analyzed increases

notably, and inclusion of data mining and intelligent systems into simulation models is required, so that relevant information can be extracted.

13. SUGGESTIONS FOR FUTURE WORK

To achieve sustainable operations, the focus of process development in the area of metals recovery needs to be shifted from 'end-of-pipe' to more systematic recycling and reuse of process streams.

In direct leaching of zinc concentrates, development of cost-effective technology to handle leaching residues properly and to recover the elemental sulfur is urgently required. This need will be a main driver of future research, and best outcomes will be achieved by developing the whole process chain such that raw material input is utilized with a minimum amount of waste. Experimental results show that increasing sulfate concentration of the leaching solution decreases the leaching rate in direct leaching of zinc concentrate, and the role of sulfates should therefore be studied more closely. The role of sulfuric acid in the course of leaching remains partly uncertain, and further studies on this issue could help to understand the leaching process more thoroughly. It has been shown by laboratory experiments and modeling that internal diffusion resistances can decrease the leach rate, but the importance of internal diffusion resistances at a plant scale require clarification.

Thiosulfate based leaching systems are relatively unstable, hence further studies are needed in the area of solution chemistry and speciation, so that the behavior of the process solution can be better understood. Knowledge of the solution chemistry is key to development of closed loop processes. Overall balances of cyanide-free gold processing need to be considered, to be able to establish optimal unit operations. Chloride leaching is considered a possible breakthrough technology for gold recovery and a combination of chloride based pre-treatment and thiosulfate leaching might enable a decrease in the amount of chemicals used on site, for instance, sodium chloride used in chloride leaching could also be used in elution of gold from resins.

References

Adams, R.W., Matthew, I.G., 1981. Leaching of metal sulfide concentrates at atmospheric pressure using SO₂/O₂ mixtures, *Proceedings of Australian Institute of Mining and Metallurgy* 280, 41–53.

Albion process, www.Albionprocess.com, 2016.

Al-Harashseh, M., Kingman, S.W., 2004. Microwave-assisted leaching – a review, *Hydrometallurgy* 73, 189–203.

Altman, K.A., Schaffner, M., McTavish, S., 2002. Agitated tank leaching selection and design. In: Mular, A.L., Halbe, D. N., Barrat, D.J. (Eds.), *Proceedings of Mineral Processing Plant Design, Practice, and Control*. Society for Mining, Metallurgy, and Exploration, Inc., pp. 1631–1643.

Aylmore, M.G., 2005. Alternative lixivants to cyanide for leaching gold ores. In: Adams, M.D. (Ed.), *Advantages in Gold Ore Processing*, Elsevier, Oxford, UK, 501 – 539.

Aylmore, M.G., Muir, D., M., 2001. Thiosulphate leaching of gold – a review. *Minerals Engineering* 14 (2), 135 – 174.

Babu, M.N., Sahu, K.K., Pandey, B.D., 2002. Zinc recovery from sphalerite concentrate by direct oxidative leaching with ammonium, sodium and potassium persulphates, *Hydrometallurgy* 64, 119–129.

Baldwin, S.A., Demopoulos, G.P., 1998. Parameter sensitivity of kinetics-based hydrometallurgical reactor models, *The Canadian Journal of Chemical Engineering* 76, 1083-1092.

Baldwin, S.A., Demopoulos, G.P., Papangelakis, V.G., 1995. Mathematical modelling of the zinc pressure leach process, *Metallurgical and Materials Transactions B* 26B, 1035-1047.

Ballester, A., Blázquez, M.L., González, F., Muñoz, J.A., 2007. Catalytic role of silver and other ions on the mechanism of chemical and biological leaching. In: Donati, E.R., Sand, W. (Eds.), *Microbial Processing of Metal Sulfides*. Springer, Netherlands. 77–101.

Braul, P., 2013. Thiosulphate going commercial, *CIM Magazine* 8. 43–46.

Breuer, B., Dai, X., Zhang, H., Hewitt, D., 2012. The increased activity in the development of thiosulfate based process for gold recovery. *ALTA 2012 Gold proceedings*, Australia, 1–13.

Brierley, C.L., 2010. Biohydrometallurgical prospects, *Hydrometallurgy* 104, 324–328.

Choi, Y., Baron, J.Y., Wang, Q., Langhans, J., Kondos, P., 2013. Thiosulfate processing – from lab curiosity to commercial application. *World Gold Conference*, Brisbane, Australia, 45–50.

Crundwell, F.K., 1988a. Effect of iron impurity in zinc sulfide concentrates on the rate of dissolution, *American Institute of Chemical Engineering Journal* 34, 1128–1134.

Crundwell, F.K., 1988b. The role of charge-transfer mechanism in the oxidative and non-oxidative dissolution of sphalerite. (Ph.D. Thesis) University of Witwatersrand, Johannesburg.

Crundwell, F.K., 1994. Micro-mixing in continuous particulate reactors. *Chemical Engineering Science* 49, 3887–3896.

Crundwell, F.K., 2005. The leaching number: its definition and use in determining the performance of leaching reactors and autoclaves. *Minerals Engineering* 18, 1315–1324.

Crundwell, F.K., 2013. The dissolution and leaching of minerals: Mechanisms, myths and misunderstandings. *Hydrometallurgy* 139, 132–148.

Crundwell, F.K., du Preez, N., Lloyd, J.M., 2013. Dynamics of particle-size distributions in continuous leaching reactors and autoclaves. *Hydrometallurgy* 133, 44–50.

Crundwell, F.K., Bryson, A.W., 1992. The modelling of particulate leaching reactors – the population balance approach. *Hydrometallurgy* 29, 275–295.

da Silva, G., 2004. Relative importance of diffusion and reaction control during the bacterial and ferric sulfate leaching of zinc sulfide. *Hydrometallurgy* 73, 313 – 324.

de Souza, A.D., Pina, P.S., Leão, V.A., 2007. Bioleaching and chemical leaching as an integrated process in the zinc industry. *Minerals Engineering* 20, 591–599.

Diamond, S., 2000. Mercury porosimetry. An inappropriate method for the measurement of pore size distribution in cement-based materials, *Cement and Concrete Research* 30, 1517–1525.

Dickinson, D.F., Heal, G.R., 1999. Solid-liquid diffusion controlled rate equations. *Thermochimica Acta* 340–341, 89–101.

Dorfling, C., Akdogan, G., Bradshaw, S.M., Eksteen, J.J., 2013. Modeling of an autoclave used for high pressure sulfuric acid/oxygen leaching of first stage leach residue. Part I: Model development, *Minerals Engineering* 53, 220–227.

Dreisinger, D.B., Peters, E., 1987. The mathematical modeling of the zinc pressure leach. The mathematical modeling of the zinc pressure leach. The Metallurgical Society Inc. *Mathematical Modeling of Materials Processing Operations*, Palm Springs, CA, USA.

Dutrizac, J.E., 2006. The dissolution of sphalerite in ferric sulfate media. *Metallurgical and Materials Transactions B* 37, 161–171.

Espiari, S., Rashchi, F., Sadrnezhad, S.K., 2006. Hydrometallurgical treatment of tailings with high zinc content. *Hydrometallurgy* 82, 54–62.

Filippou, D., 2004. Innovative hydrometallurgical processes for the primary processing of zinc, *Mineral Processing & Extractive Metallurgy Review* 25, 205–252.

Fogler, H.S., 1999. *Elements of Chemical Reaction Engineering*, 3rd Ed. Prentice Hall International, Inc. New Jersey, USA.

Fugleberg, S., 2014. Improving the competitiveness of the electrolytic zinc process by chemical reaction engineering approach. (Ph.D thesis). Åbo Akademi University, Turku.

Gbor, P.K., Jia, C.Q., 2004. Critical evaluation of coupling particle size distribution with the shrinking core model. *Chemical Engineering Science* 59, 1979–1987.

Grénman, H., Murzina, E., Rönnhom, M., Eränen, K., Mikkola, J.-P., Lahtinen, M., Salmi, T., Murzin, D.Yu., 2007. Enhancement of solid dissolution by ultrasound. *Chemical Engineering and Processing: Process Intensification* 46, 862–869.

Grénman, H., Ingves, M., Wärnå, J., Corander, J., Murzin, D.Yu., Salmi, T., 2011. Common potholes in modeling solid-liquid reactions – methods for avoiding them. *Chemical Engineering Science* 66, 4459 – 4467.

Grosse, A.C., Dicoski, G.W., Shaw, M.J., Haddad, P.R., 2003. Leaching and recovery of gold using ammoniacal thiosulfate leach liquors (a review). *Hydrometallurgy* 69, 1- 21.

Gökhan, U., 2009. Kinetics of sphalerite dissolution by sodium chlorate in hydrochloric acid. *Hydrometallurgy* 95, 39–43.

Habashi, F., 1999. *Textbook of Hydrometallurgy, Métallurgie Extractive Québec, Québec.*

Habashi, F., 2005. A short history of hydrometallurgy, *Hydrometallurgy* 79, 15- 22.

Haakana, T., Saxen, B., Lehtinen, L., Takala, H., Lahtinen, M., Svens, K., Ruonala, M., Xiao, G., 2008. Outotec direct leaching application in China. *Journal of the Southern African Institute of Mining and Metallurgy* 108, 245–251.

Herney-Ramirez, J., Lampinen, M., Vicente, M., A., Costa, C., A., Madeira, L., M., 2008. Experimental design to optimize the oxidation of orange II dye solution using a clay-based fenton-like catalyst, *Industrial & Engineering Chemistry Research* 47 (2), 284–294.

Hilson, G., Monhemius, A., J., 2006. Alternatives to cyanide in the gold mining industry: prospects for the future? *Journal of Cleaner Production* 14, 1158 – 1167.

HSC 8.1, 2015, Outotec.

International Zinc Association, www.zinc.org, 2016.

Jeffrey, M.I, Breuer, P.L., Chu, C.K., 2003. The importance of controlling oxygen addition during the thiosulfate leaching of gold ores, *International Journal of Minerals Processing* 72, 323–330.

Kaskiala, T., 2005. Studies on gas-liquid mass transfer in atmospheric leaching of sulfidic zinc concentrates, (Ph.D. Thesis) Helsinki University of Technology, Espoo.

Kerley, B.J.J., 1981. Recovery of precious metals from difficult ores. US Patent 4,269,622. Kerley Industries, United States. 4 pp.

Kingman, S.W., Rowson, N.A., 1998. Microwave treatment of minerals – a review. *Minerals Engineering* 11, 1081–1087.

Knuutila, K., 2015. Hydrometallurgy – looking good?. In: Seisko, S., Aromaa, J., Lundström, M. (Eds.), *International Hydrometallurgy Symposium in Honor of Professor Olof Forsen*, Aalto University, Helsinki, 13–24.

Kobylin, P., Kaskiala, T., Salminen, J., 2007. Modeling of $\text{H}_2\text{SO}_4\text{-FeSO}_4\text{-H}_2\text{O}$ and $\text{H}_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ systems for metallurgical applications. *Industrial & Engineering Chemistry Research* 46, 2601–2608.

Labtium, www.labtium.fi. 2016.

León y León, C., 1998. New perspectives in mercury porosimetry. *Advances in Colloid and Interface Science* 76, 341–372.

Levenspiel, O., 1999. *Chemical Reaction Engineering*. John Wiley & Sons, New York. 644pp.

Li, H., Wu, X., Wang, M., Wang, J., Wu, S., Yao, X, Li, L., 2014. Separation of elemental sulfur from zinc concentrate direct leaching residue by vacuum distillation. *Separation and Purification Technology* 138, 41–46.

Liu, H., Papangelakis, V.G., 2005a. Chemical modeling of high temperature aqueous processes, *Hydrometallurgy* 79, 48–61.

Liu, H., Papangelakis, V.G., 2005b. Thermodynamic equilibrium of the $\text{O}_2\text{-ZnSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ system from 25 to 250 °C, *Fluid Phase Equilibria* 234, 122–130.

Lochmann, J., Pedlík, M., 1995. Kinetic anomalies of dissolution of sphalerite in ferric sulfate solution. *Hydrometallurgy* 37, 89 - 96.

Luque-Garcia, J.L., Luque, de C., 2003. Ultrasound: a powerful tool for leaching, *Trend in Analytical Chemistry* 22, 41–47.

Lundström, M., Ahtiainen, R., Laihonon, P., Lindgren, M., 2015. Possibilities and challenges in gold chloride processing, in *Proceeding ALTA 2015*, 269 – 280.

Markus, H., Fugleberg, S., Valtakari, K., Salmi, T., Murzin, D.Yu., Lahtinen, M., 2004. Kinetic modelling of a solid-liquid reaction: reduction of ferric iron to ferrous iron with zinc sulphide. *Chemical Engineering Science* 59, 919–930.

Muslim, A., 2015. Modeling and simulation of gold thiosulfate elution in ammoniacal thiosulfate resin solution system, *International Journal of Modeling and Simulation* 35, 43–48.

Narayana, K.L., Swamy, K.M., Sarveswara, R., Murty, J.S., 1997. Leaching of metals from ores with ultrasound. *Mineral Processing and Extractive Metallurgy Review* 16, 239–259.

Nicol, M. J., 1993. The role of electrochemistry in hydrometallurgy. In: Hiskey, J.B., Warren, J. B. (Eds.), *Hydrometallurgy Fundamentals, Technology and Innovation*. The Metallurgical Society, Littleton, CO, 43–62.

Nikkhah, K., 1998. Autoclave design and scale-up from batch test data: a review of sizing methods and their bases. *Society of Mining Engineers of AIME Preprints* 149, 1–9.

Órfão, J.J.M, Martins, F.G., 2002. Kinetic analysis of thermogravimetric data obtained under linear temperature programming – a method based on calculations of the temperature integral by interpolation. *Thermochimica Acta* 390, 195–211.

Outotec, www.outotec.com, 2016.

Ozberk, E., Jankola, W.A, Vecchiarelli, M., Krysa, B.D., 1995. Commercial operations of the Sherrit zinc pressure leach process. *Hydrometallurgy* 39, 49–52.

Palencia-Perez. I.P., Dutrizac, J.E., 1991. The effect of iron content of sphalerite on its dissolution rate in ferric sulfate and ferric chloride media. *Hydrometallurgy* 26, 211–232.

Papangelakis, V.G., Demopoulos, G.P., 1992a, Reactor models for a series of continuous stirred tank reactors with a gas-liquid-solid leaching systems: Part I. Surface reaction control, *Metallurgical Transactions B* 23A, 847-856.

Papangelakis, V.G., Demopoulos, G.P., 1992b, Reactor models for a series of continuous stirred tank reactors with a gas-liquid-solid leaching systems: Part II. Gas transfer control, *Metallurgical Transactions B* 23B, 857-864.

Papangelakis, V.G., Berk, D., Demopoulos, G.P., 1990, Mathematical modeling of an exothermic leaching reaction system: pressure oxidation of wide size arsenopyrite particulates, *Metallurgical Transactions B* 21B, 827-837.

Pecina, T., Franco, T., Castillo, P., Orrantia, E., 2008. Leaching of zinc concentrate in H₂SO₄ solutions containing H₂O₂ and complexing agents. *Minerals Engineering* 21(1), 23 - 30.

Perera, W. N., Senanayake, G., 2004. The ammine, thiosulfate and mixed ammine/thiosulfate complexes of silver(I) and gold(I), *Inorganic Chemistry* 43, 3048–3056.

Perera, W. N., Senanayake, G., Nicol, M.J., 2005. Interaction of gold(I) with thiosulfate-sulfite mixed ligand systems, *Inorganica Chimica Acta* 358, 2183–2190.

Riekkola-Vanhanen, M., 2010, Talvivaara Sotkamo mine – bioleaching of a polymetallic nickel ore in subarctic climate, *Nova Biotechnologia* 10, 7–14.

Rohwerder, T., Gehrke, T., Kinzler, K., Sand, W., 2003. Bioleaching review part A. *Applied Microbiology and Biotechnology* 63, 239–248.

Rubisov, D.H., Papangelakis, V.G., 2000. Sulfuric acid pressure leaching of laterites – a comprehensive model for a continuous autoclave. *Hydrometallurgy* 58, 89–101.

Rönholm, M.R., Wärnå, J., Salmi, T., Turunen, I., Luoma, M., 1999. Kinetics of oxidation of ferrous sulfate with molecular oxygen. *Chemical Engineering Science* 54, 4223–4232.

Salmi, T., Grénman, H., Bernas, H., Wärnå, J., Murzin, D.Yu., 2010. Mechanistic modelling of kinetics and mass transfer for a solid-liquid system: Leaching of zinc with ferric iron. *Chemical Engineering Science* 65, 4460–4471.

Salmimies, R., Huhtanen, M., Kallas, J., Häkkinen, A., 2013. The solubility of two magnetite powders in oxalic acid: Applicability of empirical modeling, *Journal of Powder Technology*.

Senanayake, G., 2004. Gold leaching in non-cyanide lixiviant systems: critical issues on fundamentals and applications, *Minerals Engineering* 17, 785–801.

Senanayake, G., 2005, The role of ligands and oxidants in thiosulfate leaching of gold, *Gold Bulletin* 38/4, 170 – 179.

Shaw, J.A., 1982. The design of draft tube circulators. *The Australian Institute of Mining and Metallurgy*, 47–58.

Sing, K, Everett, D., Haul, R., Moscou, L., Pierotti, R., Rouquérol, J., Siemieniowska, T., 1985. Reporting physisorption data gas/solid systems with special reference to the determination of surface area and porosity, *Pure and Applied Chemistry* 4, 603–619.

Solonen, A., 2011. Bayesian methods for estimation, optimization and experimental design. (PhD Thesis), Lappeenranta University of Technology, Lappeenranta.

Suoranta, T., Zugazua, O., Niemelä, M., Perämäki, P., 2015. Recovery of palladium, platinum, rhodium and ruthenium from catalyst materials using microwave-assisted leaching and cloud point extraction. *Hydrometallurgy* 154, 56–62.

Souza, A.D., Pina, P.S., Leão, V.A., Silva, C.A., Siqueira, P.F., 2007. The leaching kinetics of a zinc sulfide concentrate in acid ferric sulfate. *Hydrometallurgy* 89, 72-81.

Svens, K. 2012. Direct leaching alternatives for zinc concentrates. In: Wang, S., Dutrizac, J.E., Free, M.L., Hwang, J.Y., Kim, D. (Eds.), T.T. Chen Honorary Symposium on Hydrometallurgy,

Electrometallurgy and Materials Characterization, 11-15 March, Florida, USA, TMS (The Minerals, Metals & Materials Society). 191–206.

Takala, H., 1999. Leaching of zinc concentrates at Outokumpu Kokkola plant, *Erzmetal* 52, 37–42.

Talonen, P., 2015. Behaviour of silica in zinc leaching circuit. In: Seisko, S., Aromaa, J., Lundström, M. (Eds.), *International Hydrometallurgy Symposium in Honor of Professor Olof Forsen*, Aalto University, Helsinki, 221–229.

Veltman, H., Robert Weir, D., 1981. Sherritt Gordon's pressure leaching technology-its industrial application. In: Davies G. A. et al.(Eds.), *Hydrometallurgy 81 Proceedings of a Society of Chemical Industry symposium held at the University of Manchester Institute of Science and Technology*, England, Society of Chemical Industry.

Verbaan, B., Crundwell, F.K., 1986. An electrochemical model for the leaching of a sphalerite concentrate. *Hydrometallurgy* 16, 345–359.

Wan, R.Y, 1997. Importance of solution chemistry for thiosulfate leaching of gold, *World Gold '97*, The Australian Institute of Mining and Metallurgy, Carlton, Vic, 159–162.

Wan, R.Y, Le Vier, M., Miller, J.D., 1993. Chapter 27: Research and development activities for the recovery of gold from non-cyanide solutions. In: *Proceedings of the Milton E. Wadsworth (IV) International Symposium on Hydrometallurgy. Hydrometallurgy: Fundamentals, Technology, and Innovations*. Society for Mining, Metallurgy, and Exploration, Salt Lake City, UT, USA.

Wang, X., Srinivasakannan, X.H., Duan, X.H., Peng, J.H., Yang, D.J., Ju, S.H., 2013. Leaching kinetics of zinc residues augmented with ultrasound, *Separation and Purification Technology* 115, 66–72.

Weisener, C.G., Smart, R.St.C., Gerson, A.R., 2004. A comparison of the kinetics and mechanism of acid leaching of sphalerite containing low and high concentrations of iron. *International Journal of Minerals Processing* 74, 239–249.

White, H.A., 1905. The solubility of gold in thiosulfates and thiocyanates, *Journal of the Chemical Metallurgical and Mining Society of South Africa* 5, 109–111.

Xu, Z.-F., Jiang, Q.-Z., Wang, C.-Y., 2013. Atmospheric oxygen-rich direct leaching behavior of zinc sulfide concentrate. *Transactions of Nonferrous Metals Society of China* 23, 3780–3787.

Zhang, L., Guo, W., Peng, J., Li, J., Lin, G., Yu, X., 2016. Comparison of ultrasonic-assisted and regular leaching of germanium from by-product of zinc metallurgy, *Ultrasonic Sonochemistry* 31, 143–149.

Zhihong, L., 2015. The oxygen pressure leaching of a gallium and germanium enriched zinc sulfide concentrate. In: Seisko, S., Aromaa, J., Lundström, M. (Eds.), *International Hydrometallurgy Symposium in Honor of Professor Olof Forsen*, Aalto University, Helsinki, 207–220.

Zwietering, T.N., 1959. The degree of mixing in continuous flow systems. *Chemical Engineering Science*, 1–15.

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Ammoniacal thiosulfate leaching of pressure oxidized sulfide gold concentrate with low reagent consumption



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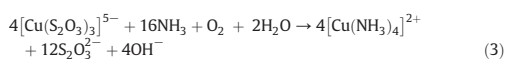
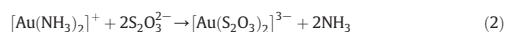
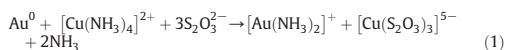
Ammoniacal thiosulfate leaching of pressure oxidized sulfide gold concentrate received from a gold mine is studied. The main chemical composition of the concentrate was Au 32 g/t, Ag 12 g/t, Fe 59%, S 21% and As 19%. The experimental variables studied were ammonia concentration, thiosulfate concentration, copper concentration, and temperature. The highest gold extraction (89%) was achieved with the following leaching solutions: 0.2 mol S₂O₃²⁻/L, 0.2 mol NH₃/L, and 0.1 g Cu/L; and with the following conditions: solids, 30 m-%; pressure, 1 atm; continuous aeration (0.2 L/min); temperature, 30 °C; and leaching time, 6 h. Measured thiosulfate and copper concentrations after 6 h of leaching were 0.19 M and 0.08 g/L, respectively. The results from the leaching experiments showed that the pressure oxidized gold concentrate was effectively leached in an ammoniacal thiosulfate leaching solution with minimal reagent consumption. The study shows that the widely reported problem of high reagent consumption can be circumvented in leaching of pressure oxidized sulfide gold concentrate by the use of low reagent concentrations. The results indicate good premises for gold recovery by ion-exchange resins, since minimal thiosulfate consumption also ensures low polythionate concentration, which is an important issue in gold recovery with ion-exchange resins. The minimal reagent consumption also indicates that there are good possibilities to circulate the leaching solution for re-use in the leaching stage after gold recovery and solid–liquid separation.

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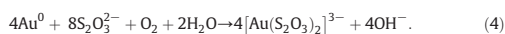
1. Introduction

The undesirable environmental and safety aspects of the prevailing cyanidation techniques used in gold production have driven study in the area towards a search for alternative lixivants. The use of thiosulfate in the presence of ammonia and copper(II) has been considered to be a suitable alternative to cyanidation techniques, and extensive research work has been carried out in this area and comprehensive reviews were presented (Aylmore and Muir, 2001; Grosse et al., 2003; Muir and Aylmore, 2004). However, widespread commercialization of thiosulfate processes has not yet been achieved. The major problems facing thiosulfate processes are the high consumption of thiosulfate and the challenges posed by the recovery of the gold after the leaching stage (Muir and Aylmore, 2004; Hilson and Monhemius, 2006). One of the challenges to evaluation and adoption of the thiosulfate process is the complicated chemistry of the leaching system, resulting from the simultaneous presence of complexing ligands (ammonia and thiosulfate), the stability of thiosulfate in the solution, and the Cu(II)–Cu(I) redox couple. The reactions that describe the leaching behavior of gold in an

ammoniacal thiosulfate system are shown below (Eqs. (1)–(4)) (Grosse et al., 2003).



The net reaction is:



Muir and Aylmore (2004) summarized published studies on thiosulfate leaching of various ores and noted that a wide range of conditions and concentrations of reagents have been used. Emphasis has been on carbonaceous ores that give poor gold recoveries using cyanide and copper–gold ores. Gold dissolution rates and recovery percentages have varied considerably, depending on the ore type and conditions

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used. Navarro et al. (2002) found that under mild conditions, thiosulfate leaching compared very favorably with cyanidation when leaching gold from flotation concentrate was studied. Muir and Aylmore (2004) studied some relatively simple Australian oxide ores and presented that while most of the gold and silver were readily leached in 2–4 h, a fraction of the cyanide-soluble gold always remained in the thiosulfate leach residue. Langhans et al. (1992) studied low grade oxidized gold ore and the results from their study indicate that copper-catalyzed thiosulfate leaching may be competitive with conventional cyanidation methods for application to heap, dump, or in-situ leaching techniques. Barrick Gold Corporation (Barrick) patented a process for recovering gold from an ore having a combination of refractory sulfide and carbonaceous material using pressure oxidation followed by thiosulfate leaching (Marchbank, 1996). Barrick subsequently patented a combined pressure oxidation, thiosulfate and resin-in-pulp process for treatment of refractory gold ores (Thomas, 1998). The patent deposited by Barrick (Thomas, 1998) included a study in which pressure-leached arsenopyrite ores from Barrick were examined and a large number of stirred tank tests carried out at pH 8–9. Gold recovery in their study varied from 50% to 95%. The work by Feng and van Deventer (2010) showed that oxidative pre-treatment of sulfide ore followed by thiosulfate leaching provided an efficient approach for the treatment of sulfide containing ore. Feng and van Deventer (2010) showed that consumption of thiosulfate in leaching was negligible after an over 1 h oxidative ammonia pre-treatment.

Muir and Aylmore (2004) stated that industry's first task in adoption of the thiosulfate system is to develop a robust overall process flowsheet that can be realistically used and costed for a range of actual ores. The efficiency of the leaching stage has a primary effect on the technical and economic success of a hydrometallurgical business (Crundwell, 2013), so it is evident that managing the leaching stage is a key issue when developing the thiosulfate system. Clearly, there is thus a need for leaching studies with different ore types and pre-treatments that can provide comprehensive data about optimal conditions and that evaluate gold recovery, reagent re-cycling or destruction, and impurity control possibilities. Efficient pre-treatment of ores/concentrates coupled with optimal leaching conditions could offer a way to overcome the problems hitherto identified in the leaching stage, as well as facilitate the following recovery stage. This work studies the leaching of pressure oxidized gold concentrate in thiosulfate solution in the presence of ammonia and copper(II). The aim of the present study is to find optimal leaching conditions for pressure oxidized sulfide gold concentrates by studying the effect of different parameters (reagent concentrations and temperature).

2. Experimental work

2.1. Materials

Pressure oxidized gold concentrate was received from a gold mine. The gold mine processes the ore to concentrate by crushing, grinding and flotation. After flotation, the concentrate consists mainly of pyrite and arsenopyrite. The concentrate from the flotation is subjected to acidic pressure oxidation in an autoclave, where sulfide minerals are oxidized to sulfate. The gold concentrate used in the experiments was taken from the process stream after pressure oxidation. The received gold concentrate was dried at 60 °C for 12–24 h. The dried concentrate was blended and divided into sub-samples, which were divided to representative samples for experimental use by a rotary splitting device. Samples were then collected for chemical analysis and size distribution characterization. Table 1 shows the elemental composition of the concentrate. Gold content was determined by fire-assay followed by ICP-OES and other elements were determined by acid digestion followed by ICP-OES. The particle size distribution of the gold concentrate was analyzed with a LS 13 320 Laser Diffraction Particle Size Analyzer. Mean particle size and particle size distribution are presented in

Table 1
Chemical composition of the pressure oxidized concentrate.

Element	Amount
Fe, mass-%	59.1
S, mass-%	21.3
As, mass-%	19.2
Au, g/t	32
Ag, g/t	12
Cu, g/t	137
Cd, g/t	3
Co, g/t	30
Cr, g/t	69
Mn, g/t	106
Mo, g/t	3
Ni, g/t	63
Pb, g/t	84
Sb, g/t	514
Zn, g/t	104

Table 2. All the chemicals used were of analytical grade and ultrapure water was used in the preparation of the solutions. Thiosulfate was added as sodium thiosulfate, copper as copper sulfate, and ammonia as ammonia water (25%) purchased from Merck.

2.2. Analytical techniques

Metal concentrations (Au, Cu) in the solutions were analyzed by atomic absorption spectroscopy (Thermo Scientific iCE 3000 Series AA spectrophotometer). Samples for gold analyses were first oxidized by hydrogen peroxide to oxidize the sulfur species to stable sulfates. After oxidation, gold sample solutions were acidified by aqua regia and boiled to ensure complete conversion of the metal species to their chloride form. The thiosulfate concentration was determined by ion chromatography (Thermo Scientific Dionex ICS-1100 Ion Chromatography System). An IonPac AS22 analytical column and IonPac AG22 guard column were used for the analyses. Rosemount Analytical PERph-X high temperature sensors were used to measure mixed solution potential (3300FT-12-30) and pH (3300HT-10-30). All potentials are given herein with respect to the Standard Hydrogen Electrode (SHE). Sensors were hooked up with a Rosemount Analytical Dual Input Analyzer. Dissolved oxygen in the solution was measured with a Marvet Fluids AJ90 analyzer.

2.3. Leaching tests

Leaching tests of the pressure oxidized concentrate were performed in a 1.1 L reactor ($d = 8.4$ cm) as batch experiments in which a total volume of 0.85 L of slurry was used. The reactor was equipped with an overhead mixer (Heidolph RZR 2041) and 4 baffles. A double-pitch-bladed turbine (4 cm diameter) was used for mixing. The stirring speed was maintained at 700 min^{-1} . The temperature in the reactor was controlled by a thermostatic oil bath. The gas was fed from the bottom of the reactor. The flow rate of the gas was controlled with a gas flow control valve (F-201 CV) hooked up with a control unit (Bronkhorst hi-tec, Type E-7100). The solution was first stabilized to

Table 2
Mean particle size and particle size distributions of the concentrate particles.

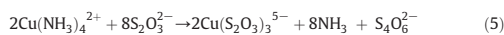
Diameter	μm
Mean	7.13
<10%	1.29
<25%	2.64
<50%	5.45
<75%	9.76
<90%	16.16

the reaction temperature. Nitrogen was fed to the solution during stabilization. After the temperature had stabilized, the concentrate was added to the reactor, mixing was started, and gas feed was changed from nitrogen to air. The first sample was taken at this point and this point was counted as the starting point of the experiment. Samples were taken continuously from the bottom valve at certain intervals during leaching. The samples were immediately vacuum filtered after sampling. The solution samples were immediately subjected to the subsequent ion chromatography and AAS analyses. In each test, the final residue was filtered, dried and analyzed for gold. Gold content was determined by fire-assay followed by ICP-OES. All the solid samples (initial oxidized gold concentrate and leaching residues) were analyzed by a commercial analytical laboratory. After calculating the final conversions based on both solution and solid analysis standard deviation 2.5% was obtained for the gold conversion. Standard deviations for thiosulfate and copper were calculated from duplicated leaching experiments. Standard deviations for thiosulfate and copper are 0.002 M and 0.004 g/L, respectively.

2.4. Experimental design

Feng and van Deventer (2010) presented that in the ammoniacal thiosulfate leaching, sulfide minerals oxidatively decompose to partially or completely release gold from the sulfide matrices. In this process, the sulfide minerals will, however, consume dissolved oxygen in the solution and catalyze the decomposition of thiosulfate. This will cause the excessive thiosulfate consumption and leaching passivation due to thiosulfate decomposition in the ammoniacal thiosulfate leaching of sulfide ores. Thus, the pressure oxidized gold concentrate used in the experiments is amenable to ammoniacal thiosulfate leaching, since the sulfide matrices are decomposed and higher gold recoveries together with low thiosulfate consumption can be expected.

A review by Muir and Aylmore (2004) of the literature on thiosulfate leaching of various ores showed that early studies used relatively high concentrations of reagents, which gave reasonable gold extraction but consumed up to 40 kg/t thiosulfate. Later studies by Langhans et al. (1992) showed that comparable extraction of gold could be achieved with dilute ammoniacal thiosulfate and identified the catalytic role played by trace amounts of copper. Low reagent concentrations are favorable for the leaching stage since high cupric ion concentrations accelerate thiosulfate degradation according to a well established undesirable side reaction in which copper(II) oxidizes the thiosulfate.



Molleman and Dreisinger (2002) found that to enable regeneration of the cupric ion, it is necessary to keep the concentration ratio of ammonia to thiosulfate within a certain range. Increasing the concentration of only one of the ligands will have a limited positive effect on the gold leaching process. The limited positive effect of the increased concentration of one ligand can however be seen only up to a certain point, after which the increased concentration may have a negative effect, as a too high ammonia concentration might stabilize copper as the copper(II)ammonia complex and a too high thiosulfate concentration might result in the stabilization of copper as the copper(I)–thiosulfate complex. These issues were presented by Molleman and Dreisinger (2002) to justify the selection of low concentrations also for thiosulfate and ammonia. In order to achieve an efficient leaching process, correct pH and oxidation potential should be maintained, together with correct concentration ratios of copper, ammonia and thiosulfate. Molleman and Dreisinger (2002) found that a pH of 9–10 is generally preferred at ambient temperature because thiosulfate appears to be less prone to degradation in this region and the copper(II)–ammonia complex is stable. Navarro et al. (2002) reported that the dissolution of gold is extremely dependent on the pH, being enhanced at pH values about 9.5 but probably hindered at pH values over 10–11, dependent on the thiosulfate

and copper concentrations used to leach the gold. Aylmore and Muir (2001) reviewed the ammoniacal thiosulfate process and concluded, based on a study by Zipperian et al. (1988), that for effective gold dissolution at high reagent concentrations, an oxidation potential of 150–200 mV with respect to SHE is required at pH 10. Eh–pH diagrams constructed by Aylmore and Muir (2001) suggested that a higher oxidation potential of 250 mV is required. At lower reagent concentrations, the optimum Eh was presented to be the same, but the pH range smaller.

The aim of the experiments in this study was to achieve $\geq 90\%$ conversion for gold while minimizing reagent consumption. Based on the above discussion, target values for pH and oxidation potential were chosen to be 10 ± 0.5 and 200 ± 50 mV (SHE), respectively. The following concentrations for reagents were chosen: NH_3 0.1, 0.2 and 0.3 M; S_2O_3 0.05, 0.1 and 0.2 M; and Cu 0.1, 0.25 and 0.5 g/L. The effect of the temperature was studied using three different temperatures: 20, 30 and 40 °C.

3. Results and discussion

3.1. Effect of initial ammonia concentration

Fig. 1 shows the effect of initial ammonia concentration on gold dissolution. Increasing the initial ammonia concentration from 0.1 M to 0.2 M increased the rate of dissolution as well as the final conversion of gold. Increasing the ammonia concentration further from 0.2 M to 0.3 M did not increase the dissolution rate or final conversion of gold.

Past studies (Navarro et al., 2002; Molleman and Dreisinger, 2002) have pointed out that maintaining pH around 10 is important for gold dissolution. Molleman and Dreisinger (2002) presented that the ammonia/thiosulfate ratio should preferably be 1–2. Fig. 2 shows the pH values measured in this study for different initial ammonia concentrations, pH ~9 was measured for slurry with initial ammonia concentration in the solution of 0.1 M and pH ~10 was measured for slurry with 0.2 M and 0.3 M. The results presented here are in agreement with past studies (Navarro et al., 2002; Molleman and Dreisinger, 2002).

Fig. 3 shows copper concentrations during leaching. From Fig. 3 it can be seen that with an initial ammonia concentration of 0.1 M almost all of the copper remains in liquid phase. When the initial ammonia concentration is increased, the trend is clearly that copper precipitates more easily. As was pointed out above, gold dissolution is sensitive to pH. Ammonia stabilizes the pH to a certain level and this is certainly one important aspect when choosing the optimum ammonia concentration. In addition to pH stabilization, another important role of ammonia is to stabilize the copper by forming a tetraammine complex with the copper, which is the primary oxidant in the leaching (Eq. (1)). Based on previous studies, Abbruzzese et al. (1995) discussed that increasing the ammonia concentration, and as a consequence the pH, reduces the area of the thermodynamic stability of $\text{Cu}(\text{NH}_3)_4^{2+}$ and $\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$ while widening the regions of the thermodynamic stability of solid copper species such as CuO and Cu_2O . Abbruzzese et al. (1995) studied the phenomenon further by elaboration of the FTIR spectra through the Kubelka Munk function and concluded that a precipitate was formed. This solid phase, attributable to $(\text{NH}_4)_3\text{Cu}(\text{S}_2\text{O}_3)_3$, reduces the oxidant activity of the cuprotetraammine complex and covers the mineral surface, hindering the thiosulfate attack.

From Figs. 1, 2 and 3, it can be concluded that the optimum ammonia concentration for gold leaching is around 0.2 M. An initial ammonia concentration of 0.2 M in the solution stabilizes pH to ~10 and has the fastest leaching rate as well as the highest final conversion of gold. Measured oxidation potential varied between 232 and 246 mV and concentration of dissolved oxygen in the slurry was between 6.5 and 7.9 mg/L during the leaching experiment with 0.2 M as the initial ammonia concentration in the solution. A drawback of increasing the

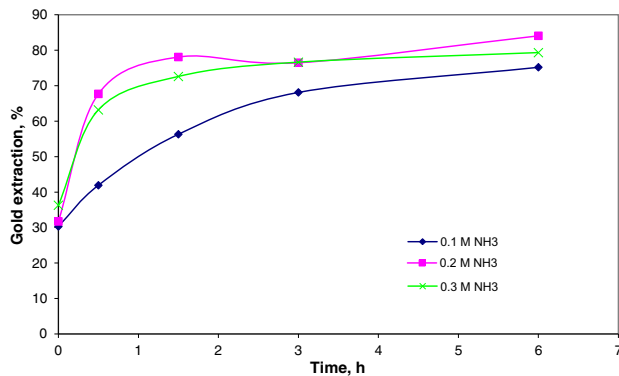


Fig. 1. Effect of initial ammonia concentration on gold dissolution. Solution: 0.1 M S_2O_3 , and 0.25 g/L Cu^{2+} . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Temperature: 30 °C. Mixing speed: 700 min^{-1} .

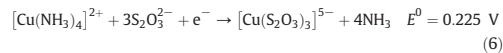
initial ammonia concentration from 0.1 to 0.2 M is that a part of the copper precipitates.

3.2. Effect of initial thiosulfate concentration

From Fig. 4, it can be seen that the initial thiosulfate concentration has only a small effect on the leaching rate and the final conversion of gold in the conducted experiments. The highest initial thiosulfate concentration (0.2 M) reaches 84% extraction after 1.5 h of leaching, while lower thiosulfate concentrations (0.05 and 0.1 M) reach only 78% extraction after 1.5 h of leaching. However, the final extraction of gold after 6 h of leaching is practically the same with concentrations of 0.05, 0.1 and 0.2 M.

Fig. 5 shows copper concentrations during leaching for different initial thiosulfate concentrations. It can be seen that, as expected, increasing the initial thiosulfate concentration stabilizes the copper. Based on previous studies done by various authors, Grosse et al. (2003) presented that in ammoniacal thiosulfate liquors, metal ions can form a range of complexes with ammonia, thiosulfate and hydroxide ions. Thiosulfate complexes are expected to predominate for gold(I), silver(I), iron(II), mercury(II) and lead(II), whereas the metal ions copper(I) and cadmium(II) should be found as an equilibrium mixture of thiosulfate

and ammine complexes. For example, copper(I) is usually reported only as $Cu(S_2O_3)_3^{5-}$, yet at concentrations of thiosulfate below 0.05 M, the primary complex is expected to be $Cu(S_2O_3)_2^{3-}$. Grosse et al. (2003) presented, based on the work done by Byerley et al. (1975), that copper(II) is almost exclusively found as $Cu(NH_3)_4^{2+}$, although it has been suggested that the triammine complex $Cu(NH_3)_3^{2+}$ may be the primary oxidizing species. Grosse et al. (2003) presented that there appears to be a maximum solubility of copper at which approximately 1 g of copper will be soluble for every 1% $(NH_4)_2S_2O_3$ (w/w) present in the leach solution. Under unfavorable conditions, precipitation of $Cu_2S_2O_3$ or mixed cuprous–ammonium thiosulfate salts may occur. Molleman and Dreisinger (2002) presented that it is evident from Eq. (6) that to enable the regeneration of the cupric ion, it is necessary to keep the concentration ratio of ammonia to thiosulfate within a certain range.



Muir and Aylmore (2004) pointed out that early work reported the precipitation of copper sulfide with high concentrations of reagents,

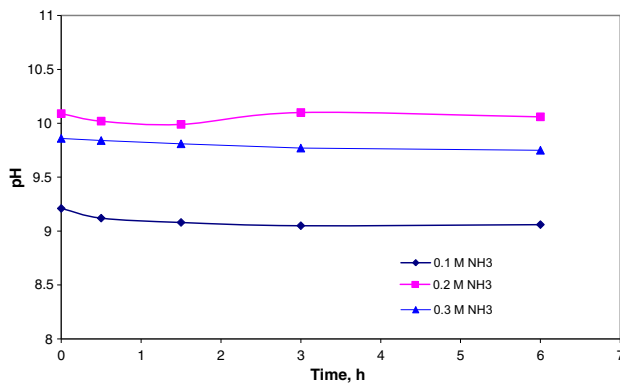


Fig. 2. Measured pH values in the gold leaching of the pressure oxidized concentrate. Solution: 0.1 M S_2O_3 , and 0.25 g/L Cu^{2+} . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Temperature: 30 °C. Mixing speed: 700 min^{-1} .

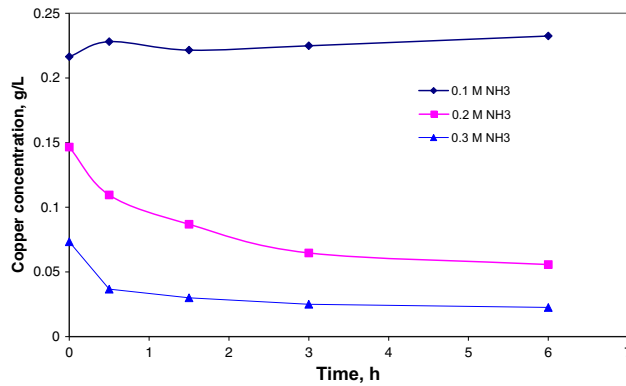
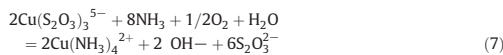


Fig. 3. Variation of copper concentration with time in the gold leaching of the pressure oxidized concentrate. Solution: 0.1 M $S_2O_3^{2-}$, and 0.25 g/L Cu^{2+} . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Temperature: 30 °C. Mixing speed: 700 min^{-1} .

but more recent work by Freitas et al. (2001) found that copper precipitated from solutions containing <0.3 M thiosulfate.

Fig. 6 presents the measured oxidation potential values during leaching. It can be seen from Fig. 6 that increasing initial thiosulfate concentration from 0.05 M to 0.1 M increases oxidation potential, but increasing initial thiosulfate concentration further from 0.1 M to 0.2 M decreases oxidation potential. The redox equilibrium between the cuprous–cupric couple in ammoniacal solution and thiosulfate is presented by the following reaction (Abbruzzese et al., 1995).



Aylmore and Muir (2001) presented that increasing the total ammonia concentration, but keeping other reagent concentrations, pH and Eh constant, increases the stability region of the $Cu(NH_3)_4^{2+}$ complex, whereas increasing the thiosulfate concentration ions increases the stability region of the $Cu(S_2O_3)_3^{5-}$. Fig. 5 shows, that increasing the initial thiosulfate concentration stabilizes the copper indicating that more $Cu(S_2O_3)_3^{5-}$ complexes are formed. $Cu(S_2O_3)_3^{5-}$ complexes settle to equilibrium with $Cu(NH_3)_4^{2+}$ complexes (Eq. (7)) and also oxidation potential increases as can be seen from Fig. 6 when the initial

thiosulfate concentration increases from 0.05 M to 0.1 M. When initial thiosulfate concentration is further increased from 0.1 M to 0.2 M the copper concentration in the solution increases as can be seen from Fig. 5. However, oxidation potential decreases as can be seen from Fig. 6 indicating that the balance between the copper complexes moves more to the right side in Eq. (7).

Fig. 7 presents the thiosulfate concentrations during leaching. From Fig. 7, it can be seen that thiosulfate concentrations do not change much in any of these experiments. Based on Figs. 4–7, it can be concluded that it is beneficial for leaching to have the initial thiosulfate concentration around 0.2 M, as this initial thiosulfate concentration reaches 84% extraction after 1.5 h of leaching and stabilizes the copper. Measured concentration of dissolved oxygen in the slurry was between 6.8 and 7.4 mg/L during the leaching experiment with 0.2 M as the initial thiosulfate concentration in the solution.

3.3. Effect of initial copper concentration

From Fig. 8, it can be seen that increasing the initial copper concentration in the leaching solution does not have a beneficial effect on the final conversion rate of the gold. Increasing the initial copper concentration from 0.1 to 0.25 g/L is beneficial for leaching during the first 1.5 h,

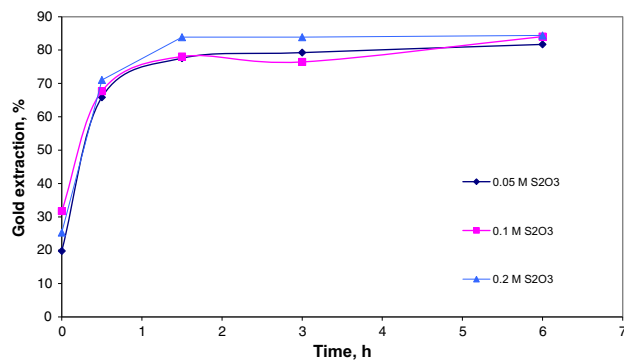


Fig. 4. Effect of initial thiosulfate concentration on gold dissolution. Solution: 0.2 M NH_3 , and 0.25 g/L Cu^{2+} . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Temperature: 30 °C. Mixing speed: 700 min^{-1} .

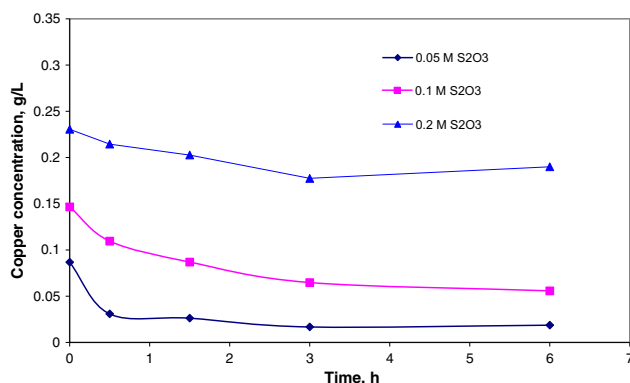


Fig. 5. Variation of copper concentration with time in the gold leaching of the pressure oxidized concentrate. Solution: 0.2 M NH_3 , and 0.25 g/L Cu^{2+} . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Temperature: 30 °C. Mixing speed: 700 min^{-1} .

but the final conversion after 6 h of leaching is slightly lower. Gold extraction reaches 84% after 1.5 h of leaching with the initial copper concentration of 0.25 g/L, while lower copper concentration (0.1 g/L) reaches only 78% extraction after 1.5 h of leaching. When the initial copper concentration is further increased to 0.5 g/L, leaching is fast during the first half an hour, but the gold concentration subsequently decreases, indicating that part of the leached gold precipitates.

Muir and Aylmore (2004) discussed that in some leach tests over an extended time there has been evidence of re-precipitation of gold, silver and copper, and lower gold recovery. They concluded that this reflects the buildup of degradation products in the solution and possible precipitation of gold and silver sulfide. Muir and Aylmore (2004) further presented that once Ag_2S is formed, it appears that the dilute thiosulfate solutions are unable to re-leach the sulfide. Senanayake (2005) presented that dissolved gold can re-precipitate in aging leach liquors due to a deficiency of thiosulfate or due to the presence of other reagents such as sulfite or sulfide. Senanayake (2005) also found that although thermodynamics predict the formation of Au_2S_3 , the X-ray diffraction analysis by West-Sells and Hackl (2005) provided evidence for the precipitation of elemental gold. From Fig. 8, it can be seen that the gold concentration decreased after the first half an hour, which suggests that the reason for precipitation is not aging of the leaching liquor. The reason for the

precipitation may be more related to the higher copper concentration in the slurry. Higher copper concentration could cause the precipitation of the gold, most likely as Au_2S_3 , and the leaching solution could be unable to re-leach the sulfide, as in the case of Ag_2S presented by Muir and Aylmore (2004). In the current study it was noticed that higher copper concentration causes instability in the solution, especially when the solution ages. Gold analysis from solution samples was not reliable after 6 h of leaching with the highest copper concentration (0.5 g/L) used in the current study. It was noticed that the solution sample after 6 h of leaching turned from clear to blurry soon after sampling, which also suggests that higher copper concentration causes precipitation of gold. Since it was not possible to get reliable results for gold from the solution samples after 6 h of leaching it was decided to repeat the experiment with the highest copper concentration with only a 3 hour leaching time in order to get reliable results.

Fig. 9 shows copper concentrations during leaching for the different initial copper concentrations used. It can be seen that with initial copper concentrations of 0.1 and 0.25 g/L almost all of the copper remains in the liquid phase. When the initial copper concentration is increased to 0.5 g/L, an increasing tendency of copper to precipitate can be clearly seen.

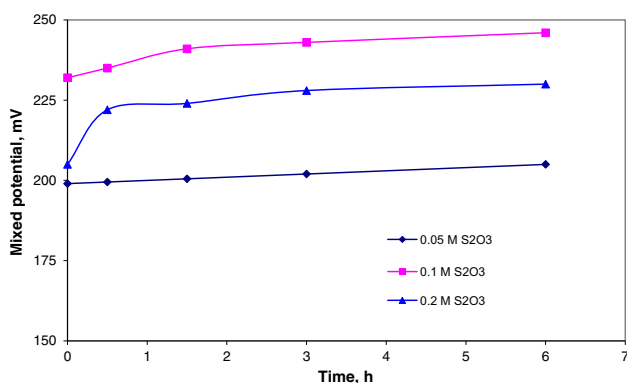


Fig. 6. Measured oxidation potential values in the gold leaching of the pressure oxidized concentrate. Solution: 0.2 M NH_3 , and 0.25 g/L Cu^{2+} . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Temperature: 30 °C. Mixing speed: 700 min^{-1} .

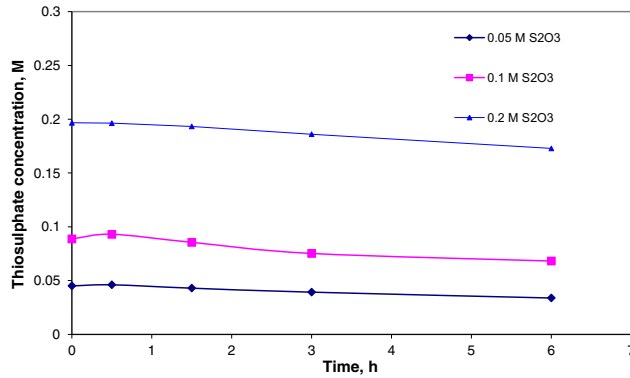


Fig. 7. Variation of thiosulfate concentration with time in the gold leaching of the pressure oxidized concentrate. Solution: 0.2 M NH_3 , and 0.25 g/L Cu^{2+} . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Temperature: 30 °C. Mixing speed: 700 min^{-1} .

Fig. 10 shows thiosulfate concentrations during leaching for the different initial copper concentrations used. It can be seen that consumption of thiosulfate is minimal with the lowest initial copper concentration (0.1 g/L). It can also be seen that when initial copper concentration increases, the oxidation rate of the thiosulfate also increases. This was expected, since the undesirable side reaction in which copper(II) oxidizes thiosulfate is well established (Eq. (5)).

Based on the results presented above, it can be concluded that low initial copper concentration in the solution (0.1 g/L) is optimal for the current case. Low initial copper concentration provides 89% conversion for the gold after 6 h of leaching and minimal reagent consumption. Measured oxidation potential varied between 199 and 215 mV and concentration of dissolved oxygen in the slurry was between 5.0 and 6.3 mg/L during the leaching experiment with 0.1 g/L as the initial copper concentration in the solution.

3.4. Effect of temperature

Experiments were carried out at three different temperatures in order to establish the effect of temperature on the gold leaching rate. Fig. 11 shows that increasing the temperature increased the rate of gold dissolution. When the temperature was increased from 20 to

30 °C the leaching rate and final conversion increased clearly. pH at these temperatures is around 10, which is optimum for gold leaching, and consequently the increase in temperature increased the leaching rate since other circumstances did not change. When the temperature was further increased from 30 to 40 °C the beneficial effect of increased temperature was no longer so clear. The measured pH at 40 °C was around 9.5, which is not the optimum pH for gold leaching. Evidently, the increase in temperature together with continuous aeration caused greater vaporization of ammonia, which can be seen as a drop in the pH. Abbruzzese et al. (1995) studied leaching at three different temperatures (25, 40 and 60 °C) and presented that an increase in temperature from 25 to 60 °C gives a decrease in gold recovery: 78.84% Au in comparison with 55.74% Au after 3 h leaching. They suggested that this decrease in gold recovery is caused by passivation due to cupric sulfide, formed by the thermal reaction between Cu(II) ions and thiosulfate. In addition, Abbruzzese et al. (1995) noted that the increase in temperature from 25 to 60 °C facilitated the loss of thiosulfate by decomposition to sulfur compounds, and as a consequence, the gold recovery fell. In contrast to Abbruzzese et al. (1995), no noticeable decrease was seen in this study in the concentrations of copper or thiosulfate during the first 1.5 h when a temperature of 40 °C was used. However, conducting experiments at 40 °C proved difficult since the gas feed line clogged

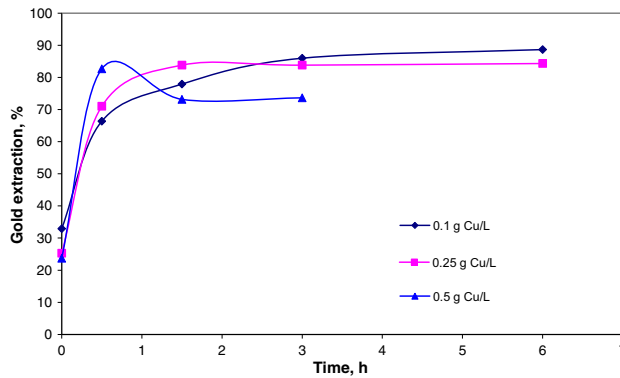


Fig. 8. Effect of initial copper concentration on gold dissolution. Solution: 0.2 M NH_3 , and 0.2 M S_2O_3 . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Temperature: 30 °C. Mixing speed: 700 min^{-1} .

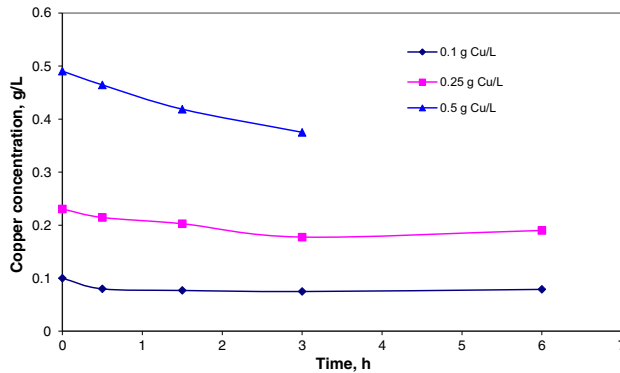


Fig. 9. Variation of copper concentration with time in the gold leaching of the pressure oxidized concentrate. Solution: 0.2 M NH_3 , and 0.2 M S_2O_3 . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Temperature: 30 °C. Mixing speed: 700 min^{-1} .

after 1.5 h of leaching. It seems that some kinds of compounds are formed at a temperature of 40 °C that stick and clog the gas feed repeatedly. It was not possible to maintain constant conditions after 1.5 h of leaching, so the repetition of the experiment at temperature 40 °C was only run for 1.5 h.

These results indicate that it is beneficial for gold leaching to maintain the leaching temperature at 30 °C. Increasing the temperature above 30 °C increases the leaching rate only slightly and different kinds of detrimental effects arise when the temperature increases beyond 30 °C, as discussed above. Using the temperature of 30 °C, 89% gold extraction was achieved in 6 h and measured thiosulfate and copper concentrations after 6 h of leaching were 0.19 M and 0.08 g/L, respectively. Measured oxidation potential varied between 199 and 215 mV and concentration of dissolved oxygen in the slurry between 5.0 and 6.3 mg/L.

Based on the current work and the study by Feng and van Deventer (2010) it can be concluded that oxidative pre-treatment followed by thiosulfate leaching is an efficient approach for the treatment of sulfide containing gold ores/concentrates. In this study, 89% gold extraction was achieved in 6 h with minimal reagent consumption for pressure oxidized gold concentrate. Feng and van Deventer (2010) conducted a

study with sulfide gold ore and achieved 94% gold extraction after 22 h of oxidative pre-treatment followed by 24 h of leaching with negligible reagent consumption. These results indicate good premises for gold recovery by ion-exchange resins, since minimal/negligible thiosulfate consumption ensures low polythionate concentration as well as facilitating recycling of the leaching solution.

4. Conclusions

Ammoniacal thiosulfate leaching experiments of pressure oxidized gold concentrate received from a gold mine showed that leaching should be carried out using low reagent concentrations. Copper concentration is critical, since increased copper concentration can lead to precipitation of leached gold. The highest gold extraction (89%) was achieved in 6 h with the following leaching solutions: 0.2 mol S_2O_3 /L, 0.2 mol NH_3 /L, 0.1 g Cu/L; and with the following conditions: solids, 30 m-%; pressure, 1 atm; continuous aeration; and temperature, 30 °C. Measured thiosulfate and copper concentrations after 6 h of leaching were 0.19 M and 0.08 g/L, respectively. Measured pH varied between 9.8 and 10, oxidation potential between 199 and 215 mV, and concentration of dissolved oxygen in the slurry between 5.0 and 6.3 mg/L.

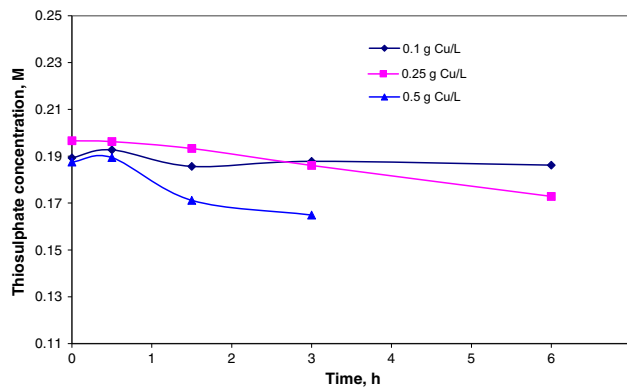


Fig. 10. Variation of thiosulfate concentration with time in the gold leaching of the pressure oxidized concentrate. Solution: 0.2 M NH_3 , and 0.2 M S_2O_3 . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Temperature: 30 °C. Mixing speed: 700 min^{-1} .

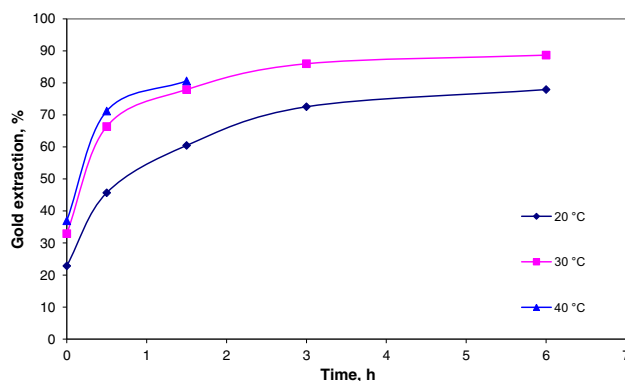


Fig. 11. Effect of temperature on gold dissolution. Solution: 0.2 M NH_3 , and 0.2 M S_2O_3 , and 0.1 g/L Cu^{2+} . Solids: 30 m-%. Pressure: 1 atm. Air flow rate: 0.2 L/min. Mixing speed: 700 min^{-1} .

The results from the leaching experiments show that pressure oxidized gold concentrate can be effectively leached in an ammoniacal thiosulfate leaching solution with minimal reagent consumption. The results indicate good premises for gold recovery by ion-exchange resins, since minimal thiosulfate consumption also ensures low polythionate concentration, which is important in metal recovery with ion-exchange resins. Minimal reagent consumption also indicates that there is a good possibility of circulating the leaching solution after gold recovery and solid-liquid separation for re-use in the leaching stage. This paper concludes that oxidative pre-treatment of sulfide containing gold ores/concentrates followed by thiosulfate leaching with low reagent concentrations offers a way to overcome the problems hitherto identified in the leaching stage and facilitate the following recovery stage.

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References

- Abbruzzese, C., Fornari, P., Massida, R., Veglio, F., Ubalini, S., 1995. Thiosulphate leaching for gold hydrometallurgy. *Hydrometallurgy* 39, 265–276.
- Aylmore, M.G., Muir, D.M., 2001. Thiosulphate leaching of gold – a review. *Miner. Eng.* 14 (2), 135–174.
- Byerley, J.A., Fouda, S.A., Rempel, G.L., 1973. Kinetics and mechanism of the oxidation of thiosulfate ions by copper(II) ions in aqueous ammonia solution. *J. Chem. Soc. Dalton Trans.* 889–893.

- Byerley, J.A., Fouda, S.A., Rempel, G.L., 1975. Activation of copper(II) ammine complexes by molecular oxygen for the oxidation of thiosulfate ions. *J. Chem. Soc. Dalton Trans.* 1329–1338.
- Crundwell, F.K., 2013. The dissolution and leaching of minerals: mechanisms, myths and misunderstandings. *Hydrometallurgy* 139, 132–148.
- Feng, D., van Deventer, J.S.J., 2010. Oxidative pre-treatment in thiosulphate leaching of sulphide gold ores. *Int. J. Miner. Process.* 94, 28–34.
- Freitas, L.R., Trindade, R.B.E., Carageorgos, T., 2001. Thiosulphate leaching of gold-copper ores from Igarape Bahia mine (CVRD). *Proc. VI SHMMT/XVIII ENTMH Conference, Rio de Janeiro.*
- Grosse, A.C., Dicoski, G.W., Shaw, M.J., Haddad, P.R., 2003. Leaching and recovery of gold using ammoniacal thiosulfate leach liquors (a review). *Hydrometallurgy* 69, 1–21.
- Hilson, G., Monhemius, A.J., 2006. Alternatives to cyanide in the gold mining industry: prospects for the future? *J. Clean. Prod.* 14, 1158–1167.
- Langhans Jr., J.W., Lei, K.P.V., Carnahan, T.G., 1992. Copper-catalyzed thiosulfate leaching of low-grade gold ores. *Hydrometallurgy* 29, 191–203.
- Marchbank, A., R., Thomas, K., G., Dreisinger, D., Fleming, C., 1996. Gold recovery from refractory carbonaceous ores by pressure oxidation and thiosulfate leaching. US patent, No. 5536297.
- Molleman, E., Dreisinger, D., 2002. The treatment of copper-gold ores by ammonium thiosulfate leaching. *Hydrometallurgy* 66, 1–21.
- Muir, D.M., Aylmore, M.G., 2004. Thiosulphate as an alternative to cyanide for gold processing – issues and impediments. *Mineral. Process. Extr. Metall. (Trans. Inst. Min. Metall. C)* 113, C2–C12.
- Navarro, P., Vargas, C., Villarroel, A., Alguacil, F.J., 2002. On the use of ammoniacal/ammonium thiosulphate for gold extraction from concentrate. *Hydrometallurgy* 65, 37–42.
- Senanayake, G., 2005. The role of ligands and oxidants in thiosulfate leaching of gold. *Gold Bull.* 38 (4), 170–179.
- Thomas, K., G., Fleming, C., Marchbank, A., R., Dreisinger, D., 1998. Gold recovery from refractory carbonaceous ores by pressure oxidation, thiosulphate leaching and resin-in-pulp adsorption. US patent, No. 5785736.
- West-Sells, P.G., Hackl, R.P., 2005. A novel thiosulfate leach process for the treatment of carbonaceous gold ores. In: Deschênes, G., Hodouin, D., Lorenzen, L. (Eds.), *Treatment of Gold Ores, Proc. 44th Annual Conference of Metallurgists of CIM Calgary, Alberta, Canada*, pp. 209–223.
- Zipperian, D., Raghavan, S., Wilson, J.P., 1988. Gold and silver extraction by ammoniacal thiosulfate leaching from rhyolite ore. *Hydrometallurgy* 19, 361–375.

Publication II

Lampinen, M., Laari, A., and Turunen, I.

Kinetic model for direct leaching of zinc sulfide concentrates at high slurry and solute concentration

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Kinetic model for direct leaching of zinc sulfide concentrates at high slurry and solute concentration



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ABSTRACT

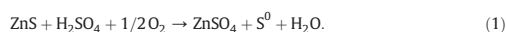
In this study, direct leaching of zinc sulfide concentrate was investigated in a solution that resembles the composition of solutions used in industrial leaching processes. The effect of different factors (temperature, Fe^{2+} – Fe^{3+} –concentration, H_2SO_4 –concentration, SO_4 –concentration, pressure, size of the concentrate particles) on the rate of the zinc sulfide concentrate leaching was studied experimentally. H_2SO_4 –concentration had no influence on the leaching kinetics. The obtained experimental data were used to model the reaction kinetics with mechanistic models as well with a more empirical model, and the reliability and the accuracy of the model parameters were studied with Markov Chain Monte Carlo (MCMC) methods. The model that best describes the leaching system ($R_2 = 97\%$) takes into account the reactions between the zinc sulfide concentrate and oxidizing agents at the reacting surface of the concentrate particles, the decrease in the active surface area of the concentrate particles as the leaching proceeds, the particle size distribution of the concentrate particles, the composition of the solution, and the oxidation rate of Fe^{2+} to Fe^{3+} . The experimental results together with the modeling results clearly demonstrate that it is important to have experimental data for the kinetics of the leaching at the conditions of the reactor.

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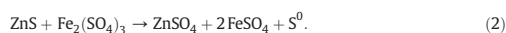
1. Introduction

The conventional method for recovering zinc from zinc ores is the Roast–Leach–Electrowin (RLE) process. An alternative to the RLE process is direct leaching, where the zinc sulfide concentrates are directly leached without roasting. Direct leaching processes can be divided into two categories, pressure leaching processes and atmospheric leaching processes. Both of these processes have many industrial applications (Haakana et al., 2008; Ozberk et al., 1995; Takala, 1999).

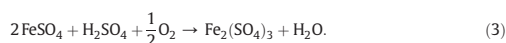
The total reaction of zinc sulfide concentrate leaching can be presented by the equation:



It is usually assumed that the reaction proceeds via an iron oxidation–reduction cycle (Eqs. (2) and (3)). First, ferric ion oxidizes sulfide sulfur and reduces to ferrous ion:



The ferrous ion is then oxidized back to ferric ion with oxygen to maintain the level of oxidant:



Ferric ion has an important role as an oxidant in the process, as can be seen from the reaction (Eq. (2)) presented above. Therefore, the kinetics of oxidation of Fe^{2+} back to Fe^{3+} (Eq. (3)) is important when the direct leaching process of zinc sulfide concentrate is studied.

Direct pressure leaching enables fast concentrate dissolution; standard residence time in the sphalerite pressure leaching process is 90 min, and operating pressures are up to 1600 kPa. Problems associated with pressure leaching are mainly found in the operation and maintenance of autoclaves (Takala, 1999; Babu et al., 2002). Atmospheric leaching is considered an option to address problems encountered in industrial pressure leaching processes. The direct atmospheric leaching process is carried out with slow kinetics requiring around 24 h for leaching, and larger reactors are therefore needed compared to pressure leaching plants (Takala, 1999). Studies of direct leaching have been performed by many authors (Rath et al., 1981; Verbaan and Crundwell, 1986; Crundwell, 1987; Corriou et al., 1988; Palencia Perez and Dutrizac, 1991; Babu et al., 2002; Dutrizac, 2006; Souza et al., 2007; Xie et al., 2007; Xu et al., 2013), and a novel reaction system has been presented (Haakana et al., 2007). New technologies

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such as ultrasound have also been explored (Grénman et al., 2007) in efforts to intensify the process, i.e., to enhance the leaching rate.

Knowledge of the chemical kinetics is crucial for the design and development of leaching processes. Mathematical modeling of leaching systems is usually used to interpret experimental results and to gain insight into the reaction mechanism. In mathematical modeling of chemical kinetics, kinetic parameters exist in the model that needs to be estimated from measured data. Obtained kinetic parameters are used to interpret the experimental data. Parameter estimates are often uncertain, since they are estimated from incomplete and noisy measurements. Hence, the uncertainty of the kinetic parameters should be closely examined. Quantifying of rate parameters is also important for the design and development of leaching reactors. The structural properties of the solid particles influence significantly the progress of the reaction, but also the reaction media has a great impact. Gbor and Jia (2004) presented that the shrinking core model (SCM) is widely used to model fluid–solid reactions such as leaching of metals from minerals. They, however, note that in most cases the particle size distribution (PSD) of the solid material is disregarded. Gbor and Jia (2004) quantified the erroneous shift in the control regime resulting from neglect of PSD. The reaction mechanisms are often considered to be very complex, comprising several unknown steps. Kinetic studies are carried out in order to develop an understanding of the mechanism of the studied reaction. Concentrations should stay constant during kinetic studies, hence studies are usually conducted in dilute solutions and with low solid content compared to the solutions and solid loads used in industrial processes. However, industrial leaching slurries are usually concentrated and contain for example considerably high amounts of sulfates (ZnSO₄, FeSO₄, MgSO₄). Previous studies have shown that the concentration of sulfates has an effect on the leaching rate (Dutrizac, 2006) as well as on the oxidation of Fe²⁺ to Fe³⁺ (Dreisinger and Peters, 1989). Crundwell and Bryson (1992) studied the modeling of particulate leaching reactors and presented that in order to produce a model that is numerically accurate, it is important to have experimental data for the kinetics of the leaching at the conditions of the reactor. Industry's first task in adoption of the leaching system is to develop a robust overall process flowsheet that can be realistically used and costed for a range of actual raw materials. It is evident that reliable chemical kinetics for process design and development purposes requires also experimental data at the conditions of the reactor and critical evaluation of the reliability of the model used for modeling and simulation purposes.

In this study, direct leaching of zinc concentrate is studied in conditions used in industrial direct leaching processes. The aim of this work is to provide premises for process development of direct leaching processes of zinc sulfide concentrates by providing experimental data for conditions close to those of an actual industrial reactor and to examine modeling aspects of the process. The performance of the mechanistic models proposed in the literature for the direct leaching system of zinc concentrates is evaluated and a model for the leaching system presented. The model takes into account the reactions between the zinc sulfide concentrate and oxidizing agents at the reacting surface of the concentrate particles, the decrease in the active surface area of the concentrate particles as the leaching proceeds, the particle size distribution of the concentrate particles, the composition of the solution, and the oxidation rate of Fe²⁺ to Fe³⁺. The reliability of the model parameters is evaluated with Markov Chain Monte Carlo (MCMC) methods.

2. Experimental work

2.1. Materials

The zinc concentrate used in the leaching experiments contains 54.2% zinc, 6.6% iron, 1.5% lead and 30.3% sulfur. The mineral composition of the zinc concentrate is: 89.6% sphalerite, 2% pyrite, 1.8% galena

and 6.1% gangue silicates and carbonates. Quantitative XRD was used to determine the mineralogy. The chemical composition of the concentrate was analyzed by ICP after digestion. Mean particle sizes and particle size distributions are presented in Table 1. Fine grinding of the concentrate particles was done in a planetary ball mill. The particle size distribution of the zinc concentrate was analyzed with an LS 13 320 Laser Diffraction Particle Size Analyzer. All the chemicals used were analytical grade, and ultrapure water was used for preparation of the solutions.

2.2. Analytical techniques

Metal concentrations (Zn, Fe, Cu) of the solution samples from the leaching experiments were analyzed by atomic absorption spectroscopy (Thermo Scientific iCE 3000 Series AA spectrophotometer). Ferrous (Fe²⁺) ion concentrations and sulfuric acid (H₂SO₄) concentrations of the solution samples from the leaching experiments were analyzed by titration with potassium dichromate and by iodometric titration with sodium thiosulfate, respectively.

2.3. Leaching tests

Leaching of the concentrate samples was conducted as batch experiments (0.7 dm³ of slurry in each batch) in a 1.1 dm³ autoclave reactor. The reactor was equipped with a stirrer and 4 baffles. A double-pitch-bladed turbine (4 cm diameter) was used for stirring. The autoclave reactor was heated by a thermostatic oil bath. The laboratory set-up consisted of a reactor, mixer, thermostatic oil bath, gas feed line for O₂ and N₂, gas mass flow controller, condenser for exhaust gas, foam trap, and pressure controller. Gas was fed from the bottom of the reactor as fine bubbles. The solution was heated to the reaction temperature and the solids (concentrate and lignosulfonate) were added to a beaker together with the hot solution. The slurry was kept in the beaker until foaming stopped. It was then poured back into the reactor and heated to the required reaction temperature. Nitrogen feed was started when the slurry was poured into the reactor. The gas feed was changed to oxygen when the required temperature and pressure were reached, and the first sample was taken at this point. The positive initial conversion for zinc in the following figures represents the amount of zinc leached before the first sample was taken. The samples (20–40 mL) were taken out from the bottom valve of the reactor at pre-set time intervals. The samples were immediately vacuum filtered after sampling and analyses were carried out on the solution samples.

2.4. Experimental design

The aim of the experiments was to provide data for the kinetics of leaching at conditions corresponding to those of an industrial atmospheric leaching reactor. Atmospheric direct leaching is carried out in large-scale mixed reactors. The reactors are tall and considerable hydrostatic pressure can be found, especially at the bottom of the reactor, as presented in a previous study (Lampinen et al., 2010). For this reason, elevated pressures were chosen for the experiments, and the selected pressure range was 200–700 kPa overpressure. Atmospheric leaching

Table 1
Mean particle size and particle size distribution of the concentrate particles.

Set	1	2	3
Diameter	µm	µm	µm
Mean	20.81	27.09	33.25
<10%	2.04	1.86	4.36
<25%	5.11	5.93	10.97
<50%	13.18	16.86	25.39
<75%	28.74	38.58	46.56
<90%	59.2	65.58	73.91

(Takala, 1999) is carried out at temperatures near the boiling point of the process solution (~100 °C). It is evident that mechanisms and phenomena in the leaching process change when the temperature rises above the melting point of elemental sulfur (115–117 °C) and the temperature range was thus selected as 70–110 °C. All the leaching experiments were conducted in a solution (Table 2) with a composition close to solutions used in industrial processes. Iron was inserted into the reactor in the form of ferrous sulfate, because stabilization of the conditions in the reactor requires time and the starting point of the leaching process could thus be controlled. Solids concentration used in the experiments was 100 g/L.

Ensuring kinetic control is the first step of kinetic experiments. Direct leaching of zinc concentrates poses a challenge since the elemental sulfur produced in the leaching reactions (Eqs. (1) and (2)) might remain on the surface of the concentrate particle and start to slow down the reaction as the reaction progresses further. Previous studies have claimed both that elemental sulfur layer has a role in the leaching process (Lochmann and Pedlik, 1995; Souza et al., 2007) and that it has no effect on the leaching (Dutrizac, 2006; Xie et al., 2007; Salmi et al., 2010). Consequently, there is no general consensus whether a shrinking particle or product layer model should be applied. In this study, the issue was addressed by suppressing any possible effect of the sulfur layer through the use of rather drastic conditions and by adding ligno-sulfonate to the slurry in each experiment. The influence of external mass transfer resistances was studied experimentally in preliminary experiments. Based on the preliminary experiments, a stirring speed of 800 1/min and oxygen flow rate of 0.4 L/min (NTP) was chosen for the actual leaching experiments. The aim of the experiments was to maximize the zinc extraction while minimizing leaching duration and to study the significance of different parameters on the zinc leaching rate. Based on a review of the results of previous zinc concentrate dissolution studies and preliminary practical observations, the experimental conditions presented in Table 3 were chosen.

3. Results and discussion

3.1. Effect of acid concentration

The effect of sulfuric acid concentration on zinc extraction was studied with two different concentrations. From Fig. 1, it can be seen that raising the sulfuric acid concentration from 110 to 150 g/L did not have a significant effect on the leaching rate of the zinc concentrate. Nevertheless, it was decided to conduct the following experiments at a sulfuric acid concentration of 150 g/L to ensure that the sulfuric acid does not become exhausted and in this way limit the leaching rate. The oxidation rate of Fe²⁺ to Fe³⁺ was slightly faster at a sulfuric acid concentration of 150 g/L. The lowest value determined for sulfuric acid concentration in the experiments conducted in this work was 50 g/L, which can be considered to be high concentration, indicating that sulfuric acid does not become exhausted nor affect leaching system in the conditions of the current work. Hence, the effect of the sulfuric acid concentration on the leaching system can be considered to be practically negligible in the conditions of the current work.

Previous studies have produced conflicting results as regards the effect of sulfuric acid concentration on the reaction rate. Salmi et al. (2010) presented that sulfuric acid concentration did not have any

Table 2

Solution used in leaching experiments. The solution also contains different amounts of iron (Fe²⁺, Fe³⁺), zinc (ZnSO₄) and sulfuric acid.

	c, g/L
Mg (MgSO ₄)	10
Mn (MnSO ₄)	3
Cu (CuSO ₄)	0.5

Table 3

Experimental conditions of the zinc concentrate leaching.

Run	T °C	Overpressure kPa	Fe ²⁺ conc. g/L	Zn-conc. g/L	H ₂ SO ₄ -conc. g/L	Mean particle size 10 ⁻⁶ m
1	70	500	20	70	150	27.09
2	95	500	20	70	150	27.09
3	110	500	20	70	150	27.09
4	95	200	20	70	150	27.09
5	95	700	20	70	150	27.09
6	95	500	10	70	150	27.09
7	95	500	40	70	150	27.09
8	95	500	40	10	150	27.09
9	95	500	40	100	150	27.09
10	95	500	20	70	110	27.09
11	95	500	20	70	150	20.81
12	95	500	20	70	150	33.25

significant influence on the reaction rate at the conditions studied in their work. Dutrizac (2006) reported that the acid concentration has no effect on the reaction rate at lower acid concentrations, but the rate increases slowly if the acid concentration exceeds 0.1 M. Crundwell (2013) presented that a frequent assumption in the literature on dissolution of minerals is that the dissolution reaction commences with an acid attack on the surface of the mineral to form hydrogen sulfide, and this hydrogen sulfide is oxidized by the oxidant in the solution (Eqs. (4) and (5)). Crundwell (2013) argued that the acid attack mechanism should be rejected and presented that the first step of the reaction is not by acid, because its rate of reaction is not fast enough and it does not successfully describe the kinetic parameters. It has also been presented (Corriou et al., 1988; Xu et al., 2013) that the dissolution reaction mechanism goes entirely through the acid attack. Corriou et al. (1988) studied pressure leaching of zinc sulfide and described the leaching by the direct acid attack mechanism. There was practically no iron available in their experiments, and they presented H₂S as being oxidized by oxygen. Dutrizac (2006) proposed that the acid attack mechanism (Eq. (4)) takes part as a parallel reaction in the leaching of sphalerite with the dissolved H₂S being oxidized by ferric ions according to Eq. (5).

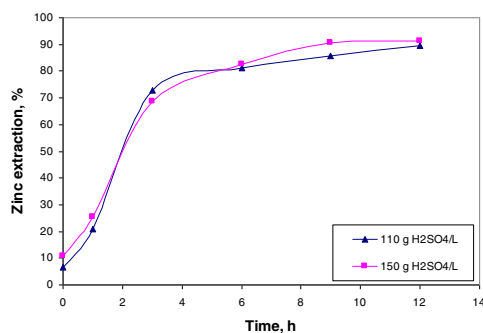
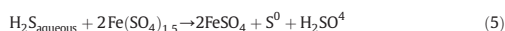


Fig. 1. Effect of sulfuric acid concentration on zinc extraction. Pressure 500 kPa overpressure, T = 95 °C, solid content 100 g/L, Fe²⁺ 20 g/L, O₂ 0.4 L/min (NTP), initial Zn-concentration 70 g/L (ZnSO₄), lignosulfonate 0.3 g/L, mean zinc concentrate particle diameter 27.09 μm. Leaching experiments were carried out in the solution presented in Table 2.

The question of the role of sulfuric acid is clearly not authoritatively answered. However, if the acid attack mechanism does occur, one would expect that the reaction rate would be strongly dependent on the concentration of the acid, as Crundwell (2013) presented. For the conditions of the current work, the sulfuric acid concentration did not have any significant influence on the reaction rate of the zinc leaching, as shown in Fig. 1, and it can thus be neglected when considering the kinetics of the zinc leaching.

3.2. Effect of temperature

The zinc leaching rate at different temperatures is presented in Fig. 2. As can be seen from Fig. 2, temperature has a significant effect on the zinc leaching rate. The leaching rate is relatively slow at 70 °C but increases significantly when the temperature is raised from 70 to 95 and further to 110 °C. The temperature effect was expected, since a similar effect has been observed in previous studies (Dutrizac, 2006; Xie et al., 2007; Souza et al., 2007; Salmi et al., 2010).

3.3. Effect of pressure

Zinc leaching rates at three different pressures are presented in Fig. 3. It can be seen that when the pressure is raised from 200 to 500 kPa overpressure the zinc leaching rate becomes faster, but raising the pressure further from 500 to 700 kPa overpressure does not have an effect on the leaching rate. Raising the pressure increases oxygen solubility, which in turn enhances the oxidation of Fe^{2+} to Fe^{3+} . This effect was confirmed by ferrous iron titrations done in the current study (Fig. 7: Run 2, 4 and 5). Increased ferric ion concentration increased the leaching rate when the pressure was raised from 200 to 500 kPa overpressure, indicating that oxidation of Fe^{2+} to Fe^{3+} is the rate limiting step. Raising the pressure above 500 kPa overpressure did not further increase the leaching rate because at these conditions the leaching rate is limited by the rate of the surface reaction.

3.4. Effect of the initial iron concentration

The zinc leaching rate at three different initial Fe^{2+} -concentrations is presented in Fig. 4. From Fig. 4, it can be seen that raising the initial Fe^{2+} -concentration decreases the rate of the zinc concentrate leaching. Raising the initial Fe^{2+} -concentration from 10 to 20 g/L does not decrease the leaching as much as raising the initial Fe^{2+} -concentration from 20 to 40 g/L. Fe^{2+} -titrations (Fig. 7: Run 2 and 7) showed that the amount of the primary oxidant (Fe^{3+}) of zinc increased throughout when the initial concentration of iron (Fe^{2+}) was 20 and 40 g/L.

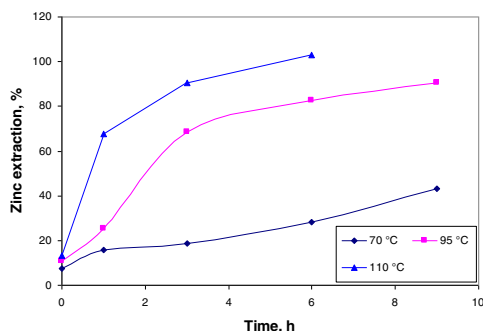


Fig. 2. Effect of leaching temperature on zinc extraction. 500 kPa overpressure, solid content 100 g/L, Fe^{2+} 20 g/L, H_2SO_4 150 g/L, O_2 0.4 L/min (NTP), initial Zn-concentration 70 g/L (ZnSO_4), liginosulfonate 0.3 g/L, mean zinc concentrate particle diameter 27.09 μm . Leaching experiments were carried out in the solution presented in Table 2.

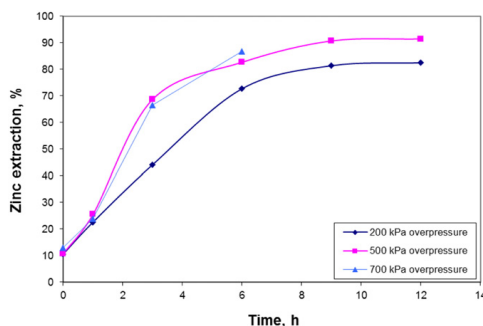


Fig. 3. Effect of leaching pressure on zinc extraction. $T = 95$ °C, solid content 100 g/L, Fe^{2+} 20 g/L, H_2SO_4 150 g/L, O_2 0.4 L/min (NTP), initial Zn-concentration 70 g/L (ZnSO_4), liginosulfonate 0.3 g/L, mean zinc concentrate particle diameter 27.09 μm . Leaching experiments were carried out in the solution presented in Table 2.

However, for an initial concentration of 10 g/L the concentration of the oxidant remained approximately constant (~ 2 g Fe^{3+} /L) between 1–3 h (Fig. 7: run 6) and then started to increase. This suggests that using initial Fe^{2+} -concentration < 10 g/L will lead to a decrease in the zinc leaching rate, because the primary oxidant level can drop to zero, in other words, the iron oxidation rate (Eq. (3)) becomes the rate limiting step. Fig. 4 shows that raising the initial Fe^{2+} -concentration significantly over 10 g/L decreases the rate of the zinc concentrate leaching, most probably because the sulfate concentration in the solution increases; this matter is discussed below. Based on the experimental results, it can be concluded that the optimal initial iron concentration for the current case is around 10 g/L.

3.5. Effect of initial sulfate concentration

Zinc leaching rates at different initial zinc sulfate concentrations are presented in Fig. 5. From Fig. 5, it can be seen that the zinc leaching rate increases when the initial zinc sulfate concentration is decreased. Dutrizac (2006) also presented in his study that increasing the initial ZnSO_4 -concentration decreases the leaching rate. He also showed that increasing the initial MgSO_4 and FeSO_4 concentrations similarly decreased the leaching rate and concluded that sulfate detrimentally affects the zinc leaching rate. Results presented in Figs. 4 and 5 are in agreement with results presented by Dutrizac (2006). The oxidation

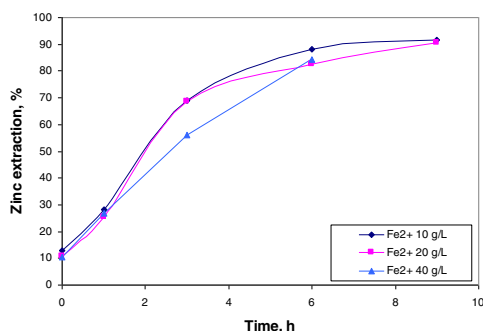


Fig. 4. Effect of initial Fe^{2+} -concentration on zinc extraction. 500 kPa overpressure, $T = 95$ °C, solid content 100 g/L, O_2 0.4 L/min (NTP), H_2SO_4 150 g/L, initial Zn-concentration 70 g/L (ZnSO_4), liginosulfonate 0.3 g/L, mean zinc concentrate particle diameter 27.09 μm . Leaching experiments were done in the solution presented in Table 2.

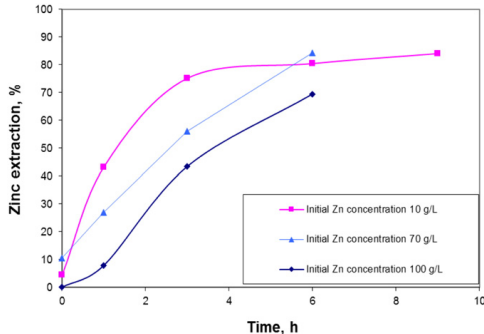


Fig. 5. Effect of initial zinc sulfate concentration on zinc extraction. 500 kPa overpressure, $T = 95\text{ }^{\circ}\text{C}$, Fe^{2+} 40 g/L, solid content 100 g/L, O_2 0.4 L/min (NTP), H_2SO_4 150 g/L, lignosulfonate 0.3 g/L, mean zinc concentrate particle diameter 27.09 μm . Leaching experiments were carried out in the solution presented in Table 2.

rate of Fe^{2+} to Fe^{3+} also increased (Fig. 7: Run 7, 8 and 9) when the initial sulfate concentration was decreased, which shows that lower sulfate concentrations are also beneficial for the ferrous ion oxidation rate.

The experimental results indicate that the composition of the solution has an effect on the leaching rate. Increasing initial Fe^{2+} - and Zn-concentrations over 10 g/L decreased the leaching rate. Fe^{2+} - and Zn were added as sulfates (ZnSO_4 and FeSO_4), which suggests that the increasing amount of sulfates is actually the reason for the deceleration of the leaching rate. If this is the case, then it would be desirable to minimize the accumulation of the sulfates when industrial leaching processes are designed, since industrial leaching processes usually contain circulation of the process solutions.

3.6. Effect of particle size

The effect of concentrate particle size on the zinc leaching rate is presented in Fig. 6. It can be seen that decrease in particle size enhanced the zinc leaching rate. Enhancement of zinc leaching as particle size decreases was expected, as the active surface area increases when the particle size is decreased. Xie et al. (2007) studied the pressure leaching kinetics of a high iron sphalerite concentrate and presented that the influence of particle size on the zinc leaching rate is remarkable. Souza

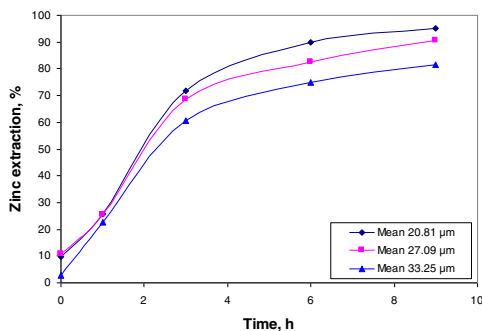


Fig. 6. Effect of the initial particle size of the concentrate on zinc extraction. 500 kPa overpressure, $T = 95\text{ }^{\circ}\text{C}$, Fe^{2+} 20 g/L, solid content 100 g/L, O_2 0.4 L/min (NTP), H_2SO_4 150 g/L, initial Zn-concentration 70 g/L (ZnSO_4), lignosulfonate 0.3 g/L. Leaching experiments were done in the solution presented in Table 2.

et al. (2007) examined the leaching kinetics of an iron-rich zinc sulfide concentrate at atmospheric pressure and presented that decrease in the particle size enhanced the zinc dissolution, but particle size plays a minor role in the leaching process.

4. Kinetic model for zinc concentrate leaching

Rönholm et al. (1999) studied the oxidation kinetics of Fe^{2+} ions to Fe^{3+} in concentrated H_2SO_4 - FeSO_4 solutions and presented a mechanistic model for the oxidation kinetics. The conditions in the current study and in the study by Rönholm et al. (1999) are quite similar, hence the model presented by Rönholm et al. (1999) is used in this study. Salmi et al. (2010) presented a mechanistic model for leaching of zinc with ferric iron. The model presented by Salmi et al. (2010) was fitted to data presented in this work. The coefficient of determination (91.37%) of the fit was reasonable, but notable uncertainty in the parameters was noticed. This was expected since Salmi et al. (2010) did not consider the effect of sulfates on the leaching kinetics, which is clearly seen in the experimental results presented in this work and in the work by Dutrizac (2006). Hence, a model for leaching of zinc was developed in this work, that takes into account also the effect of sulfates as well as the particle size distribution.

Kinetic models for oxidation of Fe^{2+} to Fe^{3+} and zinc concentrate leaching are presented below. Iron was introduced as ferrous ion, which means that the leaching process starts with iron oxidation. The rate expressions presented by Rönholm et al. (1999) were used to describe the oxidation kinetics of Fe^{2+} to Fe^{3+} . The dependency of the reaction rate on temperature is taken into account by the Arrhenius equation, which is modified to the following form to improve parameter identification (Haario, 2002):

$$r_1 = \frac{A_1 c_{\text{Fe}^{2+}}^2 c_{\text{O}_2}}{1 + (A_1/A_2) c_{\text{Fe}^{2+}}} e^{-\frac{E_1}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right)} \quad (6)$$

The rate equation presented above includes the liquid phase concentration of oxygen. Gas-liquid mass transfer was negligible in the experiments and the dissolved oxygen concentration was calculated according to Henry's law.

$$c_{\text{O}_2} = p_{\text{O}_2} / H \quad (7)$$

Oxygen solubility in the liquid phase is greatly affected by the ionic compounds present in the solution. Rönholm et al. (1999) calculated oxygen solubility in the liquid phase based on the work done by Schumpe (1993) and Weisenberger and Schumpe (1996). Kaskiala (2005) used work done by Schumpe (1993) and Weisenberger and Schumpe (1996) to calculate the oxygen solubility of two complex process solution containing different compositions of sulfuric acid, zinc sulfate and iron sulfates. Baldwin et al. (1995) used an empirical expression for Henry's constant to calculate the oxygen solubility of a zinc pressure leach process. Henry's constant for complex process solutions presented by Kaskiala (2005) are similar to those presented by Baldwin et al. (1995) for a zinc pressure leach process, so both can be used in the current case.

Oxygen partial pressure is obtained when the solution vapor pressure is subtracted from the total pressure. Rönholm et al. (1999) corrected the measured total pressure with vapor pressure of the H_2O - H_2SO_4 - FeSO_4 solution to obtain a reliable value of the partial pressure of oxygen. Rönholm et al. (1999) calculated the vapor pressure of water and used a correction factor to take into account the solvent composition. An empirical correlation related to the weight fraction of (dihydrogen) sulfate in the solution was developed by Rönholm et al. (1999). Baldwin et al. (1995) used the following correlation (Eq. (8)) for a zinc pressure leach process, which is calculated using vapor pressure data for sulfuric acid solutions activity coefficients for zinc and iron salts. The correlation presented by Baldwin et al. (1995)

for the vapor pressure of the solution is closer to the conditions used in this work and it was used in the current case.

$$p_{\text{solution}} = \exp \left[12.73323 - 0.08092 [\text{H}_2\text{SO}_4] - 0.01396 [\text{Zn}^{2+}] - 0.00991 [\text{Fe}_t] - \frac{4741.66}{T} \right] \quad (8)$$

where the concentrations are in mol dm⁻³ and p_{solution} is in atm. Fe_t in Eq. (8) is the total iron concentration.

The reduction of ferric ion back to ferrous ion by the leaching, Eq. (2), also has to be taken into account when the ordinary differential equation for the ferrous ion is written.

$$\frac{dC_{\text{Fe}^{2+}}}{dt} = -r_1 + 2 \sum_{N=1}^6 r_2 A_{i,N} n_N P_N \quad (9)$$

The zinc concentrate leaching is assumed to proceed according to reaction (2), and the reaction of the zinc is specified as a surface reaction. The zinc concentration on the solid surface of the particle is a characteristic of the concentrate and it is assumed to be constant. Therefore, k_{ZnS} can be lumped to a kinetic constant k_2 . Sulfate concentration refers to the sulfates related to ZnSO₄, FeSO₄, MgSO₄, MnSO₄, and CuSO₄, and not to sulfuric acid. This approach is adopted, because it matches the trends reported previously (Dreisinger and Peters, 1989; Baldwin et al., 1995) and for the sake of simplicity.

$$r_2 = k_{\text{ZnS}} C_{\text{Fe}^{3+}}^{n_1} C_{\text{SO}_4}^{n_2} = k_1 C_{\text{Fe}^{3+}}^{n_1} C_{\text{SO}_4}^{n_2} \quad (10)$$

The dependency of the reaction rate (Eq. (10)) on temperature is also taken into account by the Arrhenius equation.

$$k_1 = k_{1,\text{mean}} \exp \left(-\frac{E_2}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{mean}}} \right) \right) \quad (11)$$

Population balances were used when the dissolution rate of the zinc was calculated. The concentrate particles were divided into six classes. The dissolution rate for each class was calculated using an average particle size and the portion of particles in the class. Finally, all classes were summed up to obtain the overall leaching rate of the zinc. The dissolution rate of the zinc can be described by the following equation.

$$-\frac{dC_{\text{Zn}}}{dt} = \sum_{N=1}^6 r_2 A_{i,N} n_N P_N \quad (12)$$

According to the shrinking core model, the shrinkage of the core of the particle can be described with Eq. (13), where r_i and r_o denote the radius of the reacting particle and the radius of the particle at time zero, respectively. Zinc concentration at time zero is presented with $C_{\text{Zn},0}$.

$$\left(\frac{r_i}{r_o} \right)^3 = \frac{C_{\text{Zn}}}{C_{\text{Zn},0}} \quad (13)$$

Eq. (13) was used for continuous calculation of the active area of the particle. Therefore, the active area in Eqs. (9) and (12) continuously decreases as the reaction proceeds.

The ferrous ion oxidation rate (Eq. (9)) and the zinc leaching rate (Eq. (11)) are ordinary differential equations, which are numerically integrated from the initial state at time zero to the designated time from the experimental data. The differential equations were solved with a suitable ODESSA-solver (Leis and Kramer, 1988), which is a modification of the widely disseminated initial value solver LSODE. A Levenberg-Marquardt algorithm was used in the minimization of the objective function. The model parameters (A_1 , A_2 , $k_{1,\text{mean}}$, E_1 , E_2 , n_1 and n_2) were estimated by the Modest software (Haario, 2002) by

minimizing the squared difference between the simulations and the experiments.

5. Modeling results and discussion

The model presented above is fitted to experimental data presented in the study. The coefficient of determination for the model was 96.63%. Comparisons of the measured and calculated ferrous ion concentrations and conversions for zinc are presented in Figs. 7 and 8, respectively. When the pressure is 200 kPa (Fig. 7: Run 4) and when the initial zinc sulfate concentration is 100 g/L (Fig. 7: Run 9) the model calculation overestimates the rate of the ferrous ion oxidation. When the initial zinc sulfate concentration is 10 g/L (Fig. 7: Run 8) the model calculation underestimates the rate of ferrous ion oxidation. From Fig. 8 it can be seen that the measured and predicted conversions for zinc agree well.

The values of the estimated parameters are presented in Table 4. It can be seen from the table that the apparent activation energy (E_1) for oxidation of Fe^{2+} to Fe^{3+} is 25.5 kJ/mol. The rate of ferrous ion oxidation by molecular oxygen has been reported for a variety of conditions. Dreisinger and Peters (1989) reviewed studies presented in the literature for sulfate solutions and presented activation energies between 51.6–94.4 kJ/mol. Subsequently, Rönholm et al. (1999) studied the kinetics of ferrous sulfate oxidation with molecular oxygen and presented that the value for the activation energy is 34 kJ/mol. The study by Rönholm et al. (1999) was performed in concentrated H_2SO_4 – FeSO_4 solutions, at temperatures between 60–130 °C and oxygen pressures between 400–1000 kPa. It can be noted that the conditions in this study and in the study by Rönholm et al. (1999) are quite similar and the values for the activation energies are closer to each other than the values presented by Dreisinger and Peters (1989). The variation in activation energy values noted above adds weight to the notion that kinetics studies should be done at the conditions of the actual industrial application.

It can be seen from Table 4 that the apparent activation energy (E_2) for the zinc concentrate leaching is 112 kJ/mol. This value for the apparent activation energy is high, as could be expected based on the strong temperature sensitivity seen in Fig. 2. Reactions that are very temperature-sensitive have high activation energies (Levenspiel, 1972). High activation energy also indicates that the leaching is controlled by a chemical reaction on the surface of the particles. The values of activation energies reported in the literature vary widely. Rath et al. (1981) reported the activation energy to be 90.0 ± 12.5 kJ/mol in the reaction between pure zinc sulfide and ferric chloride at a temperature range of 30–70 °C. Markus et al. (2004) studied the reaction of pure zinc sulfide in ferric sulfate media and presented that activation energies vary between 63 and 97 kJ/mol, depending on the model used. Palencia Perez and Dutrizac (1991) leached sphalerite samples in both ferric iron sulfate-sulfuric acid and ferric iron chloride-hydrochloric acid solutions. The activation energy decreased as the iron content of the sphalerite increased. In ferric sulfate media, the activation energy was about 70 kJ/mol for sphalerite with an iron content of 0.04 wt.% and approximately 40 kJ/mol for sphalerite with an iron content of 12 wt.%. Verbaan and Crundwell (1986) leached a sphalerite concentrate in an acidic ferric sulfate solution and reported that the estimated activation energy was 79.4 kJ/mol at 25–85 °C. Xie et al. (2007) presented in their study that the activation energy in pressure leaching of high iron sphalerite is 55.04 kJ/mol and concluded that the leaching process is controlled by a surface chemical reaction. Dutrizac (2006) presented in his study that the activation energy in atmospheric leaching of sphalerite is 44 kJ/mol. The study concluded that the leaching process is controlled by a surface chemical reaction. Souza et al. (2007) demonstrated that atmospheric leaching of zinc sulfide proceeds in two stages. Initially, the dissolution kinetics is controlled by the chemical reaction at the surface of the zinc sulfide particles, which is followed by a second step where the leaching is controlled by diffusion of the reagents or products through the elemental sulfur layer. The activation energy of the

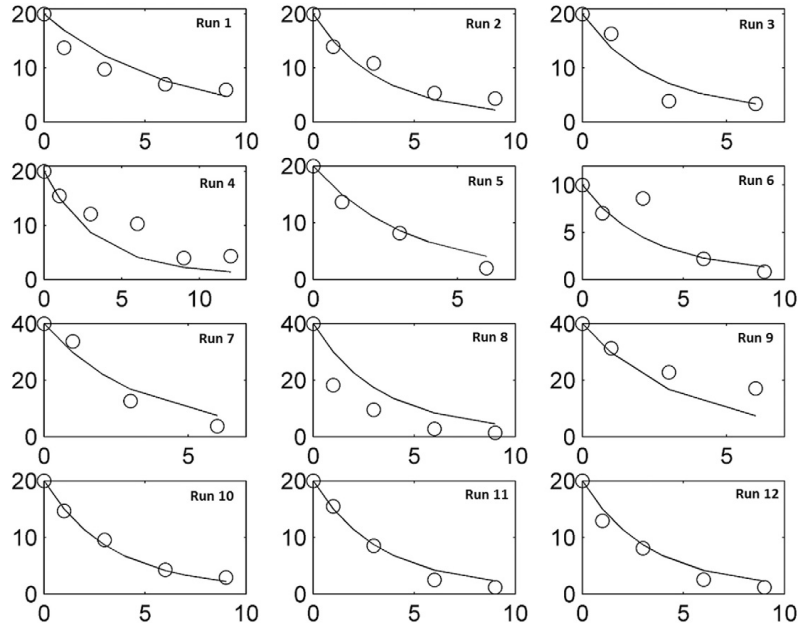


Fig. 7. Comparison of measured and predicted ferrous ion concentrations. Ferrous ion concentration (g/L) on the y-axis and time (h) on the x-axis. Experimental conditions are presented in Table 3.

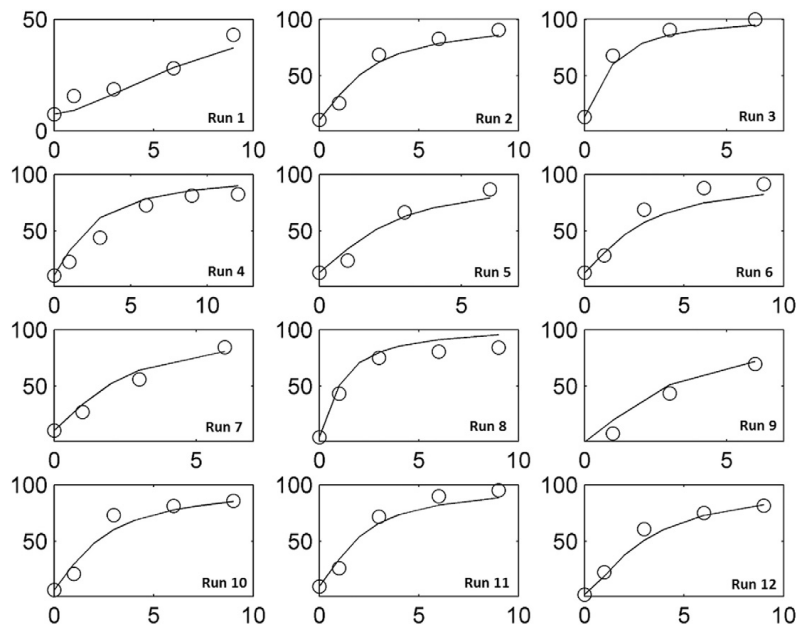


Fig. 8. Comparison of measured and predicted conversions for zinc. Conversion (%) on the y-axis and time (h) on the x-axis. Experimental conditions are presented in Table 3.

Table 4
Estimated parameters and their standard errors.

Parameter	Value	Unit	Std. error (%)
A_1	6.19	$(\text{dm}^3)^2/(\text{mol}^2\text{h})$	844.2
A_2	21.1	$\text{mol}/\text{dm}^3\text{h}$	858.2
E_1	25.5×10^3	J/mol	59.5
E_2	112×10^3	J/mol	10.1
$k_{1,\text{mean}}$	24.7×10^{-3}	$\text{mol}^{2.95}/\text{dm}^{7.85}\text{h}$	23.4
n_1	0.72	–	15.6
n_2	-2.67	–	18.8

chemical controlled step was presented as 27.5 kJ/mol and the value determined for the diffusion controlled step was 19.6 kJ/mol.

The above-mentioned studies were carried out in different conditions and with different raw materials, which explains the wide variation in the activation energies. It is evident that comparison of the different studies is difficult, because the concentrates used in the experiments have different compositions and it is possible that the experiments were conducted in significantly differing conditions. However, it should be pointed out that the composition of the concentrate particles, composition of the leaching solution and the leaching conditions are the main factors that influence the leaching kinetics. These factors should be taken into account when the chemical kinetics of leaching processes is studied.

The reliability and the accuracy of the parameters in a non-linear, multi-parameter model should always be evaluated because they affect the reliability of the model. This can be done by studying the identifiability and cross-correlation of the parameters. MCMC-methods provide good tools for evaluation of the reliability of model

parameters. In MCMC methods, all the uncertainties in the data and the modeling are treated as statistical distributions. Up-to-date adaptive computational schemes are employed in order to make the simulations as efficient as possible (Haario et al., 2001; Laine, 2008). In this work, a FORTRAN 90 software package Modest (Haario, 2002) was used for both the least squares estimation and the MCMC estimation. MCMC methods have previously been used successfully in modeling of different processes (Lampinen et al., 2010; Solonen, 2011; Vahteristo et al., 2010).

Results from the MCMC-analysis are presented in Fig. 9, which shows two-dimensional posterior distributions for the parameters. Each dot in the figure represents a sample in the Markov chain. The density of the dots represents probability. The contour lines in the figures represent 50% and 90% probability regions. Fig. 9 shows in graphical form the identifiability and cross-correlation between the parameters. In the ideal case, the dots are tightly centered in a circular form around the most probable point. The 1-dimensional projections on the axis show a sharp peak in the probability. Fig. 9 shows that most of the parameters are well identified, especially the parameters for the zinc leaching rate equation. Parameter A_1 in the ferrous ion oxidation rate equation does not have a sharp peak, which indicates that this parameter is not as well identified as the other parameters. Fig. 9 shows that parameters A_1 and A_2 cross-correlate significantly. Parameters A_1 and A_2 also have the highest values for standard errors, as can be seen from Table 4. This was expected since the process solution in the current study is more complex than in the study by Rönnholm et al. (1999). Hence the reaction mechanism can be expected to be more complex compared to one Rönnholm et al. (1999) presented. Some cross-correlation can also be seen in the parameters ($k_{1,\text{mean}}$, n_1 and n_2) of the zinc leaching rate equation.

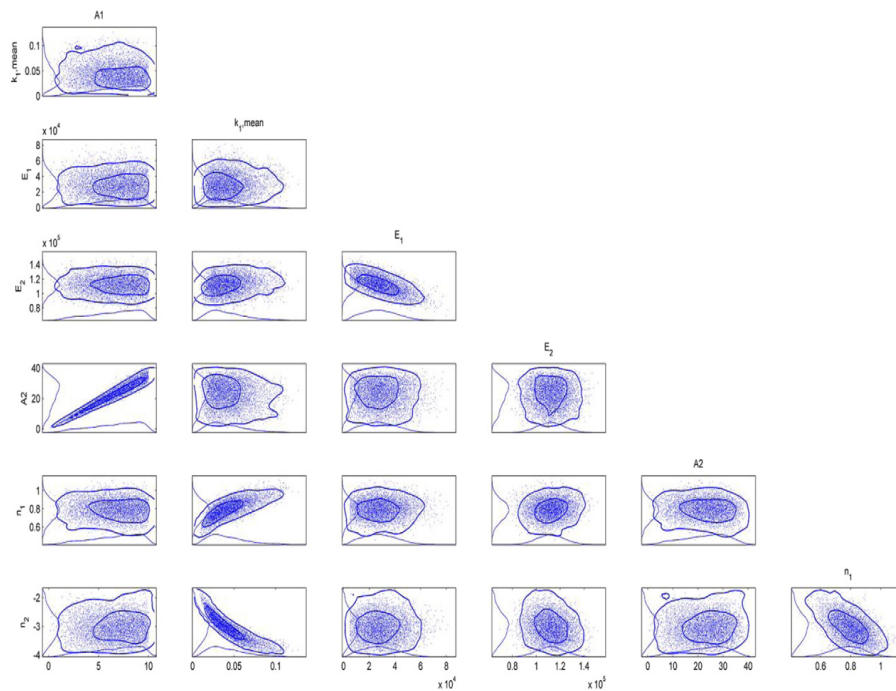


Fig. 9. Results from MCMC-analysis showing two-dimensional posterior probability distributions.

Direct oxidative leaching of zinc concentrates involves the reactions of multiple components at the reactive surface of the concentrate, decrease in the reactive area as the reactions consume some compounds in the particles, and gas–liquid and solid–liquid mass transfer. It is evident that the mechanisms of the direct leaching process are complex and modeling of the direct leaching process becomes increasingly difficult when moving towards industrial applications. In view of the complexity of the process, it can be argued that the model presented describes the leaching system well, although uncertainty can be recognized in some parameters. The high value for the coefficient of determination (96.63%), reasonable values for activation energies and well identified parameters for zinc leaching justify the claim that the model presented describes the leaching system well.

6. Conclusions

Direct leaching of zinc sulfide concentrate was studied experimentally in conditions that are similar to conditions used in industry. Results from the leaching experiments showed that temperature, pressure, particle size of the concentrate, and the iron and sulfate concentration of the slurry are the key parameters that have substantial effect on the leaching. The temperature had a great impact on the zinc concentrate leaching rate; the activation energy was calculated as 112 kJ/mol at 70–110 °C. Experimental results were used in the modeling of the direct leaching of the zinc-sulfide concentrate, and the reliability as well as the accuracy of the model parameters was studied with Markov Chain Monte Carlo (MCMC) methods. The model used in the current work takes into account reactions between the zinc sulfide concentrate and oxidizing agents on the reacting surface of the concentrate particles, the decrease of the active surface area of the concentrate particles as the leaching proceeds, the particle size distribution of the concentrate particles, the composition of the solution, and the oxidation rate of Fe^{2+} to Fe^{3+} . The model ($R_2 = 96.63\%$) described well the leaching data presented and the parameters were also identified well. Description of the oxidation rate data of Fe^{2+} to Fe^{3+} was not that good and notable uncertainty in the parameters was also recognized. The experimental results together with the modeling results showed that the solution composition, especially the sulfate concentration, has an effect on the leaching kinetics, which clearly demonstrates that it is important to have experimental data for the kinetics of the leaching at the conditions of the reactor.

List of symbols

A_i	inner surface area of particle (reactive area) (dm^2)
A_1	parameter in the kinetic expression ($(dm^3)^2/mol^2h$)
A_2	parameter in the kinetic expression (mol/dm^3h)
$C_{Fe^{2+}}$	concentration of Fe^{2+} in liquid ($mol Fe^{2+}/dm^3$)
$C_{Fe^{3+}}$	concentration of Fe^{3+} in liquid ($mol Fe^{3+}/dm^3$)
C_{O_2}	dissolved oxygen concentration ($mol O_2/dm^3$)
C_{SO_4}	sulfate concentration in liquid ($mol SO_4/dm^3$)
C_{Zn}	concentration of zinc in solids ($mol Zn/dm^3$)
$C_{Zn,ini}$	initial concentration of zinc in solids ($mol Zn/dm^3$)
$C_{Zn,S}$	concentration of zinc at solid surface ($mol Zn/dm^3$)
$C_{Zn,0}$	zinc concentration at time zero ($mol Zn/dm^3$)
E_1	activation energy (J/mol)
E_2	activation energy (J/mol)
H	Henry's constant (atm L/mol)
k_1	reaction rate constant ($mol^{2.95}/dm^{7.85} h$)
$k_{1,mean}$	reaction rate constant at mean temperature ($mol^{2.95}/dm^{7.85} h$)
n_1	reaction order for Fe^{3+}
n_2	reaction order for SO_4^{2-}
n	number of particles in reactor ($1/dm^3$)
P_N	portion of particles in the class

p_{O_2}	partial pressure of oxygen (atm)
$p_{Solution}$	vapor pressure of solution (atm)
R	gas constant (J/mol K)
r_1	reaction rate for iron oxidation (mol/dm^3h)
r_2	surface reaction rate for zinc leaching ($mol dm^2/h$)
r_i	radius of shrinking particle (dm)
r_o	radius of the particle at time zero (dm)
T	temperature (K)
T_{mean}	mean temperature of the experiments, 368 (K)

Subscripts

L	liquid phase
R	reaction (slurry) volume

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References

- Babu, M.N., Sahu, K.K., Pandey, B.D., 2002. Zinc recovery from sphalerite concentrate by direct oxidative leaching with ammonium, sodium and potassium persulphates. *Hydrometallurgy* 64, 119–129.
- Baldwin, S.A., Demopoulos, G.P., Papangelakis, V.G., 1995. Mathematical modelling of the zinc pressure leach process. *Metall. Mater. Trans. B* 26, 1035–1047.
- Corriu, J.-P., Gely, R., Viers, P., 1988. Thermodynamic study of the pressure leaching of zinc sulphide in aqueous sulfuric acid. *Hydrometallurgy* 21, 85–102.
- Crundwell, F.K., 1987. Kinetics and mechanisms of the oxidative dissolution of a zinc sulphide concentrate in ferric sulphate solutions. *Hydrometallurgy* 19, 227–242.
- Crundwell, F.K., 2013. The dissolution and leaching of minerals: mechanisms, myths and misunderstandings. *Hydrometallurgy* 139, 132–148.
- Crundwell, F.K., Bryson, A.W., 1992. The modelling of particulate leaching reactors – the population balance approach. *Hydrometallurgy* 29, 275–295.
- Dreisinger, D.B., Peters, E., 1989. The oxidation of ferrous sulphate by molecular oxygen under zinc pressure-leach conditions. *Hydrometallurgy* 22, 101–119.
- Dutrizac, J.E., 2006. The dissolution of sphalerite in ferric sulfate media. *Metall. Mater. Trans. B* 37, 161–171.
- Gbor, P.K., Jia, C.Q., 2004. Critical evaluation of coupling particle size distribution with the shrinking core model. *Chem. Eng. Sci.* 59, 1979–1987.
- Grénman, H., Murzina, E., Rönnholm, M., Eränen, K., Mikkola, J.-P., Lahtinen, M., Salmi, T., Murzin, D.Yu., 2007. Enhancement of solid dissolution by ultrasound. *Chem. Eng. Process.* 46, 862–869.
- Haakana, T., Lahtinen, M., Takala, H., Ruonala, M., Turunen, L., 2007. Development and modelling of a novel reactor for direct leaching of zinc sulphide concentrates. *Chem. Eng. Sci.* 62, 5648–5654.
- Haakana, T., Saxon, B., Lehtinen, L., Takala, H., Lahtinen, M., Svens, K., Ruonala, M., Xiao, G., 2008. Outotec direct leaching application in China. *J. South. Afr. Inst. Min. Metall.* 108, 245–251.
- Haario, H., 2002. *Modest User's Guide*. ProfMath Oy, Helsinki, Finland.
- Haario, H., Saksman, E., Tamminen, J., 2001. An adaptive metropolis algorithm. *Bernoulli* 7, 223–242.
- Kaskiala, T., 2005. Determination of mass transfer between gas and liquid in atmospheric leaching of sulphidic zinc concentrates. *Miner. Eng.* 18, 1200–1207.
- Laine, M., 2008. *Adaptive MCMC Methods with Applications in Environmental and Geophysical Model*. (Ph.D. Thesis). Finnish Meteorological Institute, Helsinki, Finland.
- Lampinen, M., Laari, A., Turunen, L., 2010. Simulation of direct leaching of zinc concentrate in a non-ideally mixed CSTR. *Can. J. Chem. Eng.* 88, 625–632.
- Leis, J.R., Kramer, M.A., 1988. ALGORITHM 658 ODESSA – an ordinary differential equation solver with explicit simultaneous sensitivity analysis. *ACM Trans. Math. Softw.* 14 (1), 61–67.
- Levenspiel, O., 1972. *Chemical Reaction Engineering*, 2nd ed. Wiley, New York.
- Lochmann, J., Pedlik, M., 1995. Kinetic anomalies of dissolution of sphalerite in ferric sulfate solution. *Hydrometallurgy* 37, 89–96.
- Markus, H., Fugleberg, S., Valtakari, D., Salmi, T., Murzin, D.Yu., Lahtinen, M., 2004. Kinetic modelling of a solid–liquid reaction: reduction of ferric iron to ferrous iron with zinc sulphide. *Chem. Eng. Sci.* 59, 919–930.
- Ozberk, E., Jankola, W.A., Vecchiarelli, M., Krysa, B.D., 1995. Commercial operations of the Sheritt zinc pressure leach process. *Hydrometallurgy* 39, 49–52.
- Palencia Perez, I., Dutrizac, J.E., 1991. The effect of the iron content of sphalerite on its rate of dissolution in ferric sulphate and ferric chloride media. *Hydrometallurgy* 26, 211–232.
- Rath, P.C., Pranguru, R.K., Jena, P.K., 1981. Kinetics of dissolution of zinc sulphide in an aqueous ferric chloride solution. *Hydrometallurgy* 6, 219–225.
- Rönnholm, M.R., Wärnå, J., Salmi, T., Turunen, L., Luoma, M., 1999. Kinetics of oxidation of ferrous sulfate with molecular oxygen. *Chem. Eng. Sci.* 54, 4223–4232.
- Salmi, T., Grénman, H., Bernas, H., Wärnå, J., Murzin, D.Yu., 2010. Mechanistic modelling of kinetics and mass transfer for a solid–liquid system: leaching of zinc with ferric iron. *Chem. Eng. Sci.* 65, 4460–4471.

- Schumpe, A., 1993. The estimation of gas solubilities in salt solutions. *Chem. Eng. Sci.* 48, 153–158.
- Solonen, A., 2011. Bayesian Methods for Estimation, Optimization and Experimental Design. (PhD thesis). Lappeenranta University of Technology, p. 62.
- Souza, A.D., Pina, P.S., Leão, V.A., Silva, C.A., Siqueira, P.F., 2007. The leaching kinetics of a zinc sulphide concentrate in acid ferric sulphate. *Hydrometallurgy* 89, 72–81.
- Takala, H., 1999. Leaching of zinc concentrates at Outokumpu Kokkola plant. *Erzmetall* 52, 37–42.
- Vahteristo, K., Sahala, K.-M., Laari, A., Solonen, A., Haario, H., 2010. Skeletal isomerization kinetics of 1-pentene over an HZSM-22 catalyst. *Chem. Eng. Sci.* 65, 4640–4651.
- Verbaan, B., Crundwell, F.K., 1986. An electrochemical model for the leaching of a sphalerite concentrate. *Hydrometallurgy* 16, 345–359.
- Weisenberger, S., Schumpe, A., 1996. Estimation of gas solubilities in salt solutions at temperatures from 273 K to 363 K. *AIChE J.* 42 (1), 298–300.
- Xie, K.-Q., Yang, X.-W., Wang, J.-K., Yan, J.-F., Shen, Q.-F., 2007. Kinetic study on pressure leaching of high iron sphalerite concentrate. *Trans. Nonferrous Metals Soc. China* 17, 187–194.
- Xu, Z.-F., Jiang, Q.-Z., Wang, C.-Y., 2013. Atmospheric oxygen-rich direct leaching behavior of zinc sulphide concentrate. *Trans. Nonferrous Metals Soc. China* 23, 3780–3787.

Publication III

Lampinen, M., Laari, A., Turunen, I., and Koiranen, T.

Determination of the role of intrinsic surface reactions and internal diffusion resistances in direct leaching of sphalerite by mechanistic modelling

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Determination of the role of intrinsic surface reactions and internal diffusion resistances in direct leaching of sphalerite by mechanistic modeling

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Abstract

A numerical kinetic model is presented based upon the shrinking core model, with the aim of determining the relative importance of diffusion, reaction and mixed control, across a range of operating conditions. The uncertainties in the model parameters are studied with Markov chain Monte Carlo (MCMC)-methods. Leaching of sphalerite with ferric iron in an acidic environment is used as a model system. The leaching process was found to be mainly diffusion controlled, thought to be due to pore diffusion and the formation of the elemental sulfur product layer. With low sulfuric acid concentrations the rate controlling step was found to change from mainly intrinsic surface reaction control to mixed control as the leaching proceeds. The rate was determined to be proportional to the sulfuric acid in the power of 1.3, which shows that the sulfuric acid has a crucial influence on the leaching kinetics. This indicates that the reaction between sphalerite and ferric ion goes through a state where sulfuric acid participates as an intermediate. The results clearly demonstrate that numerical mechanistic model with detailed analysis of the model parameters with sophisticated mathematical methods (MCMC-method) offers a good method to evaluate the rate controlling steps at different operating conditions.

Keywords: Solid-liquid reactions; Modeling; Chemical leaching; Kinetics; Parameter identification

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1. Introduction

Large amounts of chemicals and metals are produced employing solid-liquid reactions. Knowledge of the thermodynamics and the chemical kinetics is crucial for the design and development of these processes. Mathematical modeling of solid-liquid systems is commonly used to interpret experimental results and to gain insight into the reaction mechanism. Quantification of rate parameters is an important aspect of the design and development of solid-liquid reactors. However, the reaction mechanisms are often very complex and can comprise several unknown steps. Determination and monitoring of the structure of the solids and the structural changes taking place is often challenging. The kinetics and mass transfer effects are often coupled; in order to determine the intrinsic kinetics, the experiments should be free from mass transfer limitations. Creation of a strong enough turbulent effect around the particles is usually used to suppress the external mass transfer resistance, but internal mass transfer effects can still be present if the particles are porous. In view of the complexities inherent in solid-liquid reactions, modeling of dissolution reactions is usually simplified.

A number of models (Dickinson and Heal (1999); Órfão and Martins (2002); Levenspiel, 1999) for dissolution reactions have been developed, of which the major models for non-catalytic solid-liquid reactions are the shrinking core, shrinking particle, homogeneous and grain models. The shrinking core model (SCM) is widely used to model fluid-solid reactions such as leaching of metals from minerals (Gbor and Jia, 2004). Commonly, conclusions regarding particle shapes and reaction mechanisms are based on comparing different models to the experimental data and evaluating which one gives the best fit. If a shrinking sphere mechanism (SPM) is assumed, $1-(1-\alpha)^{1/3}$, (where α is conversion, Levenspiel (1999)) is plotted as a function of time for the experimental data, and if the plot gives a linear correlation, the assumption is considered to be correct. Analogously, $1-3(1-\alpha)^{2/3}+2(1-\alpha)$ is plotted for the data if a shrinking core is assumed. Usually, solid particles are assumed to follow ideal models in the sense that particles are non-porous with an ideal geometry (e.g. sphere or slab). This methodology is widely used but is not unproblematic. It has been reported (Pecina et al., 2008; Espiari et al., 2006) that, in a number of leaching

systems, investigators find it difficult to distinguish between the two reaction models of surface reaction control and liquid film diffusion control. Markus et al. (2004a) present that model discrimination per se is not enough to reveal the true mechanism of solid-liquid reactions, but detailed study of the solid particles is also needed. Grénman et al. (2011) claim that one major challenge with traditional methods is that the morphology of the particles seldom follows ideal morphology. Evidently, particles usually have an irregular geometry, some surface roughness (peaks and craters) and some porosity. Moreover, discrimination of the models can be a challenge, as several models can fit the experimental data when the parameter values are adjusted, especially if considerable experimental scattering exists. These traditional models do not allow flexible implementation of non-ideal behavior and more complex kinetics. In recent times, development of sophisticated microscopic techniques (SEM and TEM) and advanced particle size analysis methods allow more closer study of the actual particles, which can help e.g., in model discrimination. The existence of internal diffusion resistance has been reported by various researchers (Mulak et al., 2005; Safari et al., 2009; da Silva, 2004) for solid-liquid reaction systems. However, the role of internal diffusion resistance in solid-liquid reaction systems and the reactive surface area has been a challenge to determine with analytical techniques, even though analytical techniques have developed enormously in recent decades. It is therefore evident that modeling procedures need further development.

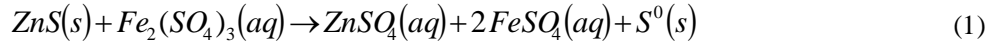
In the present work, a leaching process, namely direct leaching of zinc sulfide, is studied as a model system. Leaching processes are important in the metallurgical industry, where ore/concentrate processing involving large-scale leaching operations is common. The structural properties of the solid particles influence significantly the progress of the reaction, but also the reaction media and reaction conditions (e.g. temperature, pressure) have a great impact. Wide variety of studies for zinc sulfide leaching (Jin et al., 1984; Lampinen et al., 2010, 2015; Markus et al., 2004a, 2004b; Souza et al., 2007; Rath et al., 1981) have been conducted and parameters with a range of values have been proposed, e.g. activation energies vary from 19.6 to 112 kJ/mol, reaction order for Fe^{3+} from 0 to 1.4. Hence, it is evident that parameters should be always determined for each case separately and reliability of the parameters should be carefully studied.

Determining whether a reaction is under diffusion, chemical or mixed control is the first major step to understanding a hydrometallurgical process. The existence of internal diffusion resistance has been reported also for direct leaching of zinc sulfide (da Silva, 2004; Lochmann and Pedlík, 1995; Pecina et al., 2008; Rath et al., 1981; Weisener et al., 2004; Souza et al., 2007) and it has been mainly proposed to be due to the layer of elemental sulfur in the case of direct leaching of zinc sulfide. Souza et al., 2007 presented that the elemental sulfur produced during the sulfide dissolution has an important role in the final stages of leaching. Hence, a model that considers both the chemical reaction and diffusion of ferric ion through the elemental sulfur layer would be more realistic. Souza et al. (2007) stated that reactant porosity plays an important role if the reaction interface is diffused, meaning that oxidation reaction proceeds inside the pores. Souza et al. (2007) discussed the modeling of mixed control and presented that the simple addition of resistance terms, as used by Silva (2004), although can produce a mixed control model that fits well the experimental results, is physically bias. Souza et al. (2007) presented that the mathematical solution for mixed control, considering fractionary reaction orders usually requires a numerical solution. However, Souza et al. (2007) adopted a similar approach used by Weisener et al. (2003); Bobeck and Su (1985); Crundwell (1987). The approach was to split the extraction curve into two different segments and to perform a piecewise fitting to a chosen SCM limiting case.

It is evident that studying the kinetics of the hydrometallurgical leaching, where, non-ideal particle behavior and multiple rate determining steps most often exists, is challenging for common modeling procedure. Hence, numerical solution is needed together with detailed study of the established model parameters. In the present study, a numerical mathematical model based upon the shrinking core model for solid-liquid reactions is presented that permits evaluation of the surface reaction and internal diffusion resistance. The performance of the presented model is studied with data given in the literature by Souza et al. (2007) and the reliability of the estimated model parameters is studied by Markov chain Monte Carlo (MCMC) -methods.

2. Model development

The present work studies the leaching of zinc sulfide (sphalerite) with ferric sulfate. Elementary sulfur and ferrous sulfate are obtained as products. The reaction is carried out in an acidic environment and the overall reaction is as given below:



Competing hypotheses exist, whether the reaction happens on the solid surface according to the product layer model (Rath et al., 1981; Palencia Perez and Dutrizac, 1991; Crundwell, 1987; Suni et al., 1989; Kolodziej and Adamski, 1990) or in the liquid phase (Verbaan and Crundwell, 1986; Kammel et al., 1987; Crundwell and Verbaan, 1987; Lotens and Wesker, 1987). Chemically (Dutrizac, 2006; Göknan, 2009; Salmi et al., 2010; Souza et al., 2007) and electrochemically (Verbaan and Crundwell, 1986) controlled surface reactions have been presented in the literature and used for the modeling of the above reaction. Salmi et al., (2010) stated that for pure zinc sulfide as well as for sphalerite a chemically controlled surface reaction has been successfully applied to describe the leaching process in many studies. Moreover, there is no general agreement, whether shrinking core or shrinking particle model should be applied for zinc sulfide.

2.1 Kinetic modeling

The concentration of reagents in the solution and the temperature influence the rates of the dissolution or leaching reactions. A mechanism of dissolution is proposed based on the determined kinetic parameters. The rate of dissolution can be described with the following equation in a generalized way:

$$\text{rate} = k[c]^n \exp(-E_A/RT) \quad (2)$$

where $[c]$ represents the concentration of a reagent(s), k the rate constant, n the order of reaction, E_A the activation energy, R the gas constant, and T the temperature.

Eq. (2) describes homogeneous kinetics. However, there is a fundamental difference between homogeneous and solid-liquid kinetics: the reaction rate of a solid-phase compound dispersed in a liquid does not depend directly on the concentration of the solid in the liquid phase, but rather on the reactive surface area. Hence, a different approach is required in the case of leaching of zinc sulfide (sphalerite) with ferric sulfate. In the development of the kinetic model for zinc sulfide leaching it is assumed that the reaction between zinc and ferric iron (Eq. 1) takes place at the reactive surface of the particle. The reaction of Zn is specified as a surface reaction (mol Zn/m² min). The kinetics of the surface reaction depends on the concentration of zinc (in the solids) and on the reagent concentrations at the surface. However, zinc concentration at the solid surface of the particle is characteristic for the concentrate and can be assumed to remain constant during leaching. Therefore, $k_{Zn,S}$ can be lumped to a kinetic constant k_1 :

$$\text{rate} = r_1 = k_1 c_{Zn,S} [c]^n \exp(-E_A / RT) = k_1 [c]^n \exp(-E_A / RT) \quad (3)$$

The Arrhenius equation is commonly used to describe the temperature dependence of chemical reactions. In this study, a modified Arrhenius equation is used in order to minimize the correlation of the pre-exponential factor and the activation energy:

$$k_1 = k_{1,ref} \exp\left(-\frac{E_A}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (4)$$

The term T_{ref} is a reference temperature (often mean temperature) of the experiments and $k_{1,ref}$ is the rate constant at the reference temperature.

The dissolution rate of solids can be described by multiplying the surface reaction rate with the reactive area of the particle and the number of particles per volume of slurry:

$$-\frac{dc_A}{dt} = r_i A_i N \quad (5)$$

Based on the shrinking core model (Levenspiel, 1999), the shrinkage of the core of the particle can be described by the following equation:

$$\left(\frac{r_i}{r_o}\right)^3 = \frac{c_A}{c_{A,ini}} \quad (6)$$

It is assumed that as the leaching reaction proceeds the surface is covered with a product layer. The resistances of the surface reaction and the product layer diffusion are in series. Therefore, the concentration of oxidant, which in the current case is the ferric ion (Eq. 1), at the reacting surface $c_{Ox,s}$ has to be solved numerically from mass balance. Pseudo-steady state inside the particle are assumed, which means that the concentration profile of the oxidant is not dependent on time. This is a reasonable assumption taking into account the low reagent concentrations and the long residence time in the reactor.

The steady-state concentration profile in a spherical diffusion layer can be written as (Crank, 1975):

$$c = \frac{c_i(r_o - r)r_i + c_o(r - r_i)r_o}{r(r_o - r_i)} \quad (7)$$

From which the concentration gradient in the layer is obtained:

$$\frac{dc}{dr} = \frac{r_i r_o (c_o - c_i)}{(r_o - r_i) r^2} \quad (8)$$

The mass diffusion rate is obtained from the concentration gradient using the diffusion coefficient and can be calculated either at the inner or outer surface of the layer:

$$j_{Ox} = -D_e A_r \frac{dc}{dr} \Big|_{r=r_o} = -D_e A_{r_i} \frac{r_o (c_{Ox} - c_{Ox,s})}{(r_o - r_i) r_i} = -D_e A_{r_o} \frac{r_i (c_{Ox} - c_{Ox,s})}{(r_o - r_i) r_o} \quad (9)$$

At the reacting surface the mass balance for oxidant is then:

$$k_1 [c_{Ox,s}]^n \exp(-E_A / RT) A_i - D_e A_o \frac{r_i (c_{Ox} - c_{Ox,s})}{(r_o - r_i) r_o} = 0 \quad (10)$$

which can be solved for $c_{Ox,s}$.

The temperature dependence of the diffusion coefficient is also taken in to account.

$$D_e = D_{e,mean}(T/T_{mean}) \quad (11)$$

Eq. (6) can be used for continuous calculation of the radius of the active layer and the active area of the particle. The active area in Eqs. (5) and (10), therefore, continuously decreases as the reaction proceeds.

3. Experimental data

Experimental data reported by Souza et al. (2007) was used for kinetic modeling. Souza et al. (2007) studied experimentally the dissolution kinetics of an iron-rich zinc sulfide concentrate in an acidic ferric sulfate medium. Mineralogical analyses of the concentrate showed that sphalerite is the main mineral phase, and pyrite, quartz and galena are present in minor quantities. The effects of temperature, ferric ion and sulfuric acid concentrations, agitation speed, and particle size on the leaching kinetics were studied. Souza et al. (2007) presented that, for the conditions in their study, zinc extraction increases with increase in the ferric ion concentration, temperature and sulfuric acid concentration. Decrease in the particle size played only a marginal role in the leaching process. Souza et al. (2007) suggested that the small difference observed is probably due to the negligible increase of solid surface area with decreasing particle sizes as an effect of porosity and natural cracks and provided analyses to show porosity and natural cracks of the particles. According to Souza et al. (2007) reactant porosity plays an important role if the reaction interface is diffused, which means that the oxidation reaction proceeds inside the pores. It is evident that solid raw material used by Souza et al. (2007) is non-ideal in the sense that particles

have an irregular geometry, surface roughness (peaks and craters) and porosity, which serves a challenge for modeling. The conditions of the experimental runs are given in Table 1.

Table 1. Conditions of the experimental runs according to Souza et al. (2007).

Run	c (H ₂ SO ₄) M	c (Fe ³⁺) M	d _p μm	T °C
1	0.25	0.50	67.7	70
2	0.5	0.50	67.7	70
3	0.75	0.50	67.7	70
4	1.00	0.50	67.7	70
5	1.00	0.10	67.7	70
6	1.00	0.30	67.7	70
7	1.00	0.40	67.7	70
8	1.00	0.50	67.7	70
9	1.00	0.70	67.7	70
10	0.25	0.25	42.1	50
11	0.25	0.25	49.6	50
12	0.25	0.25	67.7	50
13	0.25	0.25	94.9	50
14	0.25	0.25	135.2	50
15	0.25	0.25	189.7	50
16	1.00	0.50	67.7	40
17	1.00	0.50	67.7	50
18	1.00	0.50	67.7	60
19	1.00	0.50	67.7	70
20	1.00	0.50	67.7	90

The traditional shrinking particle (SPM) and shrinking core model (SCM) plots were constructed for the data presented by Souza et al. (2007) and they are presented in

Appendix. From the plots it can be seen that model discrimination is not unproblematic. Some experiments give good fit for SCM (Fig. A1, A2, A14 and A15), some for SPM (A16, A17, A18 and A19) and rest of the experimental data deviates from linear plots of both SCM and SPM. The approach used by Souza et al. (2007) in the kinetic analysis was to split the extraction curve into two different segments and perform a piecewise fitting to a chosen SCM limiting case. About 40 % zinc extraction was chosen as the point where the kinetics changed from chemical to diffusion control. Scanning electron microscope (SEM) examinations of polished sections of particles after 40 % zinc extraction showed a ZnS core covered by an elemental sulfur layer, which is consistent with the proposed change in the kinetics regime. The apparent activation energy in the chemical reaction controlled step was 27.5 kJ/mol and the value obtained for the diffusion-controlled step was 19.6 kJ/mol. It was concluded that as the apparent activation energy in the initial stage of dissolution process is higher than the value observed in the final stages, this reinforces that the process is chemically controlled during the initial stage and diffusion controlled at the final stage of leaching.

The approach used by Souza et al. (2007) can be considered to be quite an approximate, since the fit of the shrinking core model presented by Souza et al. (2007) is somewhat approximate and the point where the kinetic regime changes is based on only a few SEM images. Thus, the reliability of the choice remains uncertain; does, for example, 20 % zinc extraction show a ZnS core covered by an elemental sulfur layer? The rate controlling step varies depending on leaching conditions, so it is not clear if this method can be applied in all conditions. Moreover, question remains can rate controlling step change directly from chemical reaction control to diffusion control without mixed control stage, where both have a role. Conclusions considering the values of the apparent activation energy (E_a) in the chemical reaction controlled step are somewhat contradictory. The values reported (Dutrizac, 2006, Lampinen et al., 2010, 2015; Pecina et al., 2008; Xie et al., 2007) for activation energies of reaction control vary from 39 to 112 kJ/mol, while 33–34 kJ/mol is reported (Weisener et al., 2003) as a diffusion rate controlled process. This shows that studying the kinetics of a hydrometallurgical leaching process, which often have non-ideal

features, across a range of operating conditions is a major challenge, especially with a common modeling procedure.

4. Results and discussion

The results presented by Souza et al. (2007) indicate that the leaching rate depends on the ferric iron concentration, sulfuric acid concentration, temperature, and particle size. Consequently, the concentration of ferric ion at the reaction surface and the concentration of sulfuric acid are used in this work in the rate equation (Eq. 3), which gets the form $r_1 = k_1 c_{Fe^{3+},s}^{n_1} c_{H_2SO_4}^{n_2} \exp(-E_1 / RT)$. The temperature dependence of the rate was taken into account with Eq. (4). The kinetic model for the current case consists of Eqs. (3) - (6) and Eqs. (10) and (11). The model has five parameters ($k_{1,mean}$, n_1 , n_2 , E_1 , $D_{e,mean}$) that have to be estimated by fitting to the experimental data. The zinc leaching rate equation (Eq. 5) is an ordinary differential equation that is numerically integrated from the initial state at time zero to the designated time. At each time step the surface concentration of ferric iron is solved by finding the root of Eq. (10). The model parameters were estimated with Modest software (Haario, 2002) by minimizing the squared difference between the simulations and experiments.

The coefficient of determination (Haario, 2002) for the model was 83.10 %. The experimental and the predicted zinc conversions are presented in Fig. 1. As can be seen from Fig. 1, the model mostly predicts the course of the leaching process well. From Fig. 1 it can also be seen that when the acid concentration is low (Run 1 and Run 2) the model slightly overestimates the leaching rate, and when the temperature is low (Run 16) the model overestimates the leaching rate more notably. With the largest particle sizes (Run 14 and Run 15) the model underestimates the leaching rate notably. This points out the challenge of non-ideal behavior. Ideally larger particles form thicker layers of elemental sulfur and the diffusion resistance increases as the model predicts (Run 14 and Run 15). da Silva (2004) presented that the rate of diffusion of ferric ions through the product layer increases with increasing particle size. da Silva (2004) proposed that this phenomenon is a result of the increased surface area per particle of the larger fractions. This increased

surface area results in a less coherent product layer, which begin to crack and break up. These cracks allow for increased rates of mass transfer, thus increasing its diffusion coefficient. da Silva (2004) noticed that using one value for the diffusion coefficient yields an inaccurate description of the experimental data and they therefore modeled the data using four values for the diffusion coefficient (one for each size). This approach would naturally improve the model prediction in the current study. However, over parametrization should be always avoided, hence one value for diffusion coefficient is presented.

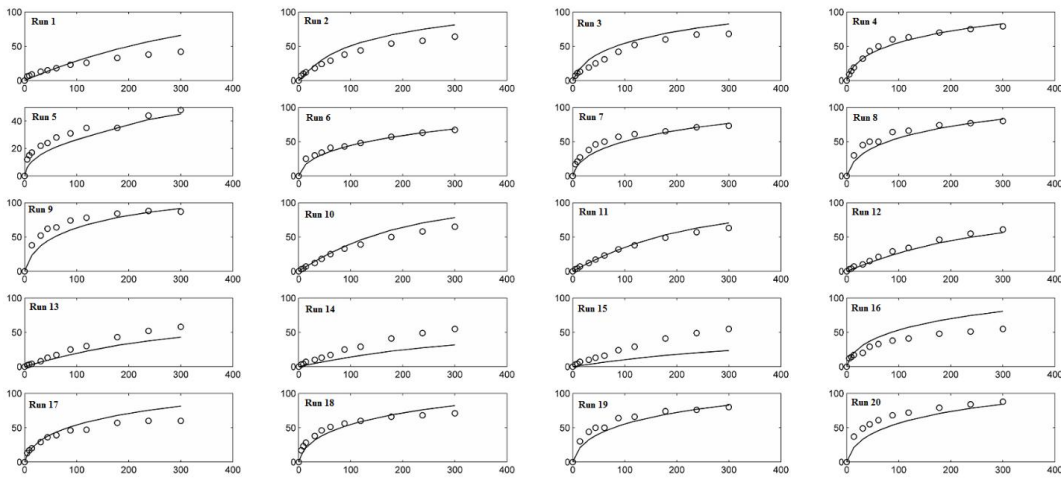


Fig. 1. The comparison of the measured and predicted conversions for zinc. Conversion (%) in the y-axis and time (min) in the x-axis. Experimental conditions are presented in table 1.

The estimated parameters are shown in Table 2.

Table 2. Estimated parameters and their standard errors.

Regression coefficient		83.10 %	
Parameter	Value	Unit	Std.error,(%)
$k_{1,\text{mean}}$	4.37×10^{-7}	$\text{mol}^{-0.41}/\text{m}^{1.37} \text{ min}$	21.5
n_1	7.84×10^{-2}	-	8.1
n_2	1.33	-	3.0
E_1	1.53×10^2	J/mol	3594.8
$D_{e,\text{mean}}$	3.52×10^{-11}	m^2/min	4.5

The presented leaching model has several parameters. For reliable model predictions it is important that the model parameters are well-identified and do not cross-correlate to each other in significant quantities. The reliability of the model parameters and the model predictions can be conveniently studied by Markov chain Monte Carlo (MCMC) methods. With MCMC, the parameter estimation problem can be resolved in a completely statistical manner. The MCMC methods are Bayesian statistical methods, which treat all the model parameters and predictions as probability distributions (Laine, 2008). With MCMC, the whole distribution of parameters can be explored, instead of obtaining point estimates and using, e.g., Gaussian approximations (Solonen, 2011). According to a Bayesian paradigm all the parametrizations of the model that statistically fit the data equally well are determined. A distribution of the unknown parameters is generated using available prior information (e.g., results obtained from previous studies or bound constraints for the parameters) and statistical knowledge of the observation noise. Computationally, the distribution is generated using the MCMC sampling approach. The length of the calculated

chain was 50 000 samples. Simple flat, uninformative priors with minimum and maximum bounds set for each parameter were used in the calculation of the chain. Up-to-date adaptive computational schemes were employed in order to make the simulations as effective as possible (Haario et al., 2001; Laine, 2008). In this study, a FORTRAN 90 software package, MODEST 15 (Haario, 2002), was used for both the least-squares and the MCMC estimation. The two methods are also implemented in a MATLAB package (Laine, 2013). The MCMC methods have been previously successfully used in process engineering problems to study the reliability of kinetic parameters in Diels-Alder reaction kinetics (Vahteristo et al., 2013), in ozonation of p-nitrophenol (Kuosa et al., 2007), in zinc sulphide leaching (Lampinen et al., 2015), and in pyrite pressure oxidation (Zhukov et al., 2015).

Results from the MCMC-analysis are shown in Fig. 2, which shows two-dimensional posterior distributions for the parameters. Each dot in the figure represents a sample in the Markov chain. The density of the dots represents probability. The contour lines in the figures represent 50 % and 90 % probability regions. Fig. 2 shows, in graphical form, the identifiability and cross-correlation between the parameters. In the ideal case, the dots are tightly centered in a circular form around the most probable point. The 1-dimensional projections on the axis also show a sharp peak in the probability. Fig. 2 shows that parameters other than E_1 have clear peaks and that there is no significant correlation between the parameters. Standard errors for parameters other than E_1 are also low, as can be seen from Table 2, so it can be concluded that the model parameters, excluding E_1 , are well identified and reliable. Parameter E_1 does not have a sharp peak in Fig. 2 and the standard error of the parameter is high, which clearly indicates that E_1 is not well identified and is not reliable.

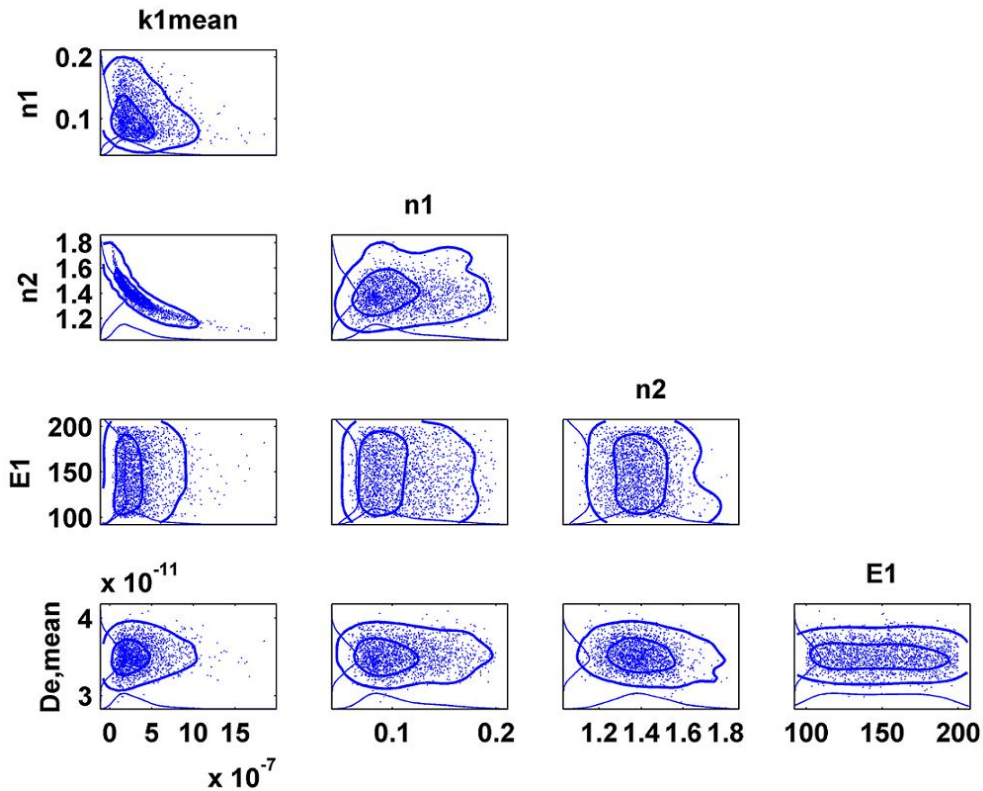


Fig. 2. Results from MCMC-analysis showing the two-dimensional posterior probability distributions.

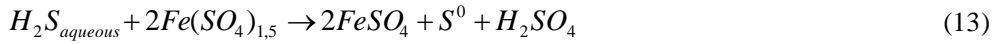
It can be seen from Table 2 that the activation energy (E_1) for intrinsic surface reaction of the zinc concentrate leaching is 0.15 kJ/mol. This value for activation energy is extremely low. The extremely low value for E_1 and poor identification of the parameter indicate that the effect of the parameter on the leaching is only marginal. From Table 2, it can also be seen that the reaction order for ferric ion surface concentration (0.0784) is small and also supports the idea that the rate limiting step is the diffusion. Jin et al., (1984) presented that the reaction order for ferric ion is 0.5 at low concentrations and zero at high concentrations of ferric ion. Salinas-Rodríguez et al. (2016) studied the kinetics of silver leaching and presented the apparent activation energy of 1.912 kJ/mol in the temperature range of 15 to 55 °C and the order of reaction with respect to the thiosulfate concentration was 0.074 in

the range studied. Salinas-Rodríguez et al. (2016) concluded that the kinetics are controlled by mass transfer of oxygen at solid-liquid surface. Hence, it can be concluded that activation energy E_1 and reaction orders n_1 are reasonable and indicate that intrinsic surface reaction has only a minor role on the leaching process in the studied conditions.

Table 2 shows that the value for the diffusion coefficient ($D_{e,mean}$) is 3.52×10^{-11} m²/min (5.87×10^{-13} m²/s). da Silva (2004) presented that the ferric sulfate oxidation of sphalerite is controlled by both the chemical reaction and product layer diffusion, with diffusion being the dominant process. Product layer diffusion was thought to arise due to formation of a layer of elemental sulfur. da Silva (2004) obtained a value for the diffusivity of ferric ions through the product layer of 3.6×10^{-15} m²/s at 21 °C compared to the value of 1.3×10^{-12} m²/s obtained by Bobeck and Su (1985) during ferric chloride leaching experiments at 87 °C. da Silva (2004) proposed that the discrepancy between the values arises from the much higher temperature of the latter experiment and from the effect of chloro-complex formation on the composition of the occlusive product layer. It is evident that the values proposed for the diffusion coefficient cannot be directly compared, since they are determined for different leaching systems. However, they give an order of magnitude for the diffusion coefficient and, hence, it can be stated that the value 3.52×10^{-11} m²/min (5.87×10^{-13} m²/s) for $D_{e,mean}$ proposed in the current work is reasonable.

The reaction order for sulfuric acid is 1.33, as can be seen from Table 2, which is reasonable, giving the value of 1.00 obtained by Souza et al. (2007) and the value of 1.5 obtained by Markus et al. (2004a). Markus et al. (2004a) stated that the order of 1.5 for sulfuric acid in the leaching reaction indicates that the reaction between zinc sulfide and ferric ion goes through a state where sulfuric acid participates as an intermediate, thus reaction takes place in the liquid phase. Weisener et al. (2003) presented that the leaching of a low Fe sphalerite is a diffusion rate controlled process in which the diffusion was associated with either the transport of Zn^{2+} out or H_3O^+ in through a surface polysulfide layer. Several studies (Corriou et al., 1988; Dutrizac, 2006; Markus et al., 2004a; Kammel et al., 1987; Verbaan and Crundwell, 1986) have proposed that the hydronium ions contribute

to the leaching by forming hydrogen sulfide, which is re-oxidized by ferric ions yielding hydronium ions, ferrous ions and elemental sulfur. Reactions can be presented as follows:



The net results of Eqs. (12) and (13) is Eq. (1). It has been proposed that the acid attack mechanism (Eqs. (12) and (13)) takes part as a parallel reaction (Dutrizac, 2006) and that the leaching mechanism goes entirely through the acid attack (Corriou et al., 1988; Xu et al., 2013). It is difficult to reveal how hydronium ions contribute to leaching reaction mechanisms, but it can be stated that hydronium ions have a strong role in the current case.

Results presented by Souza et al. (2007) and results presented in this work bring strong evidence that internal diffusion has an important role in the course of the leaching of sphalerite. However, it is not clear how important this role is and therefore it should be studied further. The model presented in this study offers a way to study the role of internal diffusion more closely. Fig. 3 presents the importance of the internal diffusion on the leaching rate. In Fig. 3, the simulated curves present the ratio (r_{SD}/r_S) of the actual leaching rate (r_{SD}) over the leaching rate (r_S) without diffusion limitations (leaching agent concentration at the surface equals the bulk leaching agent concentration).

$$\frac{r_{SD}}{r_S} = \frac{k_1 C_{Fe^{3+}}^{n_1} C_{H_2SO_4}^{n_2}}{k_2 C_{Fe^{3+}}^{n_3} C_{H_2SO_4}^{n_4}} \quad (14)$$

If the ratio presented in Fig. 3 is close to unity, the leaching is mainly controlled by the intrinsic surface reaction. If, on the other hand, the ratio is low ($\ll 1$) it means that the overall leaching rate is limited by the diffusion of leaching reagents or leaching products. Between these two cases, the leaching rate is affected by both the reaction and diffusion. Fig. 3 indicates that internal diffusion has a strong role in most of the experiments. It can

be seen that when low sulfuric acid concentration is used (Run 1-2 and 10-15) the rate controlling step is moving from intrinsic surface reaction to mixed control. In the rest of the experiments diffusion is clearly controlling the rate. Fig. 3 shows that the presented ratio is always below 1, which indicates that the internal diffusion has a role already in the beginning of the leaching process. This shows that porosity of the reactant (zinc sulfide) plays a role in the beginning of the process when the elemental sulfur layer is not yet formed. As presented above Souza et al. (2007) also discussed the possibility of the reaction to proceed inside the pores. Souza et al. (2007) proposed that the small difference in the leaching rates with different particle sizes due to the porosity and natural cracks in the particles, which leads to the negligible increase of solid surface area with decreasing particle sizes. Massaci et al. (1998) also presented the non-significance of the effect of particle size in zinc sulfide ore leaching rate is due to the natural porosity in the structure of the zinc sulfide particles.

When the sulfuric acid concentration increases, the effect of internal diffusion resistance increases. When the sulfuric acid concentration is low (0.25 M; Run 1) internal diffusion increases slowly, because the dissolution rate of sulfide is low (Fig. 1; Run 1) and the elemental sulfur layer forms slowly. On the other hand, when the sulfuric acid concentration is higher (1.0 M) the leaching rate is faster (Fig 1; Run 4), and consequently internal diffusion increases rapidly at the beginning of the reaction, when leaching is fast, and starts to slow down when the leaching rate slows down. The same trend can be seen in every experiment; when the leaching rate is fast the internal diffusion rate increases rapidly. This is consistent with Eq. (1), because a higher leaching rate results in increased production of elemental sulfur, and elemental sulfur causes the internal diffusion. In most of the experiments overall leaching rate is limited by diffusion (Run 3-9 and 16-20) and in the rest of the experiments overall rate is mainly under reaction control in the beginning and changing to mixed control as the leaching proceeds. The low value for activation energy (0.15 kJ/mol) and the results presented in Fig. 3 indicate that internal diffusion plays a major role in most of experiments.

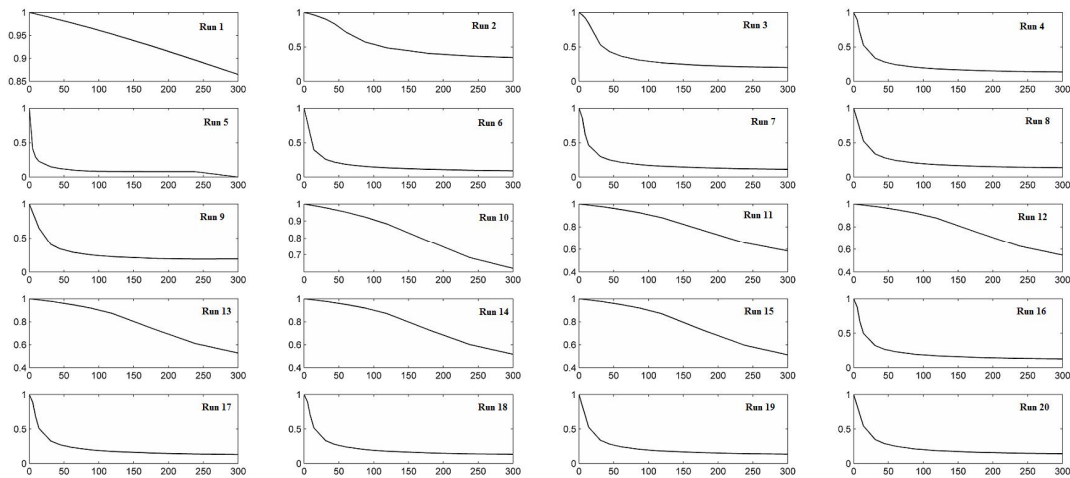


Fig. 3. Effect of internal diffusion on the leaching system. The ratio (r_{SD}/r_S) of the actual leaching rate (r_{SD}) over the leaching rate (r_S) without diffusion limitations in the y-axis and time (min) in the x-axis.

Finally, it can be concluded that the modeling results show that internal diffusion and sulfuric acid has the main role in the leaching process in the case presented by Souza et al. (2007).

4. Conclusions

A numerical kinetic model based upon the shrinking core model was presented to study the leaching of sphalerite with ferric ion in an acidic environment. The uncertainties in the model parameters were studied with Markov chain Monte Carlo (MCMC)-methods. The rate was determined to be proportional to the sulfuric acid in the power of 1.3, which shows that the sulfuric acid has a crucial influence on the leaching kinetics. This indicates that the reaction between sphalerite and ferric ion goes through a state where sulfuric acid participates as an intermediate. The leaching process was found to be mainly diffusion controlled, thought to be due to pore diffusion and formation of the elemental sulfur product layer. With low sulfuric acid concentrations the rate controlling step was found change from mainly intrinsic surface reaction control to mixed control as the leaching

proceeds. The reaction order with respect the ferric ion was 0.074 and activation energy for intrinsic surface reaction 0.15 kJ/mol, indicating a minor role of the surface reaction.

The results show that numerical mechanistic model with detailed analysis of the model parameters with sophisticated mathematical methods (MCMC-methods) offers a good method to evaluate the rate controlling steps. The presented modeling approach allows to evaluate the relative importance of reaction and diffusion at different operating conditions. This approach is required especially, when leaching is studied in large range of different conditions and with non-ideal solid material, as in the case presented in the current study.

List of symbols

A_i	inner surface area of particle (reactive area) (dm ²)
A_o	outer surface area of reacting particle (dm ²)
c	concentration (mol/dm ³)
$c_{Fe^{3+}}$	concentration of Fe ³⁺ in liquid (mol Fe ³⁺ / dmL ³)
$c_{Fe^{3+},s}$	concentration of Fe ³⁺ at the reactive surface (mol Fe ³⁺ / dmL ³)
$c_{H_2SO_4}$	concentration of H ₂ SO ₄ in liquid (mol H ₂ SO ₄ / dmL ³)
c_{Ox}	concentration of oxidant in the liquid (mol _{Ox} / dmL ³)
$c_{Ox,s}$	concentration of oxidant at reacting surface (mol _{Ox} / dmL ³)
c_A	concentration of A in solids (mol A/ dmR ³)
$c_{A,ini}$	initial concentration of A in solids (mol A/ dmR ³)
c_{ZnS}	concentration of zinc at solid surface (mol Zn/ dmR ³)
c_i	concentration at the inner surface (reacting surface) (mol/ dmL ³)
c_o	bulk concentration (mol/ dmR ³)
D_e	effective diffusivity in particles (m ² /min)

$D_{e,mean}$	effective diffusivity in particles at mean temperature (m^2/min)
E_A	activation energy (J/mol)
E_I	activation energy (J/mol)
j_{ox}	mass (molar) diffusion rate of oxidant
k	reaction rate constant
k_I	reaction rate constant ($mol^{-0.41}/dm^{1.37} min$)
$k_{I,mean}$	reaction rate constant at mean temperature ($mol^{-0.41}/dm^{1.37} min$)
k_{ref}	reaction rate at the reference temperature
n	reaction order
n_1	reaction order for Fe^{3+}
n_2	reaction order for H_2SO_4
n_3	reaction order for Fe^{3+}
n_4	reaction order for H_2SO_4
N	number of particles in reactor ($1/dm_R^3$)
R	gas constant (J/mol K)
r_I	surface reaction rate for zinc leaching ($mol dm^2/min$)
r_i	radius of the reacting surface (dm)
r_o	radius of the particle outer surface (dm)
r_s	leaching reaction rate without diffusion limitations ($mol dm^2/min$)
r_{SD}	leaching rate including diffusion limitations ($mol dm^2/min$)
T	temperature (K)
T_{ref}	reference temperature (K)
T_{mean}	mean temperature of the experiments (K)
α	conversion

Subscripts

L	liquid phase
R	reaction (slurry) volume

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References

Bobeck, G.E., Su, H., 1985. The kinetics of dissolution of sphalerite in ferric chloride solution. *Metallurgical Transactions B* 16B, 413 – 424.

Corriou, J.-P., Gely, R., Viers, P., 1988. Thermodynamic study of the pressure leaching of zinc sulphide in aqueous sulfuric acid. *Hydrometallurgy* 21, 85–102.

Crank, J., 1975. *Mathematics of diffusion*, 2nd ed Clarendon Press, Oxford.

Crundwell, F.K., 1987. Kinetics and mechanism of the oxidative dissolution of a zinc sulphide concentrate in ferric sulphate solution. *Hydrometallurgy* 19, 227–242.

Crundwell, F.K., Verbaan, B., 1987. Kinetics and mechanism of the non-oxidative dissolution of sphalerite (zinc sulphide). *Hydrometallurgy* 17, 369–384.

Crundwell, F.K., 2013. The dissolution and leaching of minerals: Mechanisms, myths and misunderstandings. *Hydrometallurgy* 139, 132 – 148.

Crundwell, F.K., Bryson, A.W., 1995. The modeling of particulate leaching reactors – the population balance approach. *Hydrometallurgy* 29, 275 – 295.

da Silva, G., 2004. Relative importance of diffusion and reaction control during the bacterial and ferric sulfate leaching of zinc sulfide. *Hydrometallurgy* 73, 313 – 324.

Dutrizac, J.E., 2006. The dissolution of sphalerite in ferric sulfate media. *Metallurgical and Materials Transactions B* 37B, 161-171.

Dickinson, D.F., Heal, G.R., 1999. Solid-liquid diffusion controlled rate equations. *Thermochimica Acta* 340–341, 89–101.

Espiari, S., Rashchi, F., Sadrnezhad, S.K., 2006. Hydrometallurgical treatment of tailings with high zinc content. *Hydrometallurgy* 82, 54–62.

Grénman, H., Ingves, M., Wärnå, J., Corander, J., Murzin, D.Yu., Salmi, T., 2011. Common potholes in modeling solid-liquid reactions – methods for avoiding them. *Chemical Engineering Science* 66, 4459 – 4467.

Gbor, P.K., Jia, C.Q., 2004. Critical evaluation of coupling particle size distribution with the shrinking core model. *Chemical Engineering Science* 59, 1979– 1987.

Grénman, H., Salmi, T., Murzin, D.Yu., 2011. Solid-liquid reaction kinetics – experimental aspects and model development. *Reviews in Chemical Engineering* 27, 53 – 77.

Gökhan, U., 2009. Kinetics of sphalerite dissolution by sodium chlorate in hydrochloric acid. *Hydrometallurgy* 95, 39–43.

Haario, H., 2002. *Modest User's Guide*, ProfMath Oy, Helsinki, Finland.

Haario, H., Saksman, E., Tamminen, J., 2001. An adaptive Metropolis algorithm. *Bernoulli* 7, 223.

Jin, Z.-M., Warren, G.W., Henein, H., 1984. Reaction kinetics of the ferric chloride leaching of sphalerite – an experimental study. *Metallurgical Transactions* 15B, 5–12.

Kammel, R., Pawlek, F., Simon, M., Xi-Ming, L., 1987. Oxidizing leaching of sphalerite under atmospheric pressure. *Metall* 41, 158–161.

Kolodziej, B., Adamski, Z., 1990. Dissolution of sphalerite in aqueous hydrochloric acid solutions under reduction conditions, *Hydrometallurgy* 24, 393–406.

Kuosa, M., Laari, A., Solonen, A., Haario, H., Kallas, J., 2007. Estimation of multicomponent reaction kinetics of p-nitrophenol ozonation in a bubble column, *Industrial & Engineering Chemistry Research* 46, 6235-6243.

Laine, M. 2008. Adaptive MCMC Methods with applications in environmental and geophysical model. (Ph.D. Thesis). Finnish Meteorological Institute, Helsinki, Finland.

Laine, M., Finnish meteorological Institute, <http://helios.fmi.fi/~lainema/mcmc> (accessed 8.11.2016).

Lampinen, M., Laari, A., Turunen, I., 2010. Simulation of direct leaching of zinc concentrate in a non-ideally mixed CSTR. *The Canadian Journal of Chemical Engineering* 88, 625–632.

Lampinen, M., Laari, A., Turunen, I., 2015. Kinetic model for direct leaching of zinc sulfide concentrates at high slurry and solute concentration. *Hydrometallurgy* 153, 160–169.

Levenspiel, O., 1999. *Chemical Reaction Engineering*. John Wiley & Sons, New York. 644pp.

Lochmann, J., Pedlík, M., 1995. Kinetic anomalies of dissolution of sphalerite in ferric sulfate solution. *Hydrometallurgy* 37, 89 - 96.

Lotens, J.P., Wesker, E., 1987. The behavior of sulfur in the oxidative leaching of sulfidic minerals. *Hydrometallurgy* 18 (1), 39–54.

Markus, H., Fugleberg, S., Valtakari, K., Salmi, T., Murzin, D.Yu., Lahtinen, M., 2004a. Kinetic modelling of a solid-liquid reaction: reduction of ferric iron to ferrous iron with zinc sulphide. *Chemical Engineering Science* 59, 919–930.

Markus, H., Fugleberg, S., Valtakari, K., Salmi, T., Murzin, D.Yu., Lahtinen, M., 2004b. Reduction of ferric to ferrous with sphalerite concentrate, kinetic modelling. *Hydrometallurgy* 73, 269–282.

Massaci, P., Recinella, M., Piga, L., 1998. Factorial experiments for selective leaching of zinc sulfide in ferric sulfate media. *International Journal of Minerals Processing* 53, 213-224.

Mulak, W., Miazga, B., Szymczycha, A., 2005. Kinetics of nickel leaching from spent catalyst in sulphuric acid solution, *International Journal of Minerals Processing* 77, 231-235.

Órfão, J.J.M, Martins, F.G., 2002. Kinetic analysis of thermogravimetric data obtained under linear temperature programming – a method based on calculations of the temperature integral by interpolation. *Thermochimica Acta* 390, 195–211.

Palencia-Perez. I.P., Dutrizac, J.E., 1991. The effect of iron content of sphalerite on its dissolution rate in ferric sulphate and ferric chloride media. *Hydrometallurgy* 26, 211–232.

Pecina, T., Franco, T., Castillo, P., Orrantia, E., 2008. Leaching of zinc concentrate in H₂SO₄ solutions containing H₂O₂ and complexing agents. *Minerals Engineering* 21(1), 23 - 30.

Rath, P.C., Paramguru, R.K., Jena, R.K., 1981. Kinetics of dissolution of zinc sulfide in aqueous ferric chloride solution. *Hydrometallurgy* 6, 219–225.

Safari, V., Arzpeyma, G., Rashchi, F., Mostoufi, N., 2009. A shrinking particle-shrinking core model for leaching of a zinc ore containing silica. *International Journal of Minerals Processing* 93, 79–83.

Salmi, T., Grénman, H., Bernas, H., Wärnå, J., Murzin, D. Yu., 2010. Mechanistic modeling of kinetics and mass transfer for a solid-liquid system: Leaching of zinc with ferric iron. *Chemical Engineering Science* 65, 4460–4471.

Souza, A.D., Pina, P.S., Leão, V.A., Silva, C.A., Siqueira, P., F., 2007. The leaching kinetics of a zinc sulphide concentrate in acid ferric sulphate. *Hydrometallurgy* 89, 72–81.

Solonen, A., 2001. Bayesian methods for estimation, optimization and experimental design, Ph.D. (Thesis), Lappeenranta University of Technology, Lappeenranta, Finland.

Suni, J., Henein, H., Warren, G.W. Reddy, D., 1989. Modeling the leaching kinetics of a sphalerite concentrate size distribution in ferric chloride solution. *Hydrometallurgy* 22, 25–38.

Vahteristo, K., Laari, A., Solonen, A., 2013. Diels–Alder reaction kinetics for production of norbornene monomers: evaluation of parameters and model reliability using Markov chain Monte Carlo methods. *Industrial & Engineering Chemistry Research* 52, 6357–6365.

Verbaan, B., Crundwell, F.K., 1986. An electrochemical model for the leaching of a sphalerite concentrate. *Hydrometallurgy* 16, 345 – 359.

Verbaan, B., Crundwell, F.K., 1986. An electrochemical model for the leaching of a sphalerite concentrate. *Hydrometallurgy* 16, 345–359.

Weisener, C.G., Smart, R.St.C., Gerson, A.R., 2003. Kinetics and mechanism of the leaching of low Fe sphalerite. *Geochimica et Cosmochimica Acta* 67 , 823–830.

Weisener, C.G., Smart, R.St.C., Gerson, A.R., 2004. A comparison of the kinetics and mechanism of acid leaching of sphalerite containing low and high concentrations of iron. *International Journal of Minerals Processing* 74, 239–249.

Xie, K-q., Yang, X-w., Wang, J-k., Yan, J-f., Shen Q-f., 2007. Kinetic study on pressure leaching of high iron sphalerite concentrate. *Transactions of Nonferrous Metals Society of China* 17, 187-194.

Xu, Z.-F., Jiang, Q.-Z., Wang, C.-Y., 2013. Atmospheric oxygen-rich direct leaching behaviour of zinc sulphide concentrate. *Transactions of Nonferrous Metals Society of China* 23, 3780-3787.

Zhukov, V. V., Laari, A., Koironen, T., 2015. Kinetic modeling of high-pressure pyrite oxidation with parameter estimation and reliability analysis using the Markov Chain Monte Carlo method, *Industrial & Engineering Chemistry Research* 54, 9920-9930.

Publication IV

Lampinen, M., Laari, A., and Turunen, I.

Simulation of direct leaching of zinc concentrate in a non-ideally mixed CSTR

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SIMULATION OF DIRECT LEACHING OF ZINC CONCENTRATE IN A NON-IDEALLY MIXED CSTR

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A simulation model for direct leaching of zinc concentrate in a continuous non-ideally mixed stirred tank reactor (CSTR) is presented. The model takes into account the surface reactions between zinc in the solids and ferric iron ions in the liquid phase, oxidation of ferrous iron back to ferric iron, gas-liquid mass transfer of oxygen, decrease of particle size as the reaction proceeds, and the effect of hydrostatic pressure on the oxygen dissolution rate. The model is pseudo-homogeneous and is approximative in the sense that it neglects the effects of particle size distributions and population balances of the concentrate particles.

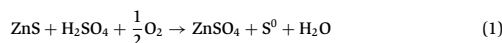
On présente un modèle de simulation pour la lixiviation directe de concentré de zinc dans un réacteur à fonctionnement continu non idéalement agité. Le modèle prend en compte les réactions en surface entre le zinc dans les solides et les ions de fer ferrique dans la phase liquide, l'oxydation du fer ferreux qui retourne en fer ferrique, le transfert de masse gaz-liquide de l'oxygène, la diminution de la taille des particules alors que la réaction se produit et l'effet de la pression hydrostatique sur la vitesse de dissolution de l'oxygène. Le modèle est pseudohomogène et est approximatif en ce sens qu'il néglige les effets des distributions de la taille des particules et des équilibres des populations des particules concentrées.

Keywords: zinc concentrate, direct leaching, modelling, parameter estimation, stirred tank

INTRODUCTION

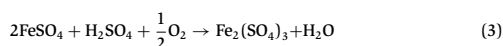
As an alternative to traditional roasting and acidic leaching of zinc from sphalerite concentrate, zinc can also be produced by directly oxidising the concentrate (direct leaching) in an acidic environment in a slurry reactor (Takala, 1999). Direct leaching of zinc concentrates has been commercially used since the 1980s and a considerable amount of research work has been done in process development. Direct leaching processes are usually divided into two categories; processes under atmospheric pressure and those under elevated pressure. On an industrial scale, leaching of zinc concentrate is carried out in several stirred tank reactors installed in series. Atmospheric direct leaching of zinc concentrates is carried out at temperatures near to the boiling point of the process solution (~100°C).

In the acidic environment of zinc leaching zinc sulfide can be directly oxidised by molecular oxygen.



However, this reaction proceeds slowly and therefore plays only a minor role in leaching chemistry.

Oxidation by ferric iron is a much faster process and the oxidation-reduction cycle of iron plays an important role in leaching. In this cycle the ferric iron is reduced by zinc sulfide to ferrous iron, which is oxidised back to a ferric form by oxygen.



Zinc leaching is usually carried out in large-scale mixed reactors. For zinc leaching process design it is very important to have a reactor model which can accurately predict the effects of temperature, pressure (including the effect of hydrostatic pressure), particle size, and non-ideal mixing in the process. Unfortunately, development of a comprehensive reactor model

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for zinc leaching is complicated and requires considerable experimental and theoretical work. Several simulation models for particulate leaching processes have been presented in literature. Papangelakis et al. (1990); and Papangelakis and Demopoulos (1992a,b,c) have developed leaching models for a series of autothermal CSTRs to solve material and energy balances for a multi-stage reactor. The changes in particle size are taken into account by solving population balance equation. The models also include the effect of particle residence time distribution. In these models it is assumed that the process is either surface reaction or gas transfer controlled. Rubisov and Papangelakis (1996) have given a simulation model for pyrite pressure oxidation as a pre-treatment of refractory gold concentrate. The model is developed for horizontal cylindrical vessels subdivided to ideally mixed compartments and accounts for gas-liquid mass transfer followed by surface oxidation reaction. Population balance equation together with shrinking-core model is used to describe the dissolution of particles. Baldwin et al. (1995) have presented a similar model for zinc pressure leaching process. The model includes the dissolution of marmatite, (Zn, Fe)S, oxidation of ferrous iron to ferric iron and precipitation of lead jarosite. The population balance method was used to solve the sulfide mineral material balances.

In a large-scale atmospheric leaching reactor, however, ideal mixing cannot be assumed, which further complicates the situation. This makes the development of reactor models with multiple reactions and a detailed description of gas-liquid mass transfer increasingly more difficult. The objective of the current work is, therefore, to develop an approximative model for zinc leaching in a large-scale non-ideally mixed reactor. This model permits evaluation of how different process conditions affect zinc atmospheric leaching and can be used in reactor design and development. In the model, the solids are treated as a pseudo-homogeneous phase and local average particle size in the reactor is calculated from the zinc conversion. The hydrodynamics is treated using axial dispersion model to describe vertical mixing in the reactor.

When studying the effects of process variables on leaching kinetics, a reaction kinetic model is required. Kinetic leaching models are complicated and include several experimental param-

eters. The reliability of these models and their parameters is very important and is reflected in the reliability of the model predictions. Novel statistical mathematical methods have been presented to study the reliability of models, including the so-called Markov Chain Monte Carlo (MCMC) methods. MCMC methods are based on Bayesian inference and treat all the parameters and model predictions as probability distributions. MCMC methods have recently been successfully used in chemical engineering to study parameter reliability in, for example, the esterification of carboxylic acids (Vahteristo et al., 2009) and chemical oxidation of polluted water by ozonation (Kuosa et al., 2007, 2009). In these studies MCMC methods have been proven to be very useful and have been shown to provide new valuable information about the processes studied. In the current work, MCMC methods are used in a similar way to study the reliability of model parameters and model predictions of zinc concentrate leaching.

REACTION KINETICS

Several authors have studied the kinetics of direct leaching of zinc sulfide concentrates. Souza et al. (2007) studied zinc concentrate leaching in acidic ferric sulfate solution. Souza et al. (2007) presented that the leaching process could be separated into two stages. Initially, the dissolution kinetics was controlled by the chemical reaction at the surface of the zinc sulfide particles followed by a second step where the reaction was controlled by diffusion of the reagents or products through the elemental sulfur layer. Aydogan et al. (2005) studied the leaching in acidic ferric chloride solution. The leaching was found to be reaction controlled and a semi-empirical correlation was proposed for the dissolution rate. Dutrizac (2006) has studied in detail the dissolution of sphalerite by ferric iron in a stirred tank under different conditions. The kinetic data presented by Dutrizac is used in this work to develop kinetic models which are in a form suitable for MCMC analysis and reactor simulation. The kinetic data obtained by Dutrizac for experimental runs carried out with different particle sizes, temperatures, and reactant concentrations are presented in Figure 1. The conditions of the experimental runs are shown in Table 1. The mixing rate in the experiments was 300 l/min.

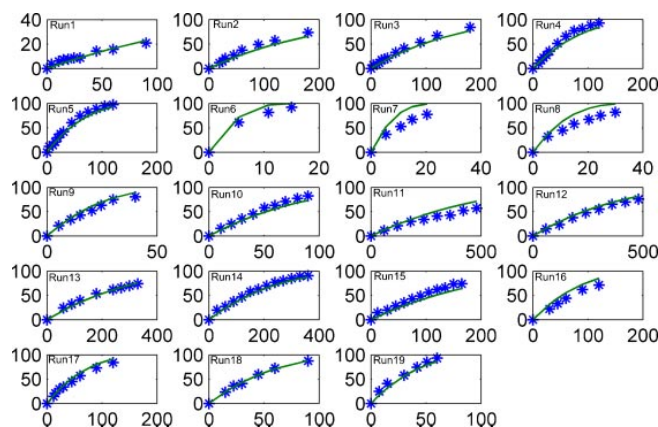


Figure 1. Comparison of the experimental and predicted zinc conversions. Time (min) on the *x*-axis and zinc extraction (%) on the *y*-axis. Experimental conditions are as shown in Table 1.

Table 1. Conditions of the experimental runs according to Dutrizac (2006)

Run	$c(\text{Fe}^{3+})$ (mol/dm ³)	dp (μm)	T (°C)
1	0.010	67.1	75
2	0.050	67.1	75
3	0.100	67.1	75
4	0.500	67.1	75
5	1.000	67.1	75
6	0.300	5.0	85
7	0.300	8.0	85
8	0.300	12.0	85
9	0.300	24.0	85
10	0.300	80.0	85
11	0.300	67.1	40
12	0.300	67.1	45
13	0.300	67.1	50
14	0.300	67.1	55
15	0.300	67.1	60
16	0.300	67.1	80
17	0.300	67.1	85
18	0.300	67.1	90
19	0.300	67.1	100

This mixing rate was chosen to eliminate external mass transfer resistance.

In the development of the kinetic model for zinc leaching it is assumed that the reaction between zinc and ferric iron takes place at the reactive surface of the particle according to Equation (2). Ferric iron diffuses through porous layer, formed by reaction products and non-reacting minerals, to the surface of the particle where it reacts with zinc sulfide generating ferrous iron and elemental sulfur. The reaction rate of Zn is specified as a surface reaction (mol Zn/m² min). The kinetics of the surface reaction depends on the concentration of zinc (in the solids), ferric iron, and sulfuric acid at the surface. However, zinc concentration at the solid surface of the particle is characteristic for the concentrate and can be assumed to remain constant during leaching. Therefore, $k_{C_{Zn,S}}$ can be lumped to a kinetic constant k_1 .

$$r_1 = k_{C_{Zn,S}} c_{\text{Fe}^{3+},s}^{n_1} c_{\text{H}_2\text{SO}_4}^{n_2} = k_1 c_{\text{Fe}^{3+},s}^{n_1} c_{\text{H}_2\text{SO}_4}^{n_2} \quad (4)$$

The dependency of the surface reaction rate on temperature is taken into account by the Arrhenius equation. The Arrhenius equation is presented in a modified form to improve parameter identification:

$$k_1 = k_{1,\text{mean}} \exp\left(-\frac{E_1}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{mean}}}\right)\right) \quad (5)$$

where T_{mean} is some mean temperature in the experiments and $k_{1,\text{mean}}$ is the rate constant at the mean temperature.

The dissolution rate of Zn can be described by multiplying the surface reaction rate with the reactive area of the particle and the number of particles per volume of slurry:

$$-\frac{dc_{Zn}}{dt} = r_1 A_i n \quad (6)$$

It is further assumed that the leaching reaction proceeds inside the particles according to the shrinking core model. Ferric iron, which is the limiting compound taking part in the reaction, must diffuse through this layer to the surface of the particle where the

reaction takes place. The concentration of ferric iron at the reacting surface, $c_{\text{Fe}^{3+},s}$, depends on the rates of the surface reaction and diffusion and has to be solved numerically from the mass balance. Pseudo-steady state conditions inside the particle are assumed, which means that the concentration profile of ferric iron in the product layer is not dependent on time. This is a reasonable assumption in view of the relatively long residence time in the reactor. At the reacting surface the mass balance for ferric iron can be written as:

$$2k_1 c_{\text{Fe}^{3+},s}^{n_1} c_{\text{H}_2\text{SO}_4}^{n_2} A_i - D_c A_o \frac{r_1 (c_{\text{Fe}^{3+}} - c_{\text{Fe}^{3+},s})}{(r_o - r_1) r_o} = 0 \quad (7)$$

Based on the shrinking core model, the shrinkage of the core of the particle can be described by the following equation:

$$\left(\frac{r_i}{r_o}\right)^3 = \frac{c_{Zn}}{c_{Zn,\text{ini}}} \quad (8)$$

This equation can be used for continuous calculation of the radius of the active layer and the active area of the particle. The active area in Equations (6) and (7), therefore, continuously decreases as the reaction proceeds.

In the modelled reactor there are two reactions that take place simultaneously. The first one is the surface reaction where zinc is leached from the concentrate due to the reaction with ferric iron according to Equation (2). The second one is a bulk reaction where ferrous iron is oxidised back to ferric iron as described by Equation (3). The kinetics (5) of this reaction has been described by Verbaan and Crundwell (1986):

$$r_2 = k_2 e^{(-E_2/RT)} c_{\text{Fe}^{2+}}^2 c_{\text{O}_2} c_{\text{H}^+}^{-0.35} \quad (9)$$

where the reaction rate r_2 is in mol/dm³ min, k_2 is $124.8 \times 10^9 \text{ dm}^{1.65} \text{ mol}^{-1.65} / \text{min}$ and E_2 is 68 kJ/mol. Concentrations are in mol/dm³.

PARAMETER ESTIMATION AND RESULTS

The kinetic model used in this study consisted of Equations from (4) to (8) and has four parameters ($k_{1,\text{mean}}$, n_1 , E_1 and D_c) which have to be estimated by fitting to experimental data. The experimental data presented by Dutrizac (2006) was used for kinetic model development. The data collected from the presented results is shown in Table 1. Dutrizac found that for a 0.3 M $\text{Fe}_2(\text{SO}_4)_3$ solution the leaching rate is independent from H_2SO_4 concentration for concentrations lower than 0.1 M H_2SO_4 . For higher H_2SO_4 concentrations the leaching rate increases. However, due to large scatter in the data it was not possible to include sulfuric acid concentration to the model and a value of 1.0 for n_2 was assumed instead. Therefore, the kinetic model should be applied with caution in other conditions than those used in the parameter estimation.

The zinc leaching rate Equation (6) is an ordinary differential equation which is numerically integrated from the initial state at time zero to the designated time. At each time step the surface concentration of ferric iron is solved by finding the root of Equation (7). The model parameters were estimated by minimising the squared difference between the simulations and experiments. The estimated parameters are shown in Table 2. The experimental and the predicted zinc conversions are compared in Figure 1. With minor exceptions, the predicted values were found to be in good agreement with the experimental data ($R_2 \approx 90\%$).

Parameter	Value	Units	Std error
$k_{1,\text{mean}}$	1.40×10^{-6}	$\text{mol}^{-0.34}/\text{m}^{-2.01} \text{ min}$	23.6
n_1	0.336	—	11.5
E_1	3.93×10^4	J/mol	3.5
D_e	4.98×10^{-5}	m^2/min	—

Regression coefficient = 89.54%.

The deviations mainly concern the smallest particle size, where the model slightly overestimates the achieved conversion.

To evaluate the accuracy of the estimated parameters in a non-linear multi-parameter model, it is important to consider possible cross-correlation and identifiability of the parameters. Classical statistical analysis giving optimal parameter values, error estimates, and correlations between them is approximate and may sometimes be quite misleading. Moreover, the question is left open of how reliable the model predictions are, that is, how accurate the modeling results are for situations other than those present in the experiments already performed. Both of these problems may be properly treated by MCMC methods. Using MCMC methods, all the uncertainties in the data and the modeling results are treated as statistical distributions. Up-to-date adaptive computational schemes are employed in order to make the simulations as effective as possible (Haario et al., 2001; Laine, 2008). A FORTRAN 90 software package MODEST (Haario, 2002) can be used for both the least squares estimation and the MCMC estimation. The referred methods are also implemented in a MATLAB package (Laine, 2008, 2009). In the current work, the reliability of the model parameters and the model predictions were studied by using the MCMC methods discussed above.

The results from the MCMC analysis are shown in Figure 2 which presents two-dimensional posterior probability distributions for the

parameters. Each dot in the figure represents a sample in the Markov chain. The density of the dots represents probability. The contour lines in the figures represent 50% and 90% probability regions. As can be seen from Figure 2, the probability region between n_1 and $k_{1,\text{mean}}$ is elongated, which means that there is considerable cross-correlation between these parameters. This lowers the reliability of these two parameters to some extent and can also be seen as a relatively high standard error in Table 2. Figure 2 also reveals that the internal diffusion coefficient is not identified and its value is relatively large. This result can be interpreted such that any value for D_e which is large enough gives an equally good fit. In other words, internal diffusion has in this case no effect on the leaching rate.

SIMULATION MODEL

The reactors where the dissolution of zinc concentrates takes place are large-scale mixed gas-liquid-solid reactors. They usually operate co-currently with the gas, and slurry (particles and reactants) is fed from the reactor bottom. Gas fed from the bottom is dispersed using a specially designed mixing element. Mixing in the reactor is intensive in order to ensure a homogeneous distribution of the particles. The reactors are tall and the considerable effect of hydrostatic pressure must be taken into account in simulations. To achieve higher conversions, there are usually a number of reactors in series, typically four. However, for the sake of simplicity, only a single reactor is considered in the current work.

The reactor model is composed of non-steady state mass balance equations for oxygen in the gas phase, for zinc concentration in the concentrate, and for dissolved oxygen, ferric iron, and ferrous iron in the liquid phase. An axial dispersion model is used to describe mixing in the reactor.

A pseudo-homogeneous model for the solids in the slurry is assumed. The mass balance for zinc in the concentrate can be

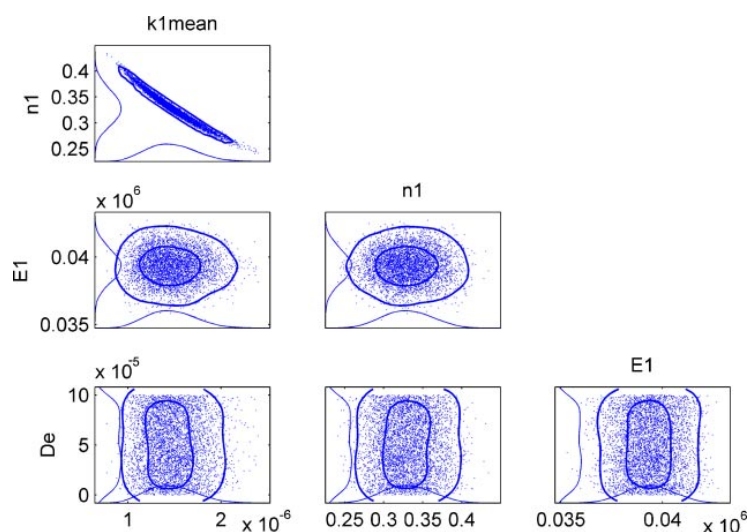


Figure 2. Two-dimensional posterior probability distributions from the MCMC analysis.

written as:

$$-\frac{dc_{Zn}}{dt} - U_L \frac{dc_{Zn}}{dz} + E_L \frac{d^2c_{Zn}}{dz^2} - r_1 A_i n = 0 \quad (10)$$

For ferric iron, ferrous iron, and dissolved oxygen in the liquid phase, the mass balances are:

$$-\frac{dc_{Fe^{3+}}}{dt} - U_L \frac{dc_{Fe^{3+}}}{dz} + E_L \frac{d^2c_{Fe^{3+}}}{dz^2} - r_1 \varepsilon_L A_i n + r_2 = 0 \quad (11)$$

$$-\frac{dc_{Fe^{2+}}}{dt} - U_L \frac{dc_{Fe^{2+}}}{dz} + E_L \frac{d^2c_{Fe^{2+}}}{dz^2} + r_1 \varepsilon_L A_i n - r_2 = 0 \quad (12)$$

$$-\frac{dc_{O_2}}{dt} - U_L \frac{dc_{O_2}}{dz} + E_L \frac{d^2c_{O_2}}{dz^2} - r_2 + k_L a (c_{O_2}^* - c_{O_2}) A_c = 0 \quad (13)$$

The boundary conditions for all compounds can be presented as:

$$\frac{dc}{dz} = \frac{U_L(c_i - c_{in})}{E_L}, \text{ for } z = 0 \quad (14)$$

$$\frac{dc}{dz} = 0, \text{ for } z = H \quad (15)$$

where c_{in} is the feed concentration of the compound and c_i is the concentration in the first cell in the reactor.

For oxygen in the gas phase, assuming plug flow, the mass balances can be written as:

$$-\frac{d\dot{n}_{O_2}}{dz} - k_L a (c_{O_2}^* - c_{O_2}) A_c = 0 \quad (16)$$

The effect of hydrostatic pressure is taken into account by the equation:

$$\frac{dp}{dz} + \rho_{SL} g \varepsilon_{SL} = 0 \quad (17)$$

In addition to the mass balances given in Equations (10)–(13), correlations are required for gas holdup and gas–liquid mass transfer to close the model equations. Yawalkar et al. (2002) have studied gas holdup in stirred tank reactors in the presence of inorganic electrolytes. The authors propose a correlation which, it is claimed, predicts gas holdup reliably for a wide range of geometrical configurations, electrolyte concentrations, and mixing speed with both radial flow and axial flow impellers.

$$\varepsilon_G = 0.1581 \left(\frac{N}{N_c} \right)^{0.734} vvm^{0.85} \quad (18)$$

where vvm is the volume of gas sparged in volume of liquid per minute and N_c is the impeller speed required for complete dispersion of the gas phase. N_c can be determined by simple methods such as by visual observation, from power input curve and mixing time studies (Rewatkar and Joshi, 1993). In the current work gas holdup in the reactor is evaluated from Equation (18) using impeller speed which is 1.5 times the minimum speed required for gas dispersion.

The volumetric gas–liquid mass transfer coefficient in the leaching reactor can be evaluated using the results presented by Kaskiala (2005). Kaskiala has studied gas–liquid mass transfer in a laboratory scale leaching reactor. Using the dynamic response method for an air–water system with a mixing speed of 300 1/min,

the following correlation was obtained between the volumetric mass transfer coefficient and superficial gas velocity.

$$k_L a = 0.497 U_G^{0.579} \quad (19)$$

The correlation of Equation (19) was obtained for an air–water system and therefore it probably underestimates the gas–liquid mass transfer that can be obtained on an industrial scale where strong electrolyte solutions are used. It should also be mentioned that Equations (18) and (19) do not take into account the presence of solids, which under process conditions can have a considerable effect on gas holdup and gas–liquid mass transfer.

Oxygen solubility in the liquid phase is greatly affected by the ionic compounds present in the solution. Oxygen solubility in the leaching solution is evaluated from the experimental correlation presented by Baldwin et al. (1995):

$$H \times 10^{-3} = -3.8 \times 10^{-5} + 0.020063T + 0.23788 [Fe^{3+}] + 0.814682 [Zn^{2+}] + 0.074723 [H_2SO_4] - 0.70314 \quad (20)$$

where the concentrations are in mol dm^{-3} and H is in $\text{atm mol}^{-1} \text{dm}^3$.

The water vapour pressure of the solution is also obtained from the experimental correlation presented by Baldwin et al. (1995):

$$p_{H_2O} = \exp \left[12.73323 - 0.08092 [H_2SO_4] - 0.01396 [Zn^{2+}] - 0.00991 [Fe_T] - \frac{4741.66}{T} \right] \quad (21)$$

where the concentrations are in mol dm^{-3} and p_{H_2O} is in atm. Fe_T in Equation (21) is the total iron concentration.

Currently, there is no detailed information about the liquid phase axial dispersion coefficient in the reactor. However, in the absence of other information, a reasonable estimate may be obtained by taking into account the height to diameter ratio of the reactor and assuming that the reactor is composed of three ideally mixed tanks in series. Using the relationship between the Peclet number and the tanks-in-series model ($Pe = 2(N_T - 1)$), a value of $1.71 \times 10^{-3} \text{ m}^2/\text{s}$ is obtained for the axial dispersion coefficient. For the gas phase, plug flow is a reasonable assumption and is used in the simulations.

The partial differential equations, Equations (10)–(17), are transformed to ordinary differential equations by dividing the reactor height into 20 classes and calculating the spatial derivatives using the Numerical Method of Lines (NUMOL) according to Schiesser (1991). The ordinary differential equations are then

Table 3. Simulation conditions and reactor dimensions

Reactor diameter	7.2 m
Reactor height	20 m
Density of concentrate	4000 kg/m ³
Zinc fraction in concentrate	33 mass%
Sulfuric acid concentration in feed	29.4 kg/m ³
Fe ³⁺ -concentration in feed	18 kg/m ³
Slurry solid content in feed	180 kg/m ³
Temperature	60–90°C
Initial particle size	30–150 μm
Volumetric flow of slurry	50–110 m ³ /h

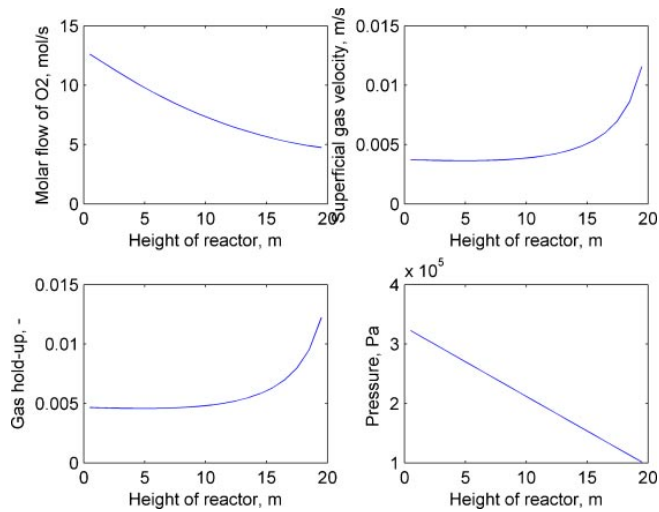


Figure 3. Profiles for molar flow of oxygen, pressure, gas holdup, and superficial gas velocity in the reactor. Initial acid (H₂SO₄) concentration 29.4 kg/m³, temperature 90°C, particle size 50 μm, volumetric flow of slurry 50 m³/h, residence time 16.3 h.

solved by integrating the model equations from the initial values to steady state.

Simulation Conditions

Simulations are carried out for a single isothermal continuous stirred tank reactor. The simulation conditions and reactor dimensions are presented in Table 3.

RESULTS

With the developed simulation model it is possible to evaluate how concentrations and different model variables change when moving from the bottom to the top of the reactor. Profiles for a 20 m high reactor are presented in Figures 3 and 4.

Figure 3 shows the combined effect of hydrostatic pressure and water vapour pressure on superficial gas velocity in the reactor.

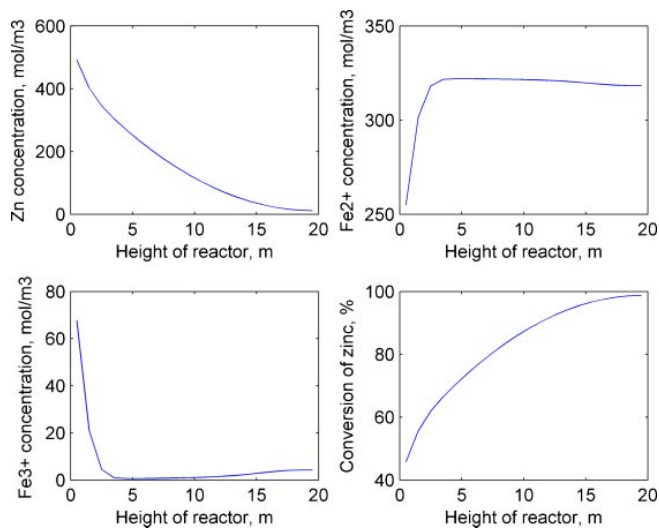


Figure 4. Profiles for zinc concentration, Fe²⁺-concentration, Fe³⁺-concentration, and conversion in the reactor. Initial acid (H₂SO₄) concentration 29.4 kg/m³, temperature 90°C, particle size 50 μm, volumetric flow of slurry 50 m³/h, residence time 16.3 h.

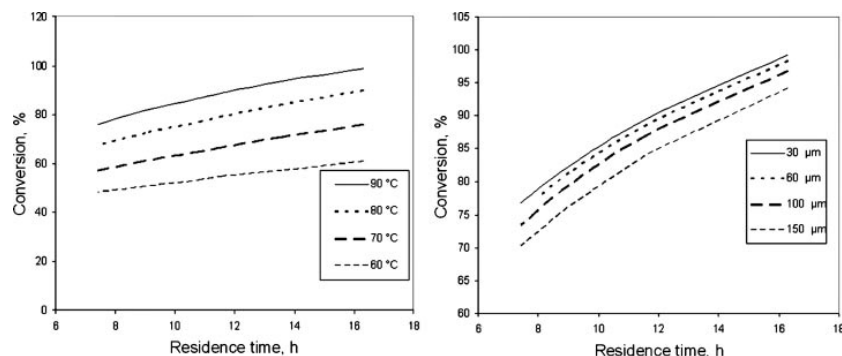


Figure 5. Conversion of zinc with different residence times, temperatures, and particle sizes. Conditions and reactor dimensions are presented in Table 3. In the left figure particle size is 50 μm and in the right figure temperature is 90 $^{\circ}\text{C}$.

The total gas pressure is a sum of oxygen partial pressure and water vapour pressure. In isothermal conditions water is vaporised until the proportion of molar water vapour flow of the total gas flow is equal to the proportion of water vapour pressure of the total pressure. Therefore, the total flow rate of gas increases as gas moves upwards in the column and the hydrostatic pressure decreases. Consequently, gas holdup is also increased. Figure 4 shows that the concentration of ferric iron rapidly decreases as the ferric iron reacts with zinc. The second reaction of ferrous iron oxidation back to ferric iron is slower and begins to increase ferric iron concentration in the upper parts of the reactor where the zinc leaching rate becomes slower.

With the developed simulation model it is possible to evaluate the effect of different parameters on conversion. In Figure 5 the effect of residence time, temperature, and particle size on conversion are presented. From these figures it can be seen that temperature has a great effect on conversion but particle size only a minor effect.

CONCLUSIONS

A pseudo-homogeneous model for direct leaching of zinc concentrate in an isothermal non-ideally mixed CSTR was developed in the current work. As the first step, a reaction kinetic model was developed based on literature data. The kinetic model describes how the leaching rate depends on particle size, temperature, and reactant concentrations. It was found that the leaching rate is controlled by the surface reaction rate. The surface reaction rate is of the order of 0.35 for ferric iron. The activation energy obtained by parameter estimation is 39.3 kJ/mol, which is in good agreement with the apparent activation energy presented in the original work of Dutrizac (2006). The role of sulfuric acid concentration on the leaching kinetics was not studied in the current work and the kinetic model is, therefore, strictly speaking only valid for the concentration used in the experiments. The developed reactor model was used to simulate the operation of the reactor at different conditions. The simulation model allows testing of the effect of different process variables on zinc conversion and can be used in process design and development. The current model is pseudo-homogeneous and it is approximative in the sense that it neglects the effects of particle size distributions, population balances, and residence time distributions of the con-

centrate particles. In addition, the model contains a number of experimental correlations which are taken from the literature. These correlations are obtained in conditions which may be significantly different from those used in industrial processes. It is recommended that before the model is used for simulation of industrial reactors, the parameters of the experimental correlations are re-estimated in conditions similar to the real process. It should be also noted that the role of mixing on the leaching kinetics is not fully covered in the current work. In a large-scale reactor the mixing conditions vary locally. The mixing rate affects the leaching kinetics by increasing the gas-liquid mass transfer and changing the hydrodynamic conditions in the reactor. More accurate description of mixing and local mass transfer in the process requires the application of CFD simulations.

NOMENCLATURE

A_c	cross-sectional area of reactor (m^2)
A_i	inner surface area of particle (reactive area) (m^2)
A_o	outer surface area of particle (m^2)
$c_{\text{Fe}^{2+}}$	concentration of Fe^{2+} in liquid ($\text{mol Fe}^{2+}/\text{m}_l^3$)
$c_{\text{Fe}^{3+}}$	concentration of Fe^{3+} in liquid ($\text{mol Fe}^{3+}/\text{m}_l^3$)
$c_{\text{Fe}^{3+},s}$	concentration of Fe^{3+} at the reacting surface ($\text{mol Fe}^{3+}/\text{m}_l^3$)
c_{O_2}	dissolved oxygen concentration ($\text{mol O}_2/\text{m}_l^3$)
$c_{\text{O}_2}^*$	dissolved oxygen concentration at saturation point ($\text{mol O}_2/\text{m}_l^3$)
c_{H^+}	concentration of H^+ in liquid ($\text{mol H}^+/\text{m}_l^3$)
$c_{\text{H}_2\text{SO}_4}$	concentration of H_2SO_4 in liquid ($\text{mol H}_2\text{SO}_4/\text{m}_l^3$)
c_{Zn}	concentration of zinc in solids ($\text{mol Zn}/\text{m}_R^3$)
$c_{\text{Zn},\text{ini}}$	initial concentration of zinc in solids ($\text{mol Zn}/\text{m}_R^3$)
$c_{\text{Zn},s}$	concentration of zinc at solid surface ($\text{mol Zn}/\text{m}_R^3$)
D_e	internal diffusion coefficient (m^2/min)
E_1	activation energy (J/mol)
E_2	activation energy (kJ/mol)
E_L	axial dispersion coefficient (m^2/s)
g	acceleration due to gravity (m/s^2)
h_R	height of reactor (m)
k_1	reaction rate constant
$k_{1,\text{mean}}$	reaction rate constant at mean temperature ($\text{mol}^{-0.34}/\text{m}^{-2.01} \text{min}$)
k_2	reaction rate constant ($\text{dm}^{1.65}\text{mol}^{-1.65}/\text{min}$)

$k_{1,a}$	volumetric mass transfer coefficient (1/s)
N	impeller speed (1/s)
N_c	impeller speed required for complete dispersion of gas phase (1/s)
N_T	number of mixed tanks in series
n_1	reaction order for Fe^{3+}
n_2	reaction order for H_2SO_4
n	number of particles in reactor ($1/\text{m}_R^3$)
\dot{n}_{O_2}	molar flow rate of oxygen (mol/s)
Pe	Peclet number ($U_L h_R / E_L$)
p	pressure (Pa)
R	gas constant (J/mol K)
r_1	reaction rate for zinc ($\text{mol m}^2/\text{min}$)
r_2	reaction rate for iron ($\text{mol m}^2/\text{s}$)
r_i	inner radius of particle (m)
r_o	outer radius of particle (m)
T	temperature (K)
T_{mean}	mean temperature (K)
t	time (s)
U_G	superficial gas velocity (m/s)
U_L	superficial slurry velocity (m/s)
v_{vm}	volume of gas sparged per unit volume of the liquid per minute (1/min)
z	axial coordinate (m)
ρ_{SL}	slurry density ($\text{kg}/\text{m}_{\text{SL}}^3$)
ε_G	gas volume fraction (holdup) ($\text{m}_G^3/\text{m}_R^3$)
ε_L	liquid volume fraction (holdup) ($\text{m}_L^3/\text{m}_R^3$)
ε_{SL}	slurry volume fraction ($\text{m}_{\text{SL}}^3/\text{m}_R^3$)

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REFERENCES

- Aydogan, S., A. Aras and M. Cambazoly, "Dissolution Kinetics of Sphalerite in Acidic Ferric Chloride Leaching," *Chem. Eng. J.* **114**, 67–72 (2005).
- Baldwin, S. A., G. P. Demopoulos and V. G. Papangelakis, "Mathematical Modelling of the Zinc Pressure Leach Process," *Metall. Mater. Trans. B* **26B**, 1035–1047 (1995).
- Dutrizac, J. E., "The Dissolution of Sphalerite in Ferric Sulfate Media," *Metall. Mater. Trans. B* **37B**, 161–171 (2006).
- Haario, H., "Modest User's Guide," ProfMath Oy, Helsinki, Finland (2002).
- Haario, H., E. Saksman and J. Tamminen, "An Adaptive Metropolis Algorithm," *Bernoulli* **7**, 223–242 (2001).
- Kaskiala, T., "Determination of Mass Transfer Between Gas and Liquid in Atmospheric Leaching of Sulphidic Zinc Concentrates," *Miner. Eng.* **18**, 1200–1207 (2005).
- Kuosa, M., A. Laari, A. Solonen, H. Haario and J. Kallas, "Estimation of Multicomponent Reaction Kinetics of p-Nitrophenol Ozonation in a Bubble Column," *Ind. Eng. Chem. Res.* **46**, 6235–6243 (2007).
- Kuosa, M., A. Laari, A. Solonen, H. Haario and J. Kallas, "Multicomponent Reaction Kinetics for Ozonation of p-Nitrophenol and Its Decomposition Products Under Acidic Conditions at Constant pH," *Chem. Eng. Sci.* **64**, 2332–2342 (2009).
- Laine, M., "Adaptive MCMC Methods With Applications in Environmental and Geophysical Model," Ph.D. Dissertation, Finnish Meteorological Institute, Helsinki, Finland (2008).
- Laine, M., "MCMC Toolbox for Matlab," www.helsinki.fi/~mjlaine/mcmc (accessed November 2009).
- Papangelakis, V. G. and G. P. Demopoulos, "Reactor Models for a Series of Continuous Stirred Tank Reactors With a Gas-Liquid-Solid Leaching Systems: Part I. Surface Reaction Control," *Metall. Trans. B* **23A**, 847–856 (1992a).
- Papangelakis, V. G. and G. P. Demopoulos, "Reactor Models for a Series of Continuous Stirred Tank Reactors With a Gas-Liquid-Solid Leaching Systems: Part II. Gas Transfer Control," *Metall. Trans. B* **23B**, 857–864 (1992b).
- Papangelakis, V. G. and G. P. Demopoulos, "Reactor Models for a Series of Continuous Stirred Tank Reactors With a Gas-Liquid-Solid Leaching Systems: Part III. Model Application," *Metall. Trans. B* **23B**, 865–877 (1992c).
- Papangelakis, V. G., D. Berk and G. P. Demopoulos, "Mathematical Modeling of an Exothermic Leaching Reaction System: Pressure Oxidation of Wide Size Arsenopyrite Particulates," *Metall. Trans. B* **21B**, 827–837 (1990).
- Rewatkar, V. B. and J. B. Joshi, "Effect of Sparger Design on Gas Dispersion in Mechanically Agitated Gas/Liquid Reactors," *Can. J. Chem. Eng.* **71**(2), 278–291 (1993).
- Rubisov, D. H. and V. G. Papangelakis, "Mathematical Modelling of the Transient Behaviour of CSTRs With Reactive Particulates: Part 2—Application to Pyrite Pressure Oxidation," *Can. J. Chem. Eng.* **74**(3), 363–371 (1996).
- Schuesser, W. E., "The Numerical Method of Lines: Integration of Partial Differential Equations," Academic Press, San Diego, USA (1991).
- Souza, A. D., P. S. Pina, V. A. Leão, C. A. Silva and P. F. Siqueira, "The Leaching Kinetics of a Zinc Sulphide Concentrate in Acid Ferric Sulphate," *Hydrometallurgy* **89**, 72–81 (2007).
- Takala, H., "Leaching of Zinc Concentrates at Outokumpu Kokkola Plant, Finland," *Erzmetall* **52**, 37–42 (1999).
- Vahteristo, K., S. Maury, A. Laari, A. Solonen, H. Haario, S. Koskimies and P. Mäkipelä, "Kinetics of Neopentyl Glycol Esterification With Different Carboxylic Acids," *Ind. Eng. Chem. Res.* **48**, 6237–6247 (2009).
- Verbaan, B. and F. K. Crundwell, "An Electrochemical Model for the Leaching of Sphalerite Concentrate," *Hydrometallurgy* **16**, 345–359 (1986).
- Yawalkar, A. A., A. B. M. Heesink, G. F. Versteeg and V. G. Pangarkar, "Gas Hold-Up in Stirred Tank Reactors in the Presence of Inorganic Electrolytes," *Can. J. Chem. Eng.* **80**(5), 791–799 (2002).

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