APPLICATION OF AMMONIUM-CITRATE-THIOSULFATE LEACHING ON
AWARUITE-BEARING SERPENTINITE ORES

by

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BASc, The University of British Columbia, 2012

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

May 2016

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Abstract

Nickel is an important alloying element of stainless steel and non-ferrous alloys. Awaruite as an alternative nickel source is gaining attention at the depletion of sulfide nickel and the high cost of laterite nickel, which are traditional nickel resources.

In view of the absence of a nickel recovery method from awaruite resources, UBC hydrometallurgy laboratory developed an in-house hydrometallurgical technology of atmospheric leaching in ammonium-citrate-thiosulfate solution. Ammonium selectively dissolves nickel in the presence of oxygen while citrate acts as a ferric chelator and thiosulfate a depassivation agent of nickel-iron alloy. In order to prepare the technology for pilot testing, in-depth batch leaching tests as well as preliminary solvent extraction tests were conducted and reported in this study.

The leaching tests on an alternative source had an optimized result of ~85% nickel extraction. The nickel leaching reactions were believed under surface reaction control as indicated by the estimated activation energy of 54.4kJ/mol through kinetic model fitting of leaching test data. However, the leaching tests with high pulp density (>10%) and recycled liquor simulating industrial settings demonstrated hindered nickel extraction due to iron accumulation. Specifically, a targeted comparison test showed that in order to retain 80% nickel extraction at 30% pulp density, simultaneous increases to four times the original ammonia concentration and six times the original citrate concentration are required in comparison with the 10% pulp density baseline test. Therefore, this technology needs to be improved on iron removal and economical leach reagents recycle for commercialization.

In the solvent extraction study, ACORGA K2000 as an ideal reagent candidate based on hydroxoyxime was tested on synthetic PLS containing 1 g/L Nickel (II), 0 – 0.8 g/L Fe (III), 0.1
– 0.5 M citrate and 1.5 – 6 M total ammonia. Hydroxyoxime has been proven effective in separating base metals from ammoniacal media. Results revealed that complete separation of nickel from iron was achieved at 5 v/o reagent solution concentration. Nickel can also be readily eluted with diluted sulfuric acid at pH = 1. The extraction kinetics was found to be relatively slow with 30 min of mixing/settling time required to reach equilibrium.
Preface

This dissertation is original, unpublished, independent work by the author, Wei Wei in May 4, 2016.
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<td>timescale constant in intrinsic kinetic models</td>
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<td>$N_{js}$</td>
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Acknowledgements

I would like to express my gratitude to my supervisor, Dr. David G. Dixon for his tremendous support throughout this study. My special thanks to Dr. Berend Wassink and Mr. Jacob Kabel for guidance on working with analytical equipment.

My appreciations also go to my colleagues and friends in the UBC Hydrometallurgy Group, namely Oscar Olvera, Laurence Dyer, Luis Quiroz, Patricia Valenzuela, Masoumeh Eghtesad, and Mariela Zuñiga for their generous help.

Last but not least, I would like to thank my parents and my fiancée for their unconditional support and love.
1. Introduction

Nickel is an important metal in modern infrastructure and technology, since it is widely used as the major alloying element for corrosion resistance in stainless steel (> 55%) and non-ferrous alloys (~15%). Nickel is also used in casting (~ 9%), electroplating (~ 9%), batteries (~5%) and other applications [1, 2]. The world consumption of nickel as of 2015 was reported more than 1.66 million tonnes per annum. China, Russia, Australia and Canada were the largest producers [3, 4].

Nickel production comes from two major sources: sulfide ores and laterite ores. Although laterite nickel makes up more than 70% of the world’s nickel resources, it only contributed to ~40% of nickel production in the world due to the difficulty and high cost of the extraction process of laterite nickel. With the sulfide nickel source depleting, alternative extraction methods and resources were demanded to satisfy the need of the market[4]. In recent decades, awaruite as a naturally occurring nickel-iron alloy started to gain attention as an alternative nickel source at the major discoveries of nickel deposits with large-tonnage awaruite reserves in Canada. However, there was not as yet an effective and economical method of nickel recovery from awaruite sources and awaruite was only sold as concentrates. UBC Hydrometallurgy lab in cooperation with Ore-Andes Eastfield patented an in-house economical hydrometallurgical process: atmospheric leaching of nickel using ammonia-citrate-thiosulfate solution. Preliminary shake flask study showed > 95% nickel extraction with synthetic awaruite and ~80% extraction with representative industrial samples [5], results which were considered promising since the average Caron nickel recovery was 85% at the expense of high cost in solution pretreatment. The objective of the current study was to prepare the technology for commercialization, details are presented in Section 3. Literature reviews on nickel resources, processing technology with an
emphasis on ammonium leaching history and thermodynamics, as well as the role of solvent extraction process in the envisaged process flow sheet and the property of ACORGA K2000, the solvent extractant candidate were presented in Section 2. Experimental setups for the leaching and solvent extraction tests are presented in Section 4. Results and discussions of the leaching and solvent extraction tests are shown in Section 5. The conclusions and recommendations are encapsulated in Section 6 and 7.
2. Literature Review

2.1 Nickel resources overview

2.1.1 Sulfide and laterite

Nickel resources exist in two major types, namely sulfide and laterite. Sulfide nickel ores contain nickel coexisting mainly with copper, iron and cobalt in sulfide forms and are often associated with precious metals such as Au, Ag and platinum group metals. Major sulfide minerals include pentlandite \((\text{Ni,Fe})_9\text{S}_8\), millerite \((\text{NiS})\), and heazlewoodite\((\text{Ni}_3\text{S}_2)\). The formation of sulfide nickel deposits is believed a result of a series of volcanic activities. Laterites are formed as a result of weathering of ultramafic rocks with varying compositions rich in iron, aluminum and magnesium and are often found as surface deposits \([4, 6]\). The various types of nickel laterite include limonite \(\{(\text{Fe,Ni})\text{O(OH)}_n\text{H}_2\text{O}\}\) and garnierites (silicate matrix). In general, sulfide nickel ores have higher nickel grades than laterite nickel ores and contain more valuable metals.

Sulfide nickel is primarily treated by pyrometallurgical means to produce nickel-containing matte for further refining or to produce ferronickel for stainless steel production. Laterite nickel ores are generally treated via reductive roasting such as rotary kiln electric furnace (RKEF), high pressure acid leaching (HPAL) or ammonia leaching. Although laterite nickel ores make up ~70% of known nickel deposits, the majority of nickel \((> 60\%)\) was extracted from sulfide deposits because of the complexity and high cost of nickel extraction from laterite ores. The energy cost of reduction pretreatment of laterite nickel alone in ammonia leaching could be as high as three times that of sulfide nickel roasting. In the recent years, however, with the sulfide nickel resource depleting and the increasing environmental restrictions over smelting processes which is the primary route of treating sulfide nickel, interest has shifted
towards the development of an effective and economic recovery process for nickel from laterite ores in recent years [4, 7, 8].

2.1.2 Awaruite

Awaruite is a greyish-white and magnetic mineral of naturally occurring iron nickel alloy (Ni$_3$Fe). It has been considered an alternative nickel resource to sulfide and laterite nickel [5]. In general, terrestrial awaruite is believed to have formed from ultramafic rocks such as peridotite which consist mainly of olivine, a magnesium iron silicate ((MgFe)$_2$SiO$_4$) containing up to 0.3% nickel. Peridotite is altered to serpentine upon exposure to weathering, a process referred to as serpentinization. More specifically, olivine in peridotite is decomposed by groundwater with carbon dioxide to form soluble magnesium, iron, and nickel, and colloidal silica. Goethite and hematite is then formed by rapid oxidation of iron in contact with air which precipitates near the surface of the deposit while the dissolved nickel and magnesium, and the colloidal silica, percolate downwards.

The first described discovery of awaruite was in 1885, along the Gorge River in Awarua Bay on the south island of New Zealand. Another well-known occurrence of awaruite is in Josephine County, Oregon, where the ore contains primarily iron-nickel nuggets < 2 cm in diameter in a serpentine matrix. The ores were analyzed to have ~77% nickel. In addition to the two occurrences described above, awaruite has been found worldwide. Awaruite also has rare occurrences in meteorites [5, 9].
In the last decade, there have been several new sites of awaruite discoveries in Canada, including the Decar project, the Dumont project and the KM26 project. Project KM26 was owned by OroAndes-Eastfield which was a collaborator in developing the ammonia-citrate-thiosulfate leaching technology of this study. Dumont project located in Quebec was the project with the largest scale of operation. It was owned by Royal Nickel Corporation. The Dumont Project reserve was estimated to have approximately 5.76 million tonnes of nickel, that is, approximately 0.27% nickel in about 1177 million tonnes of defined reserve. Dumont was expected to produce nickel at 42 ktpa as awaruite and sulfide concentrates [11]. The Decar project located in British Columbia owned by First Point Mineral Corporation was estimated to have approximately 200 million tonnes of nickel ore at 0.22% and would produce mainly awaruite concentrates with ~15% nickel concentration. In both projects, awaruite concentrates would be produced with alternating steps of grinding, magnetic separation and gravitational separation. The KM26 project was established at a previous gold deposit site based on the discovery of economical nickel ores in 2009. Based on geological survey and metallurgical tests of 11 drill cores in 2010 and 2011, awaruite was found to be one of the main economic nickel minerals, ranked after pentlandite and heazlewoodite. The KM26 project was found to have a
reserve size of approximately 300 million tonnes of 0.22% nickel, at a similar scale to the Decar project.

In absence of a readily available refining method, awaruite is currently only recovered and sold as concentrates at these projects. First Point Minerals proposed smelting the awaruite concentrates to produce ferronickel products for the stainless steel industry and had began assessment work. OroAndes Eastfield, on the other hand, began collaboration with UBC Hydrometallurgical Lab to develop a economically viable hydrometallurgical method of treating awaruite.

2.2 Ammonia leaching of nickel

2.2.1 Characteristics and principles

Ammonia leaching has been used widely for hydrometallurgical treatment of base metals including nickel and cobalt. Ammonia leaching of base metals could trace its origin to the early 20th century, pioneered by Malzac to recovery of copper and other base metals in oxygenated ammonia liquors [12]. Ammonia is an effective lixiviant which has the advantage of selectively attacking the target metals over gangue as compared to acid leaching which attacks a wide range of mineral types and therefore has limited application [4, 13]. Ammonia leaching also has advantages of low toxicity, low cost and ease of regeneration. In addition, the alkaline ammonia medium effectively rejects iron from the leach solution as iron hydroxides [14].

Ammonia leaching is applicable to sulfide nickel, oxide nickel and metallic nickel [14–16]. Sulfide and metallic nickel minerals can be directly oxidized and dissolved as ammine complexes in an alkali environment. Laterite nickel minerals such as limonite undergo a reductive process to produce metallic or sulfide nickel before nickel can be extracted by oxidative leaching in ammonia liquor [14, 17, 18].
Dissolution of nickel or nickel sulfide in ammonia solution can be represented by the following equations:

\[
Ni + (n - 2) \text{NH}_3 + 2 \text{NH}_4^+ + \frac{1}{2} O_2 \leftrightarrow \left[ \text{Ni}\left(\text{NH}_3\right)_n \right]^{2+} + \text{H}_2\text{O} \quad \text{Eq 1}
\]

\[
2 \text{NiS} + (2n - 2) \text{NH}_3 + 2 \text{NH}_4^+ + 2 O_2 \leftrightarrow 2 \left[ \text{Ni}\left(\text{NH}_3\right)_n \right]^{2+} + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \quad \text{Eq 2}
\]

In ammoniacal solutions, \(\text{NH}_3\) is in equilibrium with \(\text{NH}_4^+\), the relation of which is shown in Eq 3 and 4. \(\text{NH}_3\) dominates in solution under alkaline conditions; this can be deduced from Eq 5. \(\text{NH}_3\) stabilizes nickel in solution as ammines upon oxidation of nickel. Stability of nickel ammines at standard conditions is shown in the Pourbaix diagram of \(\text{Ni-NH}_3\text{-H}_2\text{O}\) in Figure 2 which indicates that the speciation of nickel ammines is dependent on pH, potential and the relative amount of ammonia to nickel as represented by ionic species activity.

\[
\text{NH}_4^+ \leftrightarrow (\text{NH}_3)_{aq} + H^+ \quad \text{Eq 3}
\]

\[
(\text{NH}_3)_{aq} + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad \text{Eq 4}
\]

The following relationship holds for the acid dissociation reaction of Eq 3:

\[
pH = pK_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \quad \text{where} \quad K_a = \frac{[H^+][\text{NH}_3]}{[\text{NH}_4^+]} , \quad pK_a(20^\circ\text{C}) = 9.25 \quad \text{Eq 5}
\]

In terms of the ammonium leaching kinetics of nickel, Shimakage \textit{et al.} showed that the diffusion of oxygen was rate controlling, thus the oxygen partial pressure which dictated oxygen dissolution [20] as well as temperature, stirring rate, particle surface area and \(\text{NH}_3/\text{NH}_4^+\) concentrations determined the nickel leaching rate [21]. Rotating disc studies of iron-nickel alloy tests showed that the initial rate of nickel dissolution was a function of disc rotation speed, oxygen concentration and temperature. In addition, nickel oxide and iron passivation occurred in aerated solutions which may be minimized in presence of thiosulfate. At temperatures from 20 –
110°C, the nickel leaching rate was mixed-controlled at 6 – 10 kJ/mol and shifting towards mass transfer controlled [14, 22].

![Eh-pH diagram of Ni-NH3-H2O at 25 °C, 1 atm, 1M NH3 with ionic species activity ranging 1–10⁻⁴ [19]](image)

**Figure 2**  
Eh-pH diagram of Ni-NH3-H2O at 25 °C, 1 atm, 1M NH3 with ionic species activity ranging 1–10⁻⁴ [19]

### 2.2.2 Sherritt Gordon and Caron processes

Development of ammonia leaching processes had quickly gained momentum since its initial successful application in base metal recovery. Among the many developments were the
Sherritt Gordon and Caron processes for nickel extraction. The Sherritt Gordon process was specifically designed for treating pentlandite concentrate at Sherritt’s Lynn Lake mine in northern Manitoba, which was a mixture of nickel and copper sulfides with cobalt and other value metals. The core technology of the Sherritt Gordon process was high pressure ammonia leaching which could be directly applied to nickel sulfide concentrates. It was the first successful commercial ammonia leaching of nickel sulfide concentrates. The Sherritt Gordon process was later used for nickel matte from smelting and nickel-containing alloy scraps as well. The process operated at 80 – 95°C under 850 kPa air pressure to produce nickel, cobalt and copper ammine complexes in sulfate solution with soluble thiosalts from the pentlandite concentrates. Reactive iron was oxidized and rejected to the leach residue as a hydrated oxide together with unreactive pyrite. The leach solution typically contained 50 – 60 g/L Ni, 1 – 2 g/L Co and 5 – 10 g/L Cu from which nickel powder was obtained by hydrogen reduction. Copper was precipitated as copper sulfide and sold to a copper smelter and the cobalt as sulfide was sold to cobalt refinery. Ammonia was regenerated as ammonium sulfate in the final stage [13].

The Caron process was patented in 1924 by M.H. Caron and was designed for treating laterite with low nickel grade. In a typical Caron process, laterite nickel ore was dried in a roaster at ~700°C and was reduced to produce nickel along with cobalt and iron in their metallic states, followed by cooling under non-oxidizing conditions and then oxidative leaching in an ammonium carbonate solution at atmospheric pressure, pH = 10 and 6M ammonia carbonate [16–18, 23, 24]. Cooling under an anaerobic environment was necessary to prevent passivation of ferronickel alloy [13, 18]. Nickel could then be recovered as high purity metal by hydrogen reduction or SX/EW to as high as 85% of the total nickel in the ore. Iron as an impurity was separated from solution as insoluble hydroxides to residue. However, due to the energy-intensive
reduction step and the prevailing ferronickel passivation during leaching, the Caron process suffers from marginal profitability and low cobalt recovery [13, 24]. Successful implementations of the Caron process include the commercial processes in Nicaro in Cuba, Marinduque in the Philippines and Queensland in Australia [4, 25, 26].

The Caron process as a pioneer atmospheric leaching technology could offer some insights in the development of the ammonia-citrate-thiosulfate, since they have similar leaching mechanisms and both target metallic nickel minerals. Studies of ammonia leaching of limonite and saprolite indicated optimum nickel extraction in the range of ~ 85% under careful control of pretreating conditions [17, 25]. This result may serve as a merit for evaluating the effectiveness of extraction in the development of the ammonia-citrate-thiosulfate technology targeting awaruite. In addition, effects of leach parameters have been extensively studied for improving Caron leaching, which may be relevant in understanding those of the current study. Some literature reported that excess ammonia beyond that of the stoichiometric ratio of stable nickel ammine complexes evidently favored nickel extraction, likely due to improved complexing ability of NH$_3$ at high concentrations, competition of nickel with magnesium for ammonia and notable ammonia loss to exhaust air [16–18, 27]. Nickel sulfides and oxides were shown to be leachable in ammonia solution but had much lower kinetics than that of ferronickel. Moreover, addition of Cu(II) and thiosulfate in ammonium carbonate solution were shown to have beneficial effects on iron-nickel alloy leaching [17, 18].

It has been widely accepted in the literature that the common iron precipitation in Caron processes was still a pending issue in ammonia leaching of iron-rich laterite, resulting in moderate nickel and low cobalt recovery [24, 28, 29]. Improvement in nickel and cobalt extraction rates in ammonium leaching of laterite was therefore in demand, hence the value of
this study. In addition, the theoretical advances in solvent extraction of nickel from ammoniacal liquor and readily available reagents provide a well-established ground for current study.

### 2.2.3 Ammonium-citrate-thiosulfate technology

In consideration of the absent nickel recovery method from awaruite ores, UBC patented a potentially economical hydrometallurgical route with atmospheric leaching in ammonia-citrate-thiosulfate lixiviant which renders nickel from awaruite and other non-silicate nickel amenable for further refining with readily available methods including solvent extraction [5]. This technology was developed by Dr. Adam Fischmann and Dr. David Dixon and it was envisioned for direct leaching of low-grade awaruite ores.

The leaching mechanism of this technology was based on the synergistic effect of the components of the lixiviant: It was established that ammonia-ammonium medium selectively dissolved nickel from awaruite without attacking the serpentinite matrix, the mechanism of which is demonstrated in the envisaged reaction:

\[
Ni_3Fe \, \, + \, \, 6NH_4^+ \, + \, 6NH_3 \, + \, \frac{9}{4} O_2 \, \rightarrow \, 3\left[Ni(NH_3)_4\right]^{2+} \, + \, Fe(OH)_3(s) \, + \, \frac{3}{2}H_2O \quad \text{Eq 6}
\]

Therefore the addition of excess citrate in the ammoniacal medium was necessary for keeping iron(III) partially soluble so as to alleviate iron precipitation over the awaruite particle surface in the presence of thiosulfate which acted as a catalyst for depassivating the awaruite surface in an alkaline environment [5].

Iron is thermodynamically unstable in alkaline ammoniacal solution under oxidizing conditions: it was reported soluble only as ferrous ammines under reducing conditions (\(< -0.2V\)) in alkaline ammoniacal solutions and would otherwise present as hydroxides or oxides based on the Fe-NH$_3$-H$_2$O Pourbaix diagram at 298 – 333K and 6M total ammonia [30]. In comparison,
nickel ammines were shown to have stability ranges extending beyond 0.4V at pH 7 – 11 as shown in Figure 2. Therefore iron precipitation tends to occur when nickel is leached in an oxidative ammoniacal solution. Citrate is a ferric chelator and alleviation of iron precipitation has been shown possible when citrate was in excess [31]. Ferric-citrate chemistry is complex since a wide range of ferric-citrate species with different equilibrium constants dominate at different combinations of pH, temperature, and total iron and citrate concentrations. As a result, it is difficult to map the exact ferric-citrate speciation. On the other hand, the citrate chelating mechanism of iron can be simply viewed as a competition between iron hydrolysis product and ferric citrate complexation. The solubility of ferric was found to be dictated by the iron-to-citrate molar ratio for which citrate was required to be in excess to favour iron dissolution [32]. A few other candidates of iron chelator including tartrate, oxalate, glycolate, lactate and malate were also tested in preliminary studies by Fischmann and citrate was the one with which the highest extraction rate of nickel was achieved [5].

Nickel and nickel-iron alloys have been found prone to surface passivation in ammonia solution. Studies of Ni-Fe alloys of various compositions have shown that nickel oxide and nickel-iron hydroxide passivation layers form upon exposure to alkaline as well as acidic solutions [33–35]. Thiosulfate in its reduced form of HS− and S reportedly played a catalytic role in facilitating nickel dissolution [35], likely by the formation of intermediate nickel sulfide species [36].

Preliminary shake flask tests conducted by Fischmann showed > 95% nickel extraction with synthetic awaruite and ~80% with representative industrial samples [5]. These promising results thus inspired further testing for commercialization of the ammonia-citrate-thiosulfate
technology. The details of sample mineralogy and leaching results are presented in sections 5.1.1 and 5.1.11.

2.3 Nickel refining: solvent extraction

2.3.1 Overview

The design of a nickel refining process was primarily based on two different types of nickel product with different requirements in purity: Class I and Class II. Since the primary application of nickel is as an alloying element, Class II nickel including metallized nickel oxide and ferrous nickel produced from smelting processes is used for the steel industry and other alloy productions which tolerate high levels of impurities (>15%). As for markets demanding high purity nickel metal, Class I nickel products including nickel cathodes and nickel powder are manufactured by integrated refining circuits employing methods such as solvent extraction (SX), ionic exchange, electrowinning, hydrogen reduction, cementation and the carbonyl process. In Class I nickel impurities such as antimony, arsenic, bismuth, cobalt, copper, and iron, which would have an adverse effect on the subsequent application, are reduced to << 1%. [13, 37]

SX is a well-sought after hydrometallurgical purification method of nickel due to its many advantages. Impurities can be effectively and efficiently removed in SX through relatively simple circuits of continuous and easily automated operation with minimum solids handling under atmospheric conditions [38]. Apart from being cost-effective, there are also readily available reagents and corresponding equipment for nickel extraction over a wide range of leach solution media. For chloride solutions resulting from HCl acid leaching of nickel intermediate products, tertiary amines are used to separate out cobalt from nickel. Organophosphoric, organophosphonic, organophosphinic and carboxylic acid reagents are used in sulfate solutions
produced mainly from high pressure acid leaching (HPAL) of nickel sulfides. For ammonium media from ammonia leaching processes, hydroxyoxime/phenolic oximes are used to extract nickel from the pregnant leach solution (PLS) from Caron process liquors [38, 39]. An example of ketoxime application is in QNI’s Yabulu refinery following a Caron leaching process. The ammoniacal carbonate PLS is fed to a SX circuit using LIX 87®QN to select out nickel after the PLS is treated to remove free ammonia and cobalt [40].

The primary objective of the nickel refining process design for the ammonia-citrate-thiosulfate leaching technology is to effectively extract nickel and remove iron from the PLS. The SX step is envisaged as part of the solution purification process as shown in the schematic flowsheet in Figure 3. In the solution purification process, an iron-free ammonium solution stripped of nickel is recycled to the leaching tank while the nickel-concentrated solution is fed to an electrowinning circuit to produce nickel cathode.

**Figure 3** Schematic Flowsheet of the ammonia-citrate-thiosulfate process
2.3.2 Properties of ACORGA K2000

ACORGA K2000 is a newly developed commercial reagent based on the ketoxime formulation and is manufactured by Cytec, a technical partner of this study. Ketoxime is a type of hydroxyoxime ideal for base metal extraction. Hydroxyoxime has excellent Ni/Fe selectivity while satisfactory cobalt removal is achievable with reductive stripping [41]. In view of the absence of literature on ACORGA K2000 application, much of the information such as hydroxyoxime properties and experimental design were drawn from the ample publications on Lix®84 in this study. Lix®84 and its variations are the ACORGA equivalent and they were manufactured by BASF, a competitor of Cytec.

Hydroxyoxime has a generic structure as shown in Figure 4. The phenolic oxime structure is characteristic of hydrogen bonding associating metal ions and additional oxime molecules. In terms of nickel complexation, a typical NiLₙ configuration is formed by bridging a nickel ion in the center of inter-connected oxime molecules and the structure is stabilized with hydrogen bonds [42].

![Generic Hydroxyoxime Chemical Structures](image)

**Figure 4**  Generic Hydroxyoxime Chemical Structures [43]

The extraction equilibrium by ACORGA K2000 at pH 7 – 10 may be described by Eq 7:

\[
Ni\left(\text{NH}_3\right)_{2n}^{2+} + nLH \rightarrow NiL_n + n\text{NH}_3 + n\text{NH}_4^+
\]

**Eq 7**
The equilibrium constant for Eq 7 is given as follows:

\[ K_{ex} = \frac{[\text{NiL}_n][\text{NH}_3]^n[\text{NH}_3^+]^n}{[\text{LH}]^n[\text{Ni(NH}_3)_2^{2+}]} \]

where \(2n = 1 - 5\) [14]. The reaction shown in Eq 7 reportedly has relatively slow extraction and stripping kinetics [44, 45].
3. Objective of the Present Study

The objective of this study was to evaluate and improve the performance of the ammonia-citrate-thiosulfate technology in order to prepare it for commercialization. The scope of this study included factorial leaching tests on an alternative source to that of Fischmann’s study, as well as batch leaching at high pulp density and with recycled liquor which were sought to represent industrial settings. Kinetic model fitting of the obtained data of the factorial leach tests were performed to gain understanding of the leaching kinetics. Preliminary tests on a SX reagent candidate ACORGA K2000 were also performed. Answers were sought for the following questions:

1) How do temperature, citrate concentration, total ammonia concentration, thiosulfate concentration, pH, particle size, mixing rate and pulp density affect nickel and iron leaching? Is consistent performance of leaching obtainable on an alternative source? In addition, is the nickel leaching result at room temperature (20°C) comparable to the optimized results in the preliminary study?

2) How does iron accumulation in a simulated leaching circuit using recycled leach liquor and with high pulp density affect nickel leaching?

3) What is a suitable kinetic model for describing the nickel leaching behavior obtained in this study?

4) Does the solvent extraction (SX) reagent ACORGA K2000 effectively extract nickel and separate it from iron? Can the extracted nickel be readily eluted?
4. Experimental

4.1 Leaching

(1) Sample characterization

The feedstock of all leach tests in this study came from drill cores of KM26, a nickel project located in northern BC owned by OroAndes-Eastfield. The presence of awaruite in the sample was proven by scanning the cross sections of unground bulky drill core samples with an energy dispersive X-ray analyzer [46]. The drill core samples supplied to this study were then crushed, ground in a rod mill and thoroughly mixed before being used for leaching. The material feed to the leach tests and the leach residue were dried, coned and quartered to obtain a representative sample for analysis: the particle size distribution was analyzed using a Malvern Mastersizer 2000 and the elemental composition was analyzed with acid digestion and Inductively-coupled plasma spectroscopy (ICP). The mineral phases in the processed feed material and selected residue samples were analyzed with quantitative powder X-ray diffraction analysis (QXRD) with the Rietveld method in addition to scanning electron microscope (SEM).

(2) Material

Granular ammonium sulfate ((NH₄)₂SO₄), sodium citrate (Na₃C₆H₅O₇·2H₂O) and sodium thiosulfate (Na₂O₃S₂·5H₂O) of ~99% purity produced by Fisher Scientific were used for preparing the leach solution which had a pH value of ~7 upon mixing. Thus pellets of sodium hydroxide (NaOH) with > 97% purity produced by Fisher Scientific were used for adjusting the leach solution pH to the set point pH values.
(3) Experimental set-ups and methods

In this study, the effect of parameters are assessed based on a factorial design by varying the parameter of interest while keeping all the other parameters at the same levels. The baseline conditions are listed as test M1 in Table 1 or otherwise specified. Leach tests were conducted in sealed, jacketed glass stirred-tank reactors with the setup as illustrated in Figure 5. Each 3L reactor tank was equipped with two 6-blade 45° pitched-blade axial impellers and three baffles. Applikon stirrer controller P140 was used to power the impeller to achieve complete solids suspension and gas-liquid mixing. Durable pH and Ag/AgCl ORP meters were installed at each reactor station and were connected to a laptop via an Applikon bio-controller (ADI 1030) to read and record signals for the duration of each leaching test using LabView. The analysis of pH and ORP data is shown in section A.2. Solution of ammonium sulfate, sodium citrate and sodium thiosulfate was adjusted to initial set point pH, heated and maintained at desired temperatures with a Haake DC10-P14 water bath circulating heated water through the reactor tank jacket. Continuous high purity oxygen was feed to the solution through a gas sparger and the mass flow rate was controlled by an Aalborg GFC17 gas mass flowmeter while excess oxygen exited the tank through a condenser to minimize water evaporation. The leaching experiment and its data recording commenced when temperature, pH and ORP values as well as oxygen gas flow stabilized, at which time the feed material was added to the reactor tank. Stabilization of readings was achievable within 30 min.
Solution samples were taken from the reactor tank at time intervals during leaching to test for nickel and iron extraction using Atomic absorption spectroscopy (AAS). Note that unlike iron extraction which was indicated as iron extracted per total iron in the feed material, nickel extraction was represented as per leachable nickel, which is the total non-silicate nickel determined by iodine–methanol assay (details in section 5.1.1). The kinetics of the leaching tests was compared by the extraction curves and in some cases the first hour initial rates. The leach data were also fitted to a kinetic model to facilitate the understanding of the leaching kinetics.
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<td>50</td>
<td>as is</td>
<td>~ 2.6 *</td>
<td>0.22 **</td>
<td>5</td>
<td>1200</td>
<td>32</td>
<td>150</td>
<td>10%</td>
</tr>
</tbody>
</table>
(1) Total ammonia is the sum of ammonia and ammonia species in solution, calculated from the initial ammonium sulfate concentration applied when making the leach solution.

(2) Format = RL(test#)-(cycle#) : recycled leaching with test# and cycle#, the detailed recycling procedure is explained in the Experimental section.

(3) The pH of the recycled leach solution is not adjusted and the measured values are shown and analyzed in the Result and Discussion section.

* The total ammonia concentration of a recycled leaching test is estimated based on the initial ammonia concentration (1.5M), minus the ammonia loss of <20% at each cycle, plus the compensation of 60% of initial ammonia concentration if applicable. Details are presented in the Experimental section.

** The citrate concentration of a recycled leaching test is calculated from the initial citrate concentration (0.1M) plus the compensation of 60% the initial compensation if applicable. Details are presented in the Experimental section.
4.2 Solvent extraction

(1) Test design

The selectivity of nickel from iron by ACORGA K2000 was tested at conditions shown in Table 2. The tests were all conducted at room temperature (20°C). The synthetic PLS of 1 g/L nickel(II), 0 – 0.8 g/L Fe (III), 0.1 – 0.5 M citrate and 1.5 – 6 M total ammonia was used to represent the composition of major constituents of the actual leach solution obtained from the optimal results of the leaching tests in section 5.1. Iron, citrate and ammonia concentrations were varied in the specified range to test their effects on nickel selectivity at pH 7–11 since the expected pH range of extraction was pH > 7 and soluble iron species became obsolete beyond pH = 11 [43]. The effect of other metal constituents is the subject of future study.

(2) Materials

The synthetic solution was made using ferric sulfate hydrate (Fe$_2$(SO$_4$)$_3$·xH$_2$O) with 97% purity, nickel sulfate hexahydrate (NiSO$_4$·6H$_2$O) with 99% purity, ammonia sulfate ((NH$_4$)$_2$SO$_4$) with 99% purity, and sodium citrate (Na$_3$(C$_6$H$_5$O$_7$)·2H$_2$O) with 99% purity. The loading capacity of ACORGA K2000 is 0.469 g/L nickel at 1 v/o as specified by the manufacturer Cytec. A minimum of 2.14 v/o of ACORGA K2000 was required to fully load the nickel from the synthetic PLS, thus 20 v/o was deemed sufficient and was chosen as the extractant concentration since it was easier to measure out high volumes of the extractant. Note that v/o is the ratio of volume of the extractant to the diluent as the concentration unit; in this case, ACORGA K2000 to acetone. ACORGA K2000 was dissolved in kerosene at 20 v/o and A/O = 1:1. Tests with 5 – 20 v/o were also conducted to confirm this setting as shown in section 5.2.1. The stripping solution was made of diluted sulfuric acid (H$_2$SO$_4$) with its pH adjusted by sodium hydroxide (NaOH) pellets of 97% purity.
(3) Experimental set-ups

In the extraction and the stripping procedure, the organic and aqueous solutions were mixed vigorously at 1000 rpm for 30 minutes using a magnetic stirrer followed by 30 min of settling in a separatory funnel for phase disengagement. The mixing/settling time was set based on the recommendation in Cytec’s ACORGA testing procedure [48]. For the extraction kinetics study, mixing and settling times of 20 and 10 minutes were also applied for comparison. Phase separation was conducted using a separatory funnel followed by purification of the aqueous phase using a centrifuge to eliminate the interference of residue organic droplets in the atomic absorption spectroscopy (AAS) analysis. The schematics of the phase separation setup are shown in Figure 6. The loaded organic solution was then mixed with the stripping solution followed by settling and phase separation.

![Schematics of the experimental setup for phase separation](image)

**Figure 6** Schematics of the experimental setup for phase separation [47]

The aqueous solution collected from the extraction and stripping processes were measured for equilibrium pH and analyzed for iron and nickel concentrations with AAS. The iron and nickel concentrations in the organic phase were calculated from the metal ion concentrations in the aqueous phases by mass balance.
### Table 2: Experimental conditions of solvent extraction tests

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Initial set pH (Aq)</th>
<th>Mixing/ Settling time</th>
<th>Extractant conc.</th>
<th>A/O</th>
<th>Total (^{(1)}) ammonia ([\text{NH}<em>3]</em>{\text{total}})</th>
<th>Citrate ([\text{C}_6\text{H}_5\text{O}_7^{3-}])</th>
<th>Iron ([\text{Fe}^{3+}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>X1</td>
<td>9</td>
<td>10</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X2</td>
<td>9</td>
<td>20</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X3</td>
<td>7</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X4</td>
<td>7.74</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X5</td>
<td>8.17</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X6</td>
<td>8.33</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X7</td>
<td>8.6</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X8</td>
<td>8.97</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X9</td>
<td>9</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X10</td>
<td>9.48</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X11</td>
<td>10</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X12</td>
<td>10.44</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X13</td>
<td>10.65</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X14</td>
<td>10.93</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X15</td>
<td>11</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X16</td>
<td>9</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>X17</td>
<td>9</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>X18</td>
<td>9</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>X19</td>
<td>9</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>X20</td>
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<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>X21</td>
<td>9</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>1</td>
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<tr>
<td>X22</td>
<td>9</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>0</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>X23</td>
<td>9</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>3</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>X24</td>
<td>9</td>
<td>30</td>
<td>20</td>
<td>1:1</td>
<td>6</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>X25</td>
<td>9</td>
<td>60</td>
<td>5</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X26</td>
<td>9</td>
<td>60</td>
<td>10</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X27</td>
<td>9</td>
<td>60</td>
<td>5</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X28</td>
<td>9</td>
<td>60</td>
<td>10</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X29</td>
<td>9</td>
<td>60</td>
<td>5</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>X30</td>
<td>9</td>
<td>60</td>
<td>10</td>
<td>1:1</td>
<td>1.5</td>
<td>0.2</td>
<td>0.8</td>
</tr>
</tbody>
</table>
5. Results and Discussion

5.1 Leaching

5.1.1 Mineralogy

As indicated in section 4.1 the feedstock of this study was analyzed for elemental composition by ICP. The composition of the major elements (> 0.1%) is presented in Table 3. While acid digestion method could digest all of the nickel content in the ore, only non-silicate nickel is amendable to ammonium leaching. The non-silicate nickel was dominated by awaruite and sulfide nickel as indicated in the KM26 feasibility study report [46]. Therefore nickel extractions of all the leach experiments in this study were presented as per total nickel leachable in the head sample. Leachable nickel in this study was analyzed by the means of iodine–methanol assay [49].

Fischmann applied QEM scan in addition to ICP to the feedstock of his study [5]. The feed material of Fischmann’s study came from First Point Minerals and is thus referred to as FP. Fischmann reported that no sulfide minerals were detected in his sample. The analytical result of the feedstocks from his study is compared with this study in Table 3. It is observed from Table 3 that Fischmann’s sample had greater magnesium and iron content and an absence of sulfide nickel as compared to the feedstock of this study.

The mineral phases of the feedstock KM26 were also studied with quantitative XRD. The composition of the phases was obtained and analyzed with the Rietveld method using the International Centre for Diffraction Database PDF-4 and Search-Match software by Bruker. Both the representative feed and the residue samples were identified as largely containing amorphous serpentine phase thus not possible to be directly characterized by QXRD. The amorphous serpentine phase was instead assumed a closest crystalline structure of antigorite and
its quantity estimated by its calculated diffraction contribution relative to other crystalline phases with an accuracy of 5 – 10%. It was observed that nickel phases were not detected in this case, most likely due to its insignificant presence (approx. 0.1 wt%). Therefore to the knowledge of the author of the current study, the awaruite phase of KM26 samples was only identifiable when analyzing the cross-section of bulky awaruite ores.

Table 3  Composition of major (>0.1%) elements of KM26 feedstock and Fischmann’s sample (ICP, by wt%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Total Nickel</th>
<th>Fe</th>
<th>Mg</th>
<th>Ca</th>
<th>Al</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Awaruite Nickel</td>
<td>Sulfide Nickel</td>
<td>Silicate Nickel</td>
<td>Fe</td>
<td>Mg</td>
<td>Ca</td>
</tr>
<tr>
<td>Composition (%)</td>
<td>KM 26</td>
<td>~0.10%</td>
<td>~0.11%</td>
<td>5.20 %</td>
<td>18.25 %</td>
<td>0.38 %</td>
</tr>
<tr>
<td></td>
<td>FP</td>
<td>~0.11%</td>
<td>0%</td>
<td>~0.12%</td>
<td>5.52 %</td>
<td>28.3%</td>
</tr>
</tbody>
</table>

Table 4  Results of quantitative XRD phase analysis of feedstock from project KM26 (wt. %)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Formula</th>
<th>Awaruite Ore Sample Head</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serpentine</td>
<td>Mg₃Si₂O₅(OH)₄</td>
<td>96.1</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>2.4</td>
</tr>
<tr>
<td>Ankerite/Dolomite</td>
<td>Ca(Fe²⁺,Mg,Mn)(CO₃)₂/CaMg(CO₃)₂</td>
<td>0.5</td>
</tr>
<tr>
<td>Magnesite</td>
<td>MgCO₃</td>
<td>0.3</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg₃Si₄O₁₀(OH)₂</td>
<td>0.3</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>0.4</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.0</td>
</tr>
</tbody>
</table>
5.1.2 The effect of temperature

Tests M1 – M5 were conducted to determine the effect of temperature on nickel extraction. The test conditions are listed in Table 1. Room-temperature leaching feasibility was assessed based on the comparison of the test at 20°C with other tests at various temperatures above 20°C. Considering the likely slow leaching kinetics, the 20°C test was run for 72 hrs to allow leaching to reach completion.

The extraction curves at various temperatures are compared in Figure 7 which shows that temperature had a significant effect on nickel extraction and extraction kinetics. The final nickel extraction and the extraction kinetics increased with increasing temperature. Figure 7 also reveals that nickel extraction quickly reached ~80% of completion within the first 10 hours when temperature is above 40°C. Leaching at room temperature (20°C) was more gradual and it was able to achieve a comparable level of extraction with the baseline test (50°C) after 60 hours. Therefore room temperature or near room temperature leaching is technically viable.
Figure 7   The effect of temperature on Ni and Fe extractions
5.1.3 The effect of citrate concentration

The effect of citrate concentration on feedstock from KM26 was studied via tests M9 – M11 and the baseline test M1; the results are shown in Figure 8. It is observed nickel final extraction and initial rate increased significantly at increasing citrate concentration. In addition, the iron extraction was increased simultaneously. The parallel performance of nickel and iron extraction with citrate concentration is believed to be a result of improved iron solubility with the addition of citrate which in turn depassivates the nickel mineral particle surface. In addition, based on the observed trend, the final nickel extraction could potentially be further improved with citrate concentration beyond the tested range.
Figure 8  The effect of citrate concentration on Ni and Fe extractions
5.1.4 The effect of citrate concentration at room temperature

It has been shown in Section 5.1.2 satisfactory nickel recovery which is approximately 2% lower than that of baseline test can be obtained at room temperature leaching. As an effort to improve the result, an additional room temperature test with higher citrate concentration (0.5M) was conducted as test M6 since citrate concentration was shown to have a dominant effect on nickel extraction and favours nickel extraction at higher concentrations in Section 5.1.3. The conditions of M6 are shown in Table 1. The comparison of M6 with baseline room temperature test M5 is shown in Figure 9 which shows that although increasing citrate concentration led to improved iron solubility at room temperature; it had almost no effect on nickel leaching kinetics or the final nickel extraction. Reasons for the ineffectiveness of additional citrate in this test are unclear.
Figure 9 The effect of increasing citrate concentration on Ni and Fe extractions at 20°C.
5.1.5 The effect of the total ammonia concentration

Tests M7 and M8 were conducted and compared to the baseline test M1 to show the effect of the total ammonia concentration on nickel extraction in Figure 10. The test conditions of M7 and M8 are shown in Table 1. Figure 10 shows that increasing total ammonia concentration clearly benefited the extent of nickel extraction. Therefore, nickel extraction could be improved by applying more aggressive ammonia conditions due to improved complexing ability, which is supported by the increase of stability area of nickel ammines in the Pourbaix diagram of the Ni-NH$_3$-H$_2$O system at decreasing ionic activity. However, the effect of total ammonia concentration on the initial rate of nickel and iron extraction was inconclusive from Figure 10.
Figure 10  The effect of total ammonia concentration on Ni and Fe extractions
5.1.6 The effect of thiosulfate concentration

Test M12 – 14 were conducted and compared to the baseline test M1 to investigate the effect of thiosulfate concentration. The results are shown in Figure 11.

As shown in Figure 11 the extraction curves of the tests within the comparison groups almost overlap with each other, indicating that within the tested range of concentrations thiosulfate has little or no detectable effect on nickel extraction. Since it had been shown that thiosulfate was mandatory for nickel depassivation in ammonia solution, it is believed that thiosulfate reacted with Ni to form nickel sulfide as an intermediate species which then oxidized. However, present results seem to indicate that this mechanism was not as important as initially thought [5].
Figure 11  The effect of thiosulfate concentration on Ni and Fe extractions
5.1.7 The effect of pH

The effect of pH on nickel and iron extraction were studied via tests M15 and M16 in which pH set points were set at 20°C and then the leach solution was heated to the test temperature before leaching commenced. The pH of each test was monitored throughout the leach process. Test conditions of M15 and M16 are shown in Table 1 and their results were compared with the baseline test M1 in Figure 12.

The equilibrium position of the \([\text{NH}_3]/[\text{NH}_4^+]\) ratio is affected by pH of the leach solution as indicated in Eq 5, section 2.2 and \([\text{NH}_3]\) increases at increasing pH. In addition, the solubility of Fe(III) is known to decrease at increasing pH. The \([\text{NH}_3]/[\text{NH}_4^+]\) ratio was also under the influence of temperature since both \(K_a\) and pH were temperature dependent as indicated in Eq 5.

As shown in Figure 12, while lower pH was shown to have an advantage over extraction kinetics of nickel, the final extractions over pH 7 – 10 had little difference. The Fe extraction trend, on the other hand, is much more obvious: Fe level and Fe leaching rate decreases with increasing pH. Thus it is believed that the suppressed initial rate at increasing pH was a result of decreased iron solubility. Therefore pH had limited influence over nickel extraction in the range pH 7 – 10. Based on this conclusion, leaching at near neutral pH is likely favourable in production considering the cost of reagents to adjust pH into the alkaline range.
Figure 12  The effect of pH on Ni and Fe extractions
5.1.8 The effect of particle size

The effect of particle size on nickel extraction was investigated through tests M1, M17 and M18 and the test conditions are shown in Table 1. Fischmann demonstrated that longer grinding time lead to improved nickel extraction and iron extraction provided that citrate level was sufficient for complexing iron [5]. However, no discrete particle size data were provided in his work. Therefore a suitable particle size distribution (PSD) for the leach tests of this report was determined based on the size of feed and gangue materials containing nickel sulfide and awaruite from some operating Canadian awaruite ore projects (see also section 2.1.2). As shown in Table 5, 70 – 150μm was summarized as a plausible P<sub>80</sub> range based these projects.

**Table 5** Summary of particle size in some operating awaruite projects in Canada

<table>
<thead>
<tr>
<th>Source</th>
<th>P&lt;sub&gt;80&lt;/sub&gt; after processing</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>KM 26</td>
<td>P&lt;sub&gt;80&lt;/sub&gt; = 74 μm</td>
<td>[46]</td>
</tr>
<tr>
<td>Dumont project</td>
<td>P&lt;sub&gt;80&lt;/sub&gt; = 250 μm</td>
<td>[11, 50]</td>
</tr>
<tr>
<td>Decar project</td>
<td>P&lt;sub&gt;80&lt;/sub&gt; = 75 – 600 μm</td>
<td>[51]</td>
</tr>
</tbody>
</table>

Therefore, the feed material of this study was ground with a rod mill to a P<sub>80</sub> of 150μm as the baseline PSD and was further ground to P<sub>80</sub> values of 95μm and 80μm for variable tests. The result of the effect of particle size on nickel leaching is shown in Figure 13. As shown in Figure 13, further grinding from 150μm yielded no further improvement in nickel or iron dissolution. This result was believed to be an indication that sufficient liberation of awaruite or nickel sulfide particles were achieved at 150μm.
Figure 13  The effect of particle size on Ni and Fe extractions
5.1.9 The effect of mixing rate

The effect of mixing rate on nickel and iron extraction was investigated via tests M19 and M20 and the baseline test M1. The highest mixing rate tested was 1600 rpm, which was at the capacity limit of the stirrer unit used in this experiment. The test conditions are shown in Table 1 and the results are shown in Figure 14. As observed in Figure 14, raising the mixing rate from 800 rpm to 1600 rpm had no effects on the final extraction and the leaching rate of nickel or iron. This result may be an indication that 1200 rpm was sufficient for complete solids suspension and gas-liquid mixing beyond which no substantial changes in mass transport kinetics occurred.
Figure 14  The effect of mixing rate on Ni and Fe extractions
5.1.10 The effect of pulp density

Due to limited sample amount and the difficulty of solid-liquid separation at high pulp densities, the leaching tests were run at 10% pulp density which is considerably low for an industrial process. As has been shown in Section 5.1.3, nickel extraction was directly related to iron solubility which was dictated by citrate concentration or essentially iron to citrate molar ratio. Therefore it is necessary to investigate the complexing capacity of citrate for iron at high (>10%) pulp density or essentially high iron levels.

At the same test conditions as M1 including citrate level, tests M21 – 24 were conducted with increasing pulp density up to 30% in comparison with the baseline test M1 as shown in Figure 15. The mixing rates of M21 – 24 were also adjusted to off-bottom suspension speed \( N_{js} \) which is a widely accepted criterion in the industry for minimum rate of effective mixing. \( N_{js} \) was calculated with the Zwietering equation as 1600 rpm. The detailed calculation steps are shown in Section A.1.

It is observed from Figure 15 that increasing the pulp density had an immense adverse effect on the final extraction and the kinetics of nickel and iron leaching. As shown in Figure 15, the nickel and iron extractions at 30% pulp density dropped by ~50% compared to that of 10% pulp density. It was also noticed that while nickel concentration in the leach solution continued to rise during leaching, the iron concentration seems to plateau at 0.12 g/L regardless of pulp density which was believed to be an indication of iron saturation in the leach solution.
Figure 15  The effect of pulp density on Ni and Fe extractions
Recognizing the necessity of additional citrate at high pulp densities, tests M25 and M26 were conducted to investigate the requirement of citrate. Tests M25 and M26 were essentially M22 and M24 with citrate compensations; the citrate level was raised proportionally with increasing pulp density from that of the baseline test M1 with 10% pulp density (Eq 8).

\[
[citrate]_{\text{compensation test}} = [citrate]_{\text{Test M1}} \times \frac{\text{feed solids mass of compensation test (g)}}{\text{feed solids mass of test M1 (g)}}
\]  \hspace{1cm} \text{Eq 8}

The test conditions of tests M25 and M26 are shown in Table 1 and the results of tests M1, M22, M24, M25 and M26 are compared for final extractions and first-hour leaching rates in Figure 16.
Figure 16  The effect of proportional citrate compensation at high pulp densities
Figure 16 demonstrates that nickel extraction was improved by citrate compensation. However, although the iron extraction was fully restored to baseline levels, nickel extraction still degraded noticeably. In addition, citrate levels in M25 and M26 were believed to be in excess — Spiro et al. reported that the iron (III) precipitates in ammonia solution at pH 7–10.8 became non-detectable as the citrate-to-iron molar ratio went over 20:1 [31]. The citrate-to-iron molar ratio in tests M22, M24, M25 and M26 exceeded this level as shown in Table 6. Therefore it seems that citrate deficiency was not the only factor contributing to the degradation in nickel extraction at high pulp densities. Ammonia deficiency was suspected to be the cause of the ineffectiveness of citrate compensation and the test results of this hypothesis are shown in Section 5.1.12.

Table 6  Citrate to iron concentration molar ratio of test M22, M24, M25 and M26

<table>
<thead>
<tr>
<th>Citrate : Fe Molar Ratio</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>20% pulp density</td>
<td>48:1</td>
</tr>
<tr>
<td>20% pulp density + citrate</td>
<td>72:1</td>
</tr>
<tr>
<td>30% pulp density</td>
<td>46:1</td>
</tr>
<tr>
<td>30% pulp density + citrate</td>
<td>86:1</td>
</tr>
</tbody>
</table>

5.1.11 Comparison of the effects of leach parameters on an alternative source

The effects of leach parameters on KM26 samples as an alternative source to Fischmann’s representative industrial sample are compared in Figure 17, for which the data were extracted from section 5.1.2 – 5.1.8 of this thesis and Fig 17 of Fischmann’s report [5]. The range of variable values and baseline test conditions were the same for both studies except for particle size: temperature (20 – 80°C), total ammonia (1.5 – 3.0 M), citrate (0 – 250 mM),
thiosulfate (0 – 50 mM), pH (7 – 10) and pulp density (~10%); the baseline test (50°C, 1.5M total ammonia, 0.1M citrate, 5mM thiosulfate, pH 9, 10% pulp density. The same experimental setup was used in both studies. Mixing rate and pulp density were constants in Fischmann’s study, thus the tests of these two parameters were not included in the comparison.

Notice that the KM26 final nickel extractions are shown as that of the total nickel instead of leachable nickel, so that they are on the same scale in comparison of Fischmann’s results. In addition, in absence of the particle size distribution (PSD) data of Fischmann’s sample, the PSD of this study was estimated based on known awaruite projects and with which sufficient liberation was achieved (see Section 5.1.8).
Based on Figure 17, the nickel extraction of KM26 at the baseline condition was at ~10% per total nickel greater than that of Fischmann’s study. This result indicated that the lixiviants were effective on KM26 as an alternative awaruite resource. While temperature was shown to be the dominant parameter in Fischmann’s results, citrate concentration had the most significant effect on KM26 samples assessed by the sensitivity in nickel extraction to citrate concentration increase. The results from both studies were otherwise very similar.
5.1.12 Aggressive ammonia and citrate leaching

As shown in Section 5.1.10, citrate compensation at high pulp densities did not yield satisfactory results – nickel extraction at 30% pulp density failed to be restored to the level at 10% pulp density despite the citrate compensation and the resulting improved iron extraction as compared to the baseline test (Figure 16). Moreover, in the Caron process the optimized total ammonia level was ~6M which seems to be an indication of high ammonia requirements in the leaching of nickel and nickel-iron alloys. Therefore, it was suspected that ammonia deficiency could have been the cause of the low extraction rate. To prove this hypothesis, aggressive citrate and ammonia concentrations greater than the concentration applied in Sections 5.1.3 and 5.1.5 were used. This is to verify if satisfactory nickel extraction is obtainable at high pulp density and consequently determine if the technology under investigation is technically plausible and economically feasible to be further pursued.

In the aggressive citrate and ammonia leaching study, test M1 and tests M26–29 were used and the test conditions are shown in Table 1. M1 was selected as the baseline test as the standard of satisfactory nickel extraction for this study. M26 was selected as the blank test, which showed unsatisfactory nickel extraction in spite of citrate compensation. M27 with only aggressive ammonia level and M29 with both aggressive ammonia and citrate levels at otherwise similar conditions as M26 were conducted to see if ammonia deficiency was indeed the problem. In addition, M28 with the same conditions as M27 but at baseline test (M1) citrate level was also performed to test for the effect of only applying aggressive ammonia conditions. The results are presented in Figure 18.
Figure 18  The effect of aggressive ammonia and citrate compensations on Ni and Fe extractions

It is clearly shown in Figure 18 that only at simultaneous citrate and ammonia compensation at an aggressive amount was nickel extraction restored close to the baseline level.
at 30% pulp density. In addition, nickel extraction rate was closely related to iron extraction level which once again indicated that improvement in nickel extraction was based on favorable Fe dissolution.

5.1.13 Recycled leaching

In industrial processes, leach solution runs through leaching cycles so that the concentrations of the pay metals reach economical levels before entering the recovery step. At the same time, the concentrations of other constituents of the leach solution also rise. Therefore iron accumulation becomes a potential problem for the commercialization of this leaching technology since it could cause citrate deficiency and consequently decrease the nickel extraction rate. In order to test the performance of repeated leaching, tests RL1 to RL3 were conducted with conditions specified in Table 1. RL1 to RL3 are three groups of recycled leaching tests and each group ran through three consecutive cycles of batch leaching. The test cycles were thus labeled RLX-a, RLX-b, RLX-c. Leach solution was recycled while the residue was removed and a fresh batch of feed material was added at each cycle to maintain the same pulp density. RL1 was first conducted with all cycles commenced at baseline conditions as in M1. Nickel extraction decreased at each cycle along with iron extraction which is evident from Figure 19. Therefore citrate was compensated in the second and third cycles so that the total citrate concentration increased 60% at each cycle in RL2. This increase in citrate concentration was arbitrarily assigned for a preliminary quantitative assessment. It was also measured from RL1 that there was a <20% ammonia loss at each cycle. The leach solution samples were sent to a local analytical laboratory (SGS) for analysis and ammonia loss as the difference of the total ammonia
was measured using a Skalar Segmented Flow Autoanalyzer. Similar values of ammonia loss were reported in Zuniga’s study on the ammonia leaching of limonite [24]. Therefore ammonia compensation via a 60% increase of the total ammonia concentration at each cycle was also made in addition to citrate compensation in RL3. A summary of the final nickel and iron extractions of RL1 to RL3 are shown in Figure 19.

Figure 19 shows as much as 20% decrease in the extraction of the total leachable nickel despite citrate and ammonia compensations in RL2 and RL3 after each leach cycle. However, it was also observed that the decrease was significantly retarded for iron and moderately retarded for nickel with the compensation of citrate and ammonia. The degradation in extraction rate was also evidently slower with the compensation of ammonia in RL3 as compared to RL2. Therefore the results of RL1 to RL3 showed that the accumulation in iron must be countered with an increase in citrate concentration as well as ammonia concentration accordingly to prevent iron precipitation which consequently hinders nickel leaching [5]. This finding coincided with that in aggressive ammonia and citrate leaching tests as shown in Section 5.1.12. It was necessary to maintain sufficiently high citrate-to-iron molar ratios in solution to prevent iron precipitation. The role of ammonia compensation was unclear but tests RL1 to RL3 clearly showed its importance in facilitating nickel extraction.
Figure 19  
Ni and Fe extractions in recycled leaching tests with various reagent compensations (blank test = no compensations)
5.1.14 pH and ORP data analysis

The pH and potential of leach solution (ORP in mV Ag/AgCl) of leaching tests M1–20 and RL1 to RL2 were analyzed to facilitate the understanding of the effects of leaching parameters on nickel extraction. In summary, the pH and ORP values are unaffected by other leaching parameters except temperature. This response is believed to be a result of both the change in pH meter reference solution [59] and the equilibrium position of hydrogen concentration in water dissociation to form hydrogen and oxygen under the influence of the strong sodium hydroxide. They were also stable over the course of each leaching test with no correlation to the leaching curve. The decrease in pH over the cycles in recycled leaching was likely an indication of the deprotonation of citrate complexing with Fe(III) [32]. For reference the complete analysis is presented in Section A.2.

5.1.15 Modeling of leaching kinetics

In order to facilitate the understanding of the leaching kinetics of nickel, the conversion data obtained in tests M1–29 were fitted for a general particle leaching model as shown in Eq 9 for which the solution was given as Eq 10. This model was developed by Dixon et al. from previously established intrinsic models. It was based on the assumptions of discrete spherical ore particles, unsteady-state diffusion and rate-controlling reagents and is therefore suitable for describing the leaching reactions in this study with which citrate concentration has a prominent effect on nickel extraction as shown in Section 5.1.3. \( \tau \) is known as the time scale constant at specific temperature and reagent concentrations which represents the time for complete leaching of a particle of the mean size calculated from the PSD of sample. The model also incorporates the integration of particle size distribution in the exponent \( \varphi \) so that \( 1 - X \) represents the total
conversion of nickel. Dixon has demonstrated that $\varphi$ is applicable to a wide range of particle size distributions [52].

\[
\frac{dX}{dt} = \frac{(1 - X)^\varphi}{\tau} \hspace{2cm} \text{Eq 9}
\]

\[
X = \begin{cases} 
1 - \left(1 - \frac{(1 - \varphi)\tau}{\varphi}(1 - \varphi)^{1 - \varphi}\right) & \text{at } \varphi \neq 1 \\
1 - \exp\left(-\frac{t}{\tau}\right) & \text{at } \varphi = 1
\end{cases} \hspace{2cm} \text{Eq 10}
\]

The model fitting was achieved by the means changing $\tau$ values specific to each test and the universal $\varphi$ value with EXCEL solver to minimize the accumulated difference $\Sigma(P_i - O_i)^2$ between the model evaluated nickel conversion ($P_i$) and the corresponding experimental data ($O_i$). The best-fit model $\tau$ and $\varphi$ values are shown in Table 7 and the conversion curves plotted with these parameters are shown in comparison with the experimental data in Figure 20 – 26 to illustrate the fit.
Table 7  Summary of fitted $\tau$, $\phi$ and $\Sigma(P_i - O_i)^2$ values

(Baseline: 50°C, 1.5M total ammonia, 0.1 M total citrate, 5 mM thiosulfate, 1200 rpm, pH 9)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Test #</th>
<th>$\tau$</th>
<th>$\phi$</th>
<th>$\Sigma(P_i - O_i)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>M1</td>
<td>44.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 °C</td>
<td>M5</td>
<td>262.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>M2</td>
<td>46.15</td>
<td></td>
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<tr>
<td>60 °C</td>
<td>M3</td>
<td>17.19</td>
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<td></td>
</tr>
<tr>
<td>70 °C</td>
<td>M4</td>
<td>9.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>total Ammonia concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 M</td>
<td>M7</td>
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<tr>
<td>3 M</td>
<td>M8</td>
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<td>total citrate concentration</td>
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<tr>
<td>0M</td>
<td>M9</td>
<td></td>
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<td></td>
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<tr>
<td>0.05 M</td>
<td>M10</td>
<td></td>
<td></td>
<td>4.73</td>
</tr>
<tr>
<td>0.2 M</td>
<td>M11</td>
<td></td>
<td></td>
<td>1.96</td>
</tr>
<tr>
<td>mixing rate</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>800 rpm</td>
<td>M19</td>
<td></td>
<td></td>
<td>47.92</td>
</tr>
<tr>
<td>1600 rpm</td>
<td>M20</td>
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<td>44.37</td>
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<tr>
<td>thiosulfate concentration</td>
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</tr>
<tr>
<td>0mM</td>
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<td></td>
<td></td>
<td>60.76</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>M15</td>
<td></td>
<td></td>
<td>15.91</td>
</tr>
<tr>
<td>10</td>
<td>M16</td>
<td></td>
<td></td>
<td>16.43</td>
</tr>
<tr>
<td>PSD</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80µm</td>
<td>M17</td>
<td></td>
<td></td>
<td>67.65</td>
</tr>
<tr>
<td>95µm</td>
<td>M18</td>
<td></td>
<td></td>
<td>77.47</td>
</tr>
</tbody>
</table>
Figure 20  Model fitting for nickel extraction curves at various temperatures (tests M1–5)

Figure 21  Model fitting for nickel extraction curves at various total ammonia concentrations (tests M1, M7–8)
Figure 22  Model fitting for nickel extraction curves at various citrate concentrations  
(tests M1, M9–11)

Figure 23  Model fitting for nickel extraction curves at various thiosulfate concentrations (tests M1, M12–14)
Figure 24  Model fitting for nickel extraction curves at various pH (tests M1, M15–16)

Figure 25  Model fitting for nickel extraction curves at various PSD (tests M1, M17–18)
The activation energy of the nickel leaching reactions of Eq 2 and 6 as an average was estimated based on the Arrhenius equation shown in Eq 12. Since the reaction rate constant $k$ is inversely proportional to $\tau$ ($k \propto 1/\tau$). The activation energy $E$ was calculated using Eq 11 to be 54.4 kJ/mol which indicates a surface reaction control in the nickel leaching kinetics. The plot of Eq 11 to obtain the activation energy is show in Figure 27. This result seems to be in contradiction of the assumption that citrate was a rate controlling reagent. This mismatch in the assumption and result could be due to taking the activation energy as an average of the involved nickel reactions including awaruite and nickel sulfides. Therefore the leaching data of individual minerals could be isolated before applying the kinetic model to improve accuracy. However, this
is impossible without exact awaruite phase identification and quantification which is yet not achievable.

\[
\frac{d(Ln \frac{1}{T})}{d \left( \frac{1}{T} \right)} = -\frac{E}{R} \quad \text{Eq 11}
\]

\[
k = A \exp\left( -\frac{E}{RT} \right) \quad \text{Eq 12}
\]

![Arrhenius plot to determine the activation energy](image)

Figure 27  Arrhenius plot to determine the activation energy

<table>
<thead>
<tr>
<th>E/R/1000</th>
<th>E/R</th>
<th>R</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.54</td>
<td>6540</td>
<td>8.31</td>
<td>54.38</td>
</tr>
</tbody>
</table>
5.2 Solvent extraction

5.2.1 Extraction

Pre-tests of the preliminary SX study were conducted with synthetic solution of 1 g/L nickel, 0.8 g/L iron, 0.2 M citrate and 1.5 M total ammonia at 20 v/o, A:O = 1, 30 min mixing/settling time and initial set pH = 7, 9 and 11. From the pre-tests, 99.8% nickel recovery was obtained at pH = 9. Test conditions of all SX preliminary tests are shown in Table 2.

Based on the above findings, the selectivity graph was refined with tests at additional pH values. As indicated in Section 4.2, 20 v/o and 30 min mixing/settling time were chosen based on manufacturer specified properties. These two parameters were varied to study their effects. At pH = 9, A:O = 1 with 30 min mixing/settling time, extraction of nickel at 5, 10 and 20 v/o corresponding to tests X25, X26 and X2 were obtained as 95.6%, 98.3% and 99.8% respectively as shown in Figure 28. This result indicated that 5 v/o was sufficient to extract nickel from the synthetic solution.

![Figure 28](image)

**Figure 28** The Effect of extractant concentration on nickel extraction
To demonstrate SX extraction kinetics of ACORGA K2000, tests with 10 – 30 min mixing/settling time were conducted as tests X1, X2 and X9. As observed in Figure 29, a minimum of 30 min was required for the nickel extraction reaction to reach equilibrium, which was believed to be the evidence for the slow extraction kinetics of ACORGA K2000. Although ACORGA K2000 application has been seldom reported, many papers indicate that oximes have slow kinetics of nickel extraction [53]. The effects of pH, salt concentrations, and iron concentration on nickel extraction were studied at A:O = 1:1, 20 v/o, 30 min mixing/settling time and are shown in the following sections.

![Figure 29](image)

**Figure 29**  Effect of mixing/settling time on nickel extraction

### 5.2.1.1 Selectivity of nickel and iron

Based on the preliminary selectivity tests the varied pH was set at ~0.5 increments for a complete selectivity graph of nickel and iron via tests X3–15. The obtained nickel and iron
extraction data at various initial pH values and the measured equilibrium pH are shown in Figure 30.

**Figure 30** Selectivity graph of ACORGA K2000 with nickel and iron

Figure 30 shows that the extraction of nickel increased at rising pH due to deprotonation of the oxime molecule (Eq 7). It also shows 99.8% nickel recovery with <1.5% iron co-extraction at pH 9 ± 0.5 based on which the separation factor was calculated as 1570, indicating that complete nickel separation from iron is possible with ACORGA K2000.

5.2.1.2 The effect of iron precipitation

Fe (III) is the predominant species in the leach solution and it has low solubility at pH > 7. A speciation diagram of iron in leach solution was not obtainable due to elusive iron citrate...
speciation data. In order to study the possible iron precipitation and its effect on nickel extraction, synthetic PLS was adjusted from pH 7 to 11 to assess precipitation formation and nickel and iron loss. It revealed that the solution color gradually changed from blue to green over the range of pH 7−10, and beyond pH 10 the solution quickly turned brown and darkened until observable brown precipitate appeared at ~pH 11. Precipitation of dark brown iron hydroxide likely induced the color change, the iron loss was ~5% at pH <10.6 and it increased to ~25% at pH 11 as indicated in Figure 31. Figure 31 also shows that nickel loss was < 0.5%.

![Figure 31](source)

**Figure 31  Synthetic PLS at pH 7−11 and the corresponding nickel and iron loss**

In addition, since iron showed some affinity to oxime ligand over the nickel extraction pH range as indicated in Figure 30, the effect of iron concentration was studied via tests X9 and X19–21. The nickel extraction obtained from these results was consistently 99.8% which showed no effect from iron concentration at the given extractant concentration.

**5.2.1.3 The effects of salts**

The effect of citrate and total ammonia concentration on nickel extraction was studied via tests X16–19 and X22–24 with conditions specified in Table 2. The iron concentration was
maintained at zero to exclude its effect. Results showed consistent 99.8% extraction of nickel. Therefore the change in citrate and ammonia concentrations had no effects on nickel extraction.

5.2.2 Stripping

The loaded organic phases from the extraction tests at 5, 10 and 20 v/o were stripped of nickel using sulfuric acid solution at pH 0–7. As shown in Figure 32, nickel could be readily stripped at pH < 1 from 5 v/o loaded organic solution and stripping became increasingly more difficult at increasing extractant concentration.

![Diagram](image)

Figure 32  %nickel stripped from loaded ACORGA K2000 solutions at
(a) 20v/o  (b) 10v/o   (c) 5v/o   (d) comparison of Ni recovery at 5 – 20v/o, pH = 1
6. Conclusions

This study reported findings of batch leaching tests of a new ammonia-citrate-thiosulfate nickel leaching technology on an alternative source (awaruite) and with laboratory simulation of industrial settings in order to prepare for the pilot test of this technology. Results of preliminary SX tests with ACORGA K2000 as an ideal reagent candidate were also presented. ACORGA K2000 was formulated from hydroxyoxime which has been proven effective in separating base metals including copper and nickel from ammonium media.

Leaching tests were conducted on an alternative source of awaruite ore (from Project KM26) in stirred reactors with controlled parameters including temperature, citrate concentration, total ammonia concentration, thiosulfate concentration, pH, particle size, mixing rate and pulp density. The test results indicated an optimum nickel extraction of 85% per leachable nickel. Besides temperature, citrate played the most important role which is believed to be a result of the mechanism of citrate facilitated iron dissolution which was evident through the close correlation of nickel to iron extraction at the increase of citrate concentration shown in Section 5.1.3, Section 5.1.12 and Section 5.1.13. More specifically, nickel extraction rate was improved as more mineral particle surface was alleviated from ferric hydroxides with citrate stabilizing more ferric anions in solution as ferric hydroxides. In addition, room temperature leaching was considered a possible option since approximately 70% final nickel extraction was obtained.

However, with the accumulation of iron in leach solution in batch leaching tests with recycled liquor as well as tests at high pulp density (>10%), the demand for citrate and ammonia increased significantly in order to retain nickel extraction at ~80%. Increase of citrate and ammonia concentration proportional to the increase in feed solids mass was not sufficient. A comparison test conducted at 30% pulp density showed that at approximately three times the
feed material input from the 10% pulp density baseline test, similar nickel extraction with <5% difference was only obtainable at simultaneous increase to four times the original ammonia concentration and six times the original citrate concentration. This finding revealed that iron accumulation is an obstacle in the commercialization of the new ammonium-citrate-thiosulfate leaching technology, a potentially effective and economical process.

The activation energy of the nickel leaching reaction was estimated to be 54.4 kJ/mol based on experimental data obtained from test M1 – 29 utilizing a kinetic model developed by Dixon et al. [52]. This result indicated surface reaction control in the leaching reactions which seems to counter the assumption of citrate as a rate-controlling reagent. This mismatch in the assumption and result could be due to taking the activation energy as an average of the involved nickel reactions including awaruite and nickel sulfides. Therefore the leaching data of individual minerals could be isolated before applying the kinetic model to improve accuracy. However, this is impossible without exact awaruite phase identification and quantification which is yet achievable.

In solvent extraction tests with ACORGA K2000 on synthetic PLS solution containing 1 g/L Nickel (II), 0 – 0.8 g/L Fe (III), 0.1 – 0.5 M citrate and 1.5 – 6 M total ammonia to simulate the leaching solution, results showed complete separation of nickel from iron at 5 v/o reagent solution concentration. Nickel can also be readily eluted with diluted sulfuric acid at pH of about 1. The extraction was found to be relatively slow, since 30 min mixing and settling time was required to reach equilibrium.
7. Recommendations for Future Work

Based on this study, future work based on the following topics is recommended:

(1) Development of an iron removal method from the leaching circuit without sacrificing the nickel level

(2) Economical recycling of reagents, especially ammonia and citrate

(3) SX tests with ACORGA K2000 with real solution at economical nickel levels as well as the construction of an isotherm of extraction to provide the basis for SX process design and flow sheet optimization

(4) Pilot leaching test of the ammonium-citrate-thiosulfate technology
Bibliography


no. 973. 2005, pp. 1–12.


Appendix A

A.1 Off-bottom suspension mixing speed calculation

Off-bottom suspension point is the minimum mixing power required for suspending all solid particles off the bottom of agitation. At this point, maximum surface area of solid is exposed for solid-liquid mass transport and chemical reaction. Beyond this point, the effect of mixing power on solid-liquid mass transport quickly diminishes until complete uniformity of particle concentration and size distribution are attained and increasing mixing power no longer yields substantial change in the mass transport coefficient as demonstrated in Figure 33. Thus the off-bottom point has been widely used in the industry as the criterion of the minimum mixing rate requirement [54–56] and has been most commonly described by the Zwietering equation as a function of pulp density, tank geometry, particle size and geometry.

![Graph showing effect of agitation on relative solid-liquid mass transport coefficient](image)

**Figure 33**  The effect of agitation on relative solid-liquid mass transport coefficient [56]

Given the schematics of tank geometry used in this study as shown in Figure 34, a modified form of the Zwietering equation was used to calculate the critical off-bottom suspension rate $N_{js}$ (Eq 13).
Figure 34  Schematics of the tank geometry (6-blade 45° pitched-blade impeller) [56]

Modifications were made to include the effect of gas sparging via term $Q_g$ [57] and the power to pulp density via term $m$. The power to pulp density has been shown to differ for solids by their densities and particle sizes [54] to as high as ~0.32; therefore the power to pulp density has been modified to 0.32 from 0.13 in the original Zwietering equation. For this reason the calculated $N_{js}$ is likely to be greater than the actual requirement. Note that although Eq 13 was derived based on a single impeller design [58], an additional impeller in this configuration shown in Figure 34 was indicated to have minimal effect on $N_{js}$ [56], thus Eq 13 is still valid.

$$\left(\frac{T}{D}\right)^{0.1}D^{0.2}\left(\frac{\rho_p - \rho}{\rho}\right)^{0.45}\frac{X^n}{D^{0.85}}(0.83 + 0.31Q_g)$$

Eq 13

In which
- $N_{js}$ = impeller speed at off-bottom suspension point (s⁻¹)
- $T$ = tank diameter (m)
- $C$ = impeller clearance from tank bottom (m)
- $D$ = impeller diameter (m)
- $v$ = dynamic viscosity (m²s⁻¹)
- $d_p$ = Sauter mean particle size (m)
- $g$ = specific gravity (ms⁻²)
- $\rho$ = liquid density
- $\rho_p$ = solid density
- $X$ = pulp density by solid to liquid ratio (%)
- $Q_g$ = gas sparging rate per tank volume (ml/min)

$$S = 2.28\left(\frac{T}{D}\right)^{0.83}\exp(0.65\frac{C}{T})$$

For 6-blade 45° pitched-blade impeller
A summary of all the input values of Eq 13 are shown in Table 8 based on which the critical off-bottom suspension rate $N_{js}$ at pulp density range 10 – 30% is shown in Figure 35. Based on these calculations, the minimum effective mixing rate was determined to be ~1600 rpm at 30% pulp density.

**Table 8  Summary of input values of Eq 13**

<table>
<thead>
<tr>
<th>$T$</th>
<th>$D$</th>
<th>$C$</th>
<th>$v$</th>
<th>$d_P$</th>
<th>$\rho_P$</th>
<th>$\rho$</th>
<th>$Q_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>m</td>
<td>m</td>
<td>m/s</td>
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<td>kg/m$^3$</td>
<td>kg/m$^3$</td>
<td>ml/min</td>
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<tr>
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<td>0.045</td>
<td>1.00E−06</td>
<td>1.50E−04</td>
<td>1.63E+03</td>
<td>1.00E+03</td>
<td>0.0189</td>
</tr>
</tbody>
</table>

**Figure 35  The critical mixing rate for off-bottom suspension at variable pulp densities**
A.2 Analysis of pH and ORP data

In order to illustrate the effect of parameters reflected on pH or ORP values, tests of the same variable group were compared in the same graph as shown in Figure 36. Calibration was performed with each probe for each test to ensure the highest possible accuracy.

(1) pH

An overview of the pH data of the leaching tests M1–20 as shown in Figure 36–42 indicates that the pH value of the leach solution tends to stabilize with little variation (< 0.25) throughout the leaching process. There was a lack of correlation between the pH trend and the leaching curves. Recall that the pH of all leaching tests was adjusted to the set point pH value at 20°C as shown in Table 1, therefore the monitored pH value at elevated temperatures were lower than the set point pH values under the effect of temperature on pH measurement [59].

The pH values were shown to be uniformly ~8.15 and unaffected by the total ammonia concentration, citrate concentration, thiosulfate concentration, the particle size distribution and the mixing rate. However, while at the same temperature (50°C) the temperature correlated pH readings dropped from the initial set pH for tests M1 and M16, the pH reading of M15 increased. Since sodium hydroxide used for pH adjustment was not added to M15 which had neutral pH, the rise in pH of M15 was attributable to the shift in the chemical equilibrium position of ammonia/ammonium in the absence of the strong base sodium hydroxide. As for the recycled leaching tests shown in Figures 42 and 43, the pH value over each leaching cycle is shown to be relatively consistent but the average pH level decreases over the cycles. The decrease in pH was likely a result of deprotonation of citrate complexing with Fe(III) [32].
Figure 36  pH vs time at various temperatures

Figure 37  pH vs time at various total ammonia concentrations
Figure 38  pH vs time at various citrate concentrations
Figure 39  pH vs time at various thiosulfate concentrations

Figure 40  pH vs time at various initial pH values
Figure 41  pH vs time at various particle sizes

Figure 42  pH vs time at various mixing rate
**Figure 43**  pH vs time of recycled leaching with no reagent compensations (tests RL1)

**Figure 44**  pH vs time of recycled leaching with citrate compensations (tests RL2)
(2) **ORP**

An overview of the ORP data of the leaching tests M1–20 as well as the recycled leaching tests RL1 and RL2 as shown in Figure 45–Figure 53 indicates that the ORP value of the leach solution stabilized (variations < 40mV) over the course of leaching. As indicated in Figure 52 by the comparison of M1 and RL1-a which had identical test conditions, the reproducibility of the ORP measurements was greater than ±40mV, thus making the differences observed in Figure 45–Figure 53 negligible. The insensitivity of the leach solution potential to the change in leaching parameters could be an indication of surplus oxygen fed. There was also a lack of correlation between the ORP trend and the leaching curves. The abrupt changes in ORP values were due to instrumental malfunctions.
Figure 45  ORP (mV vs. Ag/AgCl) vs time at various temperatures

Figure 46  ORP (mV vs. Ag/AgCl) vs time at various total ammonia concentrations
Figure 47  ORP (mV vs. Ag/AgCl) vs time at various citrate concentrations

Figure 48  ORP (mV vs. Ag/AgCl) vs time at various thiosulfate concentrations
Figure 49  ORP (mV vs. Ag/AgCl) vs time at various initial pH values

Figure 50  ORP (mV vs. Ag/AgCl) vs time at various particle sizes
Figure 51  ORP (mV vs. Ag/AgCl) vs time at various mixing rates

Figure 52  ORP (mV vs. Ag/AgCl) vs time of recycled leaching tests with no reagent compensations (tests RL1)
Figure 53  ORP (mV vs. Ag/AgCl) vs time of recycled leaching with citrate compensations (tests RL2)