Green Processing and Waste Valorization:
Sulfur Removal and Hematite Recovery from High Pressure Acid Leach Residue for Steelmaking

by

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ABSTRACT

The current study investigates a novel and environmentally friendly waste valorization process to refine hematite from the residue of the high-pressure acid leaching (HPAL) of nickel laterite ore. The process consists of an alkaline leaching step utilizing sodium hydroxide to reduce the sulfur impurity content in the HPAL residue. This novel process is very efficient because it runs at room temperature with a significantly short residence time (10 min). The refined HPAL residue has a sulfur content below the threshold accepted by the steelmaking industry; hence, it can potentially be used as a raw material. The proposed waste valorization process has the double advantage of generating a commercially valuable product from a waste stream and simultaneously providing environmental benefits by reducing the amount of scrapped leach residue and costs associated with constructing and maintaining storage facilities.
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TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................................................................................... III

TABLE OF CONTENTS ............................................................................................................ IV

LIST OF TABLES .................................................................................................................... VI

LIST OF FIGURES ................................................................................................................... VII

NOMENCLATURE ................................................................................................................... X

CHAPTER 1  INTRODUCTION ...................................................................................................... 1
  1.1  HIGH PRESSURE ACID LEACH (HPAL) RESIDUE ......................................................... 1
      1.1.1  HPAL Process and Production of HPAL Residue ....................................................... 1
      1.1.2  Properties of HPAL Residue ..................................................................................... 4
      1.1.3  Disposal of HPAL Residue ...................................................................................... 5
      1.1.4  Reutilization of HPAL Residue ................................................................................ 6
  1.2  RESEARCH OBJECTIVES ............................................................................................... 8
  1.3  THESIS OVERVIEW ...................................................................................................... 9

CHAPTER 2  LITERATURE REVIEW .......................................................................................... 10

CHAPTER 3  MATERIALS AND EXPERIMENTAL PROCEDURES ......................................... 13
  3.1  MATERIALS .................................................................................................................... 13
  3.2  CHARACTERIZATION OF HPAL RESIDUE ................................................................ 14
      3.2.1  Aqua Regia Digestion and Inductively-Coupled Plasma Optical Emission
             Spectrometry (ICP-OES) ......................................................................................... 14
      3.2.2  Scanning Electron Microscopy Energy Dispersive Spectroscopy ....................... 14
      3.2.3  X-Ray Diffraction (XRD) ...................................................................................... 14
      3.2.4  X-Ray Fluorescence (XRF) ................................................................................... 15
      3.2.5  Particle Size Distribution ...................................................................................... 15
      3.2.6  Electron Probe Microanalyzer (EPMA) ................................................................ 15
  3.3  LEACHING EXPERIMENTS .......................................................................................... 15

CHAPTER 4  RESULTS AND DISCUSSION .............................................................................. 17
  4.1  CHARACTERIZATION OF HPAL RESIDUE ................................................................ 17
  4.2  LEACHING OF HPAL RESIDUE .................................................................................. 21
      4.2.1  Reaction Stoichiometry .......................................................................................... 21
      4.2.2  Investigation of Optimum S/L Ratio ...................................................................... 22
      4.2.3  Leaching using NaOH .......................................................................................... 23
4.2.4 Leaching using KOH ........................................................................................................24
4.2.5 Leaching using Na₂CO₃ and NaHCO₃ .................................................................25
4.2.6 Leaching using Ca(OH)₂ ..........................................................................................26
4.3 EXTRACTION OF ALUMINUM .....................................................................................27
4.3.1 Extraction of Aluminum Using NaOH as Leachant ..................................................27
4.3.2 Extraction of Aluminum Using KOH as Leachant ....................................................28
4.4 EXTRACTION OF SILICON .............................................................................................29
4.5 CHARACTERIZATION OF LEACHED HPAL RESIDUE .................................................30
4.6 INVESTIGATION OF THE KINETICS OF THE LEACHING PROCESS .........................33

CHAPTER 5 PRELIMINARY ECONOMIC ANALYSIS .........................................................36
CHAPTER 6 CONCLUSIONS .................................................................................................37
CHAPTER 7 RECOMMENDATIONS FOR FUTURE WORK ..............................................38
REFERENCES ..................................................................................................................39

APPENDIX A: Effect of Base Concentration on the Extraction of Sulfur .........................42
APPENDIX B: Effect of Residence Time on the Extraction of Sulfur .................................43
APPENDIX C: Effect of Reaction Temperature on the Extraction of Sulfur ......................44
APPENDIX D: Effect of Utilizing Recycled Sodium Hydroxide as Leachant ..................45
APPENDIX E: Magnetic Separation of Hematite from Impurities ....................................46
APPENDIX F: Additional SEM-EDS Images of the HPAL Residue .................................47
LIST OF TABLES

Table 1 - Experimental matrix for sulfur leaching experiments from HPAL residue. ................................................................. 16

Table 2 - Elemental composition of HPAL residue. ......................................................................................................................... 17

Table 3 - Chemical compositions of the original HPAL residue and leached HPAL using 1 M NaOH at 25 °C for 10 min with S/L of 1/2 measured by ICP-OES. ........................................................................................................ 31

Table 4 - Preliminary cost analysis for processing 1 tonne of HPAL residue. ................. 36

Table 5 - Average reported price for the bases used in this study. 44,46,47  ......................... 36
LIST OF FIGURES

Figure 1 - Block flow diagram of HPAL process employed at Vale New Caledonia. ..............................................................3

Figure 2 - (a) Vale New Caledonia Nickel Plant, (b) Kwe West Residue Storage Facility. ..........................................................5

Figure 3 - Dried HPAL Residue. .........................................................................................................................13

Figure 4 - X-ray diffraction pattern of HPAL residue. .................................................................................................17

Figure 5 - Secondary electron images of HPAL residue. (a) and (b) SEM images of agglomerated silica and hematite, (c) and (d) nanosized hematite particles, (e) natroalunite particle in agglomerated hematite particles. ..........18

Figure 6 - (a) SEM Backscattered image of HPAL residue; elemental maps for (b) iron, (c) silicon, (d) aluminum, (e) sulfur, and (f) sodium. ..............................................................19

Figure 7 - Particle size distribution of the HPAL residue on a logarithmic scale. ..................20

Figure 8 - Color-coded electron probe microanalyzer (EPMA) compositional results................................................................20

Figure 9 - Theoretical S/L ratio as a function of M NaOH .................................................................................................22

Figure 10 - The content of the remaining sulfur in the leached HPAL residue at various S/L ratios using 1 M NaOH at 25 °C and 30 min residence time. Error bars represent the standard error of the mean for three replicates. ....23

Figure 11 - Concentration of extracted sulfur as a function of residence time at various temperatures, using 1 M NaOH with S/L of 1/2 as the leaching agent. Error bars represent the standard error of the mean for three replicates ........................................................................24

Figure 12 - Concentration of extracted sulfur as a function of time at various temperatures using 1 M KOH at S/L of 1/2 as the leaching agent. Error bars represent the standard error of the mean for three replicates ..................................................25

Figure 13 - The concentration of extracted sulfur in the leach solution using NaHCO₃ (1 M, S/L=1/2, 80 °C), Na₂CO₃ (1 M, S/L=1/2, 65 °C, 80 °C), and NaOH (1 M, S/L=1/2, 80 °C) as the leaching agent. Error bars represent the standard error of the mean for three replicates ..................26

Figure 14 - The concentration of the extracted sulfur in the leached solution using Ca(OH)₂ (0.02 M, S/L=1/22, 25 °C and 80 °C), NaHCO₃ (1 M, S/L=1/2, 80 °C), Na₂CO₃ (1 M, S/L=1/2, 65 °C, 80 °C), and NaOH (1 M, S/L=1/2, 80 °C) as the leaching agent. Error bars represent the standard error of the mean for three replicates. ........................................27
Figure 15 - Concentration of extracted aluminum as a function of time at various temperatures using 1 M NaOH as leaching agent at 25, 45, 65, and 80 °C. Error bars represent the standard error of the mean for three replicates.

Figure 16 - Concentration of extracted aluminum as a function of time at various temperatures using 1 M KOH as leaching agent at 25, 45, 65, and 80 °C. Error bars represent the standard error of the mean for three replicates.

Figure 17 - Concentration of extracted silicon as a function of time at various temperatures using 1 M NaOH as leaching agent at 25, 45, 65, and 80 °C. Error bars represent the standard error of the mean for three replicates.

Figure 18 - XRD pattern of the leached vs. original HPAL residue. Leaching conditions:

Figure 19 - SEM-EDS elemental maps of sulfur and aluminum in the original and leached HPAL.

Figure 20 - a) Concentration of sulfur as a function of time at various temperatures using 1 M NaOH, S/L=1/2 as the leaching agent. (b) Plot of \( dc/dt \) (i.e., reaction rate) as a function of log \( c \), where the intercept is log \( k \). (c) Arrhenius equation plot to determine the apparent activation energy \( (E) \) of the leaching reaction using 1 M NaOH, S/L=1/2. Error bars represent the standard error of the mean for three replicates.

Figure 21 - a) Concentration of sulfur as a function of time at various temperatures using 1 M KOH at S/L=1/2 as the leaching agent. (b) Plot of \( dc/dt \) (i.e., reaction rate) as a function of log \( c \), where the intercept is log \( k \). (c) Arrhenius equation plot to determine the apparent activation energy \( (E) \) of the leaching reaction using 1 M KOH with S/L=1/2. Error bars represent the standard error of the mean for three replicates.

Figure 22 - The effect of NaOH concentration on the extraction of sulfur, aluminum, iron.

Figure 23 - The effect of residence time on the extraction of sulfur, aluminum and iron.

Figure 24 - The effect of reaction temperature on the extraction of sulfur, aluminum and iron.

Figure 25 - The effect of utilizing recycled sodium hydroxide as leachant.

Figure 26 - The comparison of X-Ray Diffraction (XRD) pattern between magnetoically separated HPAL residue and original HPAL residue.
Figure 27 - SEM image and EDS elemental mapping of HPAL residue. ..........................47
Figure 28 - SEM image of HPAL residue indicating (a) hematite, natroalunite, and
(b) magnesium silicate particles morphology. ............................................................47
Figure 29 - Low magnification SEM image of HPAL residue and EDS elemental
mapping. ....................................................................................................................48
NOMENCLATURE

LIST OF SYMBOLS

\( M \)  
Molarity (mol/L)

\( C \)  
Instantaneous concentration at time \( t \) (mol/L)

\( k \)  
Rate constant (1/min)

\( t \)  
Time (min)

\( A \)  
Frequency factor (1/min)

\( E \)  
Activation energy (kJ/mol)

\( R \)  
Universal gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\))

\( T \)  
Temperature (K)

ABBREVIATIONS

HPAL  
High Pressure Acid Leach

XPS  
X-ray Photoelectron Spectroscopy

XRD  
X-ray Diffraction

SEM  
Scanning Electron Microscopy

XRF  
X-ray Fluorescence

EDS  
Energy Dispersive Spectroscopy

ICP-OES  
Inductively Coupled Plasma Optical Emission Spectrometry

DI Water  
Deionized Water

S/L  
Solid-to-Liquid ratio

PSD  
Particle Size Distribution

PVC  
Polyvinyl chloride

USD  
United States Dollar

RPM  
Revolutions Per Minute

SUBSCRIPTS

\( \text{aq} \)  
Aqueous phase

\( s \)  
Solid phase

\( g \)  
Gaseous phase

\( l \)  
Liquid phase
CHAPTER 1 INTRODUCTION

Steel is a versatile product and fundamental to the development of modern human civilization. Conventional steelmaking produces crude steel by reducing iron ore in the form of hematite (Fe₂O₃), magnetite (Fe₃O₄), and wüstite (FeO) with coke in blast furnaces. Crude steel is then refined in a basic oxygen furnaces to obtain steel with desirable properties. Economic growth in China over the past decade has driven the demand for steel and in 2016, the demand for steel was reported to be 1501 Mt and thus is forecasted to double by 2050. The annual demand for steel has increased at a compound growth rate of 5% over the last 20 years, surpassing the growth rate of other materials. At the same time, in recent years, obtaining good quality iron ore has become difficult. Because of the growth in demand and decreasing quality of iron ore, new approaches are required to find and utilize secondary resources for iron oxide.

1.1 HIGH PRESSURE ACID LEACH (HPAL) RESIDUE
1.1.1 HPAL Process and Production of HPAL Residue

High pressure acid leach residue, which consists of mainly of hematite (Fe₂O₃), is a byproduct produced during nickel production by the high pressure acid leach (HPAL) process. 40-50% of the global nickel is extracted with the HPAL process. Whittington and Muir have reviewed the chemistry of the HPAL process. In this process, laterite ore is first screened to reject large ore and rock by adding water and stirring. The ore slurry is then decanted to obtain a thickened pulp. Sulfuric acid is added to the thickened pulp and heated to 260 °C at a pressure of 45 bar. The pulp is then injected into a titanium autoclave at 270 °C and metals, such as cobalt and nickel, are dissolved. Impurities, such as iron and aluminum, undergo hydrolysis and precipitate, largely in the form of hematite (Fe₂O₃) and alumite (XAl₃(SO₄)₂(OH)₆, X=Na,K,H,O,NH₄). The mechanism of the HPAL process is as follows: iron and aluminum exist in the laterite as trivalent ions, in the form of goethite, iron oxide hydroxide (FeO(OH)), and boehmite, aluminium oxide hydroxide (γ-AlO(OH)), respectively. Nickel and cobalt exist as assumed form of oxides. According to the following reactions (1-4), all compounds dissolve during high pressure acid leaching.
FeO(OH)_{s} + 3H_{aq}^{+} → Fe^{3+}_{aq} + 2H_{2}O_{l} \hspace{1cm} (1)

AlO(OH)_{s} + 3H_{aq}^{+} → Al^{3+}_{aq} + 2H_{2}O_{l} \hspace{1cm} (2)

NiO_{s} + 2H_{aq}^{+} → Ni^{2+}_{aq} + H_{2}O_{l} \hspace{1cm} (3)

CoO_{s} + 2H_{aq}^{+} → Co^{2+}_{aq} + H_{2}O_{l} \hspace{1cm} (4)

During the leaching process, nickel and cobalt oxides dissolve and remain in the aqueous phase as sulfates.\(^{13,14}\) However, ferric and aluminum cations hydrolyze, producing solid products.\(^{15}\) During hydrolysis, ferric cations directly form hematite (reaction 5) or basic ferric sulfate (reaction 6), which can transform to hematite (reaction 7).\(^{14,16}\) These reactions result in the generation of the acid consumed by the dissolution of goethite (reaction 1).\(^{17}\)

\[
2Fe^{3+}_{aq} + 2H_{2}O_{l} \rightarrow Fe_{3}O_{4} + 6H^{+}_{aq} \hspace{1cm} (5)
\]

\[
Fe^{3+}_{aq} + SO_{4}^{2-}_{aq} + H_{2}O_{l} \rightarrow Fe(OH)SO_{4} + H^{+}_{aq} \hspace{1cm} (6)
\]

\[
2Fe(OH)SO_{4} + H_{2}O_{l} \rightarrow Fe_{3}O_{4} + 2SO_{4}^{2-} + 4H^{+}_{aq} \hspace{1cm} (7)
\]

During hydrolysis, aluminum cations form basic aluminum sulfate (at temperatures above 270°C) (reaction 8) or alunite (in most cases) (reaction 9 and 10). Similar to the hydrolysis of the ferric cations, the hydrolysis of the aluminum cations also regenerates most of the acid consumed during the dissolution (reaction 2).\(^{17}\)

\[
3Al^{3+} + 2SO_{4}^{2-} + 7H_{2}O_{l} \rightarrow (H_{2}O)Al(SO_{4})(OH)_{5} + 5H^{+}_{aq} \hspace{1cm} (8)
\]

\[
3Al^{3+} + 2SO_{4}^{2-} + X^{+} + 6H_{2}O_{l} \rightarrow (X)Al(SO_{4})(OH)_{5} + 6H^{+}_{aq} + X = Na, K, HSO_{4}, NH_{4} \hspace{1cm} (9)
\]

\[
Al^{3+} + SO_{4}^{2-} + H_{2}O_{l} \rightarrow Al(OH)SO_{4} + H^{+}_{aq} \hspace{1cm} (10)
\]

After the leaching process, the residue is gradually cooled and separated from the liquor by counter-current decantation. The leach solution, enriched with nickel and cobalt, is sent to a neutralization stage to remove iron and aluminum and recover the soluble nickel and cobalt.\(^{16,19}\) HPAL residue, consisting of mainly hematite and impurities, such as silica and alunite, is channeled to tailing ponds for storage. The HPAL process utilized in Goro, New Caledonia comprises six main stages: feed preparation, leaching, counter-current
decantation, neutralization, solvent extraction, and pyro-hydrolysis. Figure 1 shows the HPAL process employed at the Goro plant.

![Block flow diagram of HPAL process employed at Vale New Caledonia.](image)

At present, for every tonne of nickel extracted, approximately 100 tonnes of HPAL residue are generated. Production of HPAL residue at Vale New Caledonia alone is about 5.6 million tonnes per annum at full production. Currently, the HPAL residue is stored in tailing ponds constructed near the production facilities, occupying hundreds of acres of land. HPAL slurry stored in the ponds is also known to contain harmful heavy metals, such as manganese and chromium (VI), which can contaminate drinking-water sources and endangering terrestrial organisms. Thus, it is very important to manage these tailings properly.
1.1.2 Properties of HPAL Residue

Depending on the leaching conditions, HPAL residue consists of mainly hematite (Fe₂O₃), with impurities, including silicon dioxide (SiO₂), natroalunite, (NaAl₃(SO₄)₂(OH)₆), and silicates, such as serpentine (Mg₃SiO₅(OH)₄), derived from the laterite ore. The residue may also contain basic ferric sulfate (FeOHSO₄), iron sulfate (Fe₂(SO₄)₃), gypsum (CaSO₄·2H₂O), and iron-alumino-chromite (Al₉Fe₄Cr₂O₁₄) as minor phases. Trace metals, such as manganese, chromium, copper, and zinc are also present in the residue.

HPAL residue generally has a very fine particle size. The average size of hematite particles, a major component in HPAL residue, is about 1 µm. Other impurities, including silicates and gypsum, tend to have a larger particle sizes. The fine particle size of HPAL residue results in very poor drainage properties. The moisture content of HPAL residue is about 60%. HPAL residue has low permeability because of re-precipitation of Fe compounds, which results in increased saturation in the tailing ponds. The high saturation of HPAL residue reduces the ability of the impoundment to support the weight of the ground equipment on it.

Fresh HPAL residue generated from the autoclave is very acidic and contains a surplus of sulfuric acid. The pH is adjusted to an appropriate level for solid-liquid separation by counter-current decantation. The solid obtained from the counter-current decantation process has pH of 2-3 (measured in this work). Because of the high level of manganese (Mn) content and low pH, HPAL residue can have a harmful impacts on the environment. Environmental concerns related to HPAL residue have been a serious challenge for the HPAL process. Due to the presence of heavy metals, such as Mn and Cr, in the slurry poses a threat to the underground water system. Erosion, infiltration, and leaching into surface and ground water are the main routes for transport into the environment.
1.1.3 **Disposal of HPAL Residue**

Currently, HPAL residue has no commercial value, and it is currently stored in tailing impoundments. At the present, there are two management options for the residue. The residue can either be filtered and dry-stacked in a pit, requiring minimal or no structural containment, or stored as wet slurry in conventional tailing pond or in-pit disposal. The process water is usually not reused, as it has very high levels of sulfate and manganese. The construction of HPAL tailing ponds requires careful design and engineering. HPAL residue tends to have a very small particle size and this causes the material to have high saturation. A sturdy base is required to withstand the weight of the residue. A complete environmental containment system, such as base liner, drains, and closure cap is also required to resist physical, mechanical, and chemical stress caused by HPAL residue, and prevent the wastewater from coming in contact with the soil and underground water supply.

The current project was supported by Vale Ltd. (a Brazilian mining company). The mine is located at Goro in the south of New Caledonia, near the township of Yaté, Prony Bay, in the South Province. The tailings are currently stored in a tailings dam (Kwe dam) in the form of wet slurry, which covers 1.3 km² and having a storage capacity of 40 Mm³. Figure 2a depicts Vale’s New Caledonia Nickel Plant and Figure 2b shows a view of Kwe West Residue Storage Facility at Goro.

![Figure 2](image)

Figure 2 – (a) Vale New Caledonia Nickel Plant, (b) Kwe West Residue Storage Facility.

Disposal of HPAL residue by dry stacking involves pressure filtration of slurry to remove excess moisture and transportation by truck or conveyor belt to a stack. Dry stacking is not practiced at present, because of the high cost of filtration and presence of hygroscopic materials, such as gypsum, in the tailings.
1.1.4 Reutilization of HPAL Residue

Rapid economic growth in developing countries, such as India and China, and the decreasing supply of good quality iron ore has sparked an initiative towards the reutilization of secondary sources. Currently, HPAL residue has little commercial value and almost all residue generated is channeled into tailing ponds. Although hematite, the major component of HPAL residue, is generally stable and nontoxic, the amount of land required to store the residue is a major environmental concern.

Some potential reuses of HPAL residue include the utilization of hematite as aggregates in Portland cement, production of brick and tiles, and pigments for paint. Some research has been done on utilizing iron tailing as aggregates in Portland cement. Chen et al. studied the utilization of hematite tailing for the production of fired bricks. The study prepared fired brick utilizing a combination of 84% of hematite tailings and 12-15% water and firing the mixture at 980 °C to 1030 °C for 2 h. The resultant brick achieved a mechanical strength of up to 20.0-22.9 MPa. Zhao et al. investigated the potential of utilizing hematite as the main raw material to prepare ultra-high performance concrete. 40% hematite tailings was shown as the optimum replacement mixture for concrete production.

Another potential application of HPAL residue is in the production of red pigment. Iron oxide red pigment has found its application in the construction industry, inorganic dyes, ceramics, pigments, and adsorbents in the paper industry, lacquers or plastics. Pereira et al. utilized iron tailings as pigment for ceramics and concluded that it is a suitable ceramic pigment as the residue is thermally stable from 500 °C to 1100 °C, which is the firing temperature of the ceramic.

HPAL residue can also be used as a seeding agent for impurity removal in the HPAL process to increase the settling rate of hematite in the pregnant leach solution. Addition of 50 wt.% to 80 wt.% of HPAL residue obtained from the counter-current decantation stage is beneficial for the precipitation of iron impurities in the pregnant leach solution.

The major consumer of hematite is the steel industry. Therefore, to have a widespread reclamation of HPAL residue as a valuable product, it must find its application as a feedstock in the steelmaking industry. To make HPAL residue a suitable feedstock for this industry, its sulfur content must be suppressed to less than 1 wt.%.
from becoming brittle at high temperature (hot shortness).

The current study focuses on developing an innovative, resource-efficient, and cost-effective process for refining HPAL residue from Vale’s New Caledonia nickel plant. The refining process is based on the direct leaching of alunite from the HPAL residue using alkaline leachant to lower sulfur content to below 1 wt.% and increase iron content to above 56 wt.% The process produces high purity hematite that can be used as a feedstock for steelmaking. The results and findings from this study provide insight for further development of an efficient hematite recovery process from HPAL residue with potential for large-scale implementation.
1.2 RESEARCH OBJECTIVES

The main objective of this research project was to develop a green, resource-efficient, cost effective, and industrially viable hydrometallurgical process to valorize HPAL residue produced at Vale’s Goro plant, and produce it into a suitable feedstock for the steelmaking industry.

The project consisted of four project segments:

Project Segment (I) focused on a thorough characterization of HPAL residue, using various characterization techniques, including aqua-regia digestion, followed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Electron Probe Microanalysis (EPMA), Scanning Electron Microscopy Energy Dispersive Spectroscopy (SEM-EDS), and Particle Size Analysis (PSA). The results provided an in-depth insight into the composition, crystal phases, elemental distribution, morphology, and particle size.

Project Segment (II) focused on systematic leaching experiments utilizing NaOH as the leaching agent to determine the optimum operating conditions, in terms of residence time, concentration, temperature, and solid-to-liquid ratio (pulp density).

Project Segment (III) focused on utilizing leaching agents other than NaOH to determine the most efficient and cost effective leachant for the process. KOH, Na₂CO₃, NaHCO₃, and Ca(OH)₂ were studied.

Project Segment (IV) focused on a kinetic investigation and mechanism elucidation of the leaching processes utilizing NaOH or KOH as the leaching agents.
1.3 THESIS OVERVIEW

The present thesis is composed of six chapters, which are structured as follows:

- Chapter 1 presents an introduction to the research project.
- Chapter 2 presents a literature review of previous research performed on the recovery and reutilization of iron tailings/residue.
- Chapter 3 presents the material and experimental procedure used in this work.
- Chapter 4 presents the results and discussions.
- Chapter 5 summarizes the major conclusions drawn from this work.
- Chapter 6 outlines the suggestions for future work.
- Appendices present the development process that led to the optimized process.

This thesis was prepared on the basis of the following published refereed journal publications. The results of this work have been presented in two conferences. We are in the process of preparing second manuscript that will be submitted to Analytical Chemistry.

Journal Publications

Refereed Conference Publications

Conference Presentations
CHAPTER 2 LITERATURE REVIEW

Several studies have been conducted to reuse iron tailings produced by the mining industry. Das et al. have investigated the possibility of utilizing iron tailings as one of the materials in ceramic tiles production. At a firing temperature of 1200 °C with 40 wt.% iron tailing, a ceramic tile with comparable scratch hardness and strength to commercial tiles was produced.8

Pereira et al. considered the utilization of untreated iron tailing as a ceramic colorant for glazes. Iron residue is a suitable ceramic pigment because of its thermal stability at high temperature (500-1100 °C). It was also found that addition of iron residue in transparent frits does not produce substantial color change. However, addition of iron residue to the white and matte frits significantly changed the glaze color and tonality with increasing temperature. Therefore, it was concluded that to utilize iron tailing as red pigment, 1050 °C and 1100 °C were optimum firing temperatures for white and matte glaze and transparent glaze, respectively.27

Ropenack et al. investigated a method to valorize jarosite \((XFe^{3+}_3(OH)\_6(SO\_4)_2) (X=Na\ or\ K)\)-containing residues to saleable products.31 By subjecting jarosite-containing residue and zinc sulfides in an autoclave at a temperature of 130-170 °C to an oxygen partial pressure of 1000 kPa and 40 to 100 g/L of free sulfuric acid, jarosite-containing residues and zinc sulfides were dissolved. The leachate was then introduced into a leach circuit for zinc electrolysis and iron was the precipitated as hematite.

Dutrizac has performed a thorough investigation on the conversion of sodium jarosite \(((NaFe^{3+}_{3}(OH)\_6(SO\_4)_2))\) to hematite through hydrothermal processes. To attain complete conversion of sodium jarosite to a low-sulfur content hematite product, the optimum conditions were determined to be 225 °C with a residence time of 1 h, and an acid concentration of less than 0.5 M of H\(_2\)SO\(_4\).32

Dutrizac et al. studied the precipitation of hematite from ferric chloride media at a temperature of less than 100 °C at ambient pressure.33 The presence of hematite seed was determined to be essential to favor the precipitation of hematite instead of akageneite (β-FeO·OH), regardless of the reaction temperature. Although prolonged reaction times favored the precipitation of hematite, the presence of hematite seed significantly shortened the reaction
time required for the exclusive precipitation of hematite. Addition of hematite seed in proportion to the amount of product formed was also found to be beneficial to precipitate only hematite product. Presence of CaCl₂ or NaCl reduced the amount of precipitate formed and had minor effects on the composition of hematite formed. In contrast, presence of ZnCl₂ had no significant effects on the composition of hematite precipitates.

Ma et al. conducted an investigation on utilizing nitric acid to substitute sulfuric acid in the HPAL process. Extraction efficiency of Ni and Co was above 82 % for limonitic laterite ore and above 98 % for saprolitic laterite ore. This process offers the advantage of producing hematite residue with low sulfur content, making it a suitable feedstock for steelmaking.34

Ozaki et al. designed a process to recover magnesium from HPAL leachate to produce magnesium oxide for the neutralization step in HPAL process. By utilizing magnesium-based neutralizing agents, precipitation of sulfate salts could be avoided, thus reducing the sulfur content of HPAL residue. After the HPAL process, the leachate was neutralized and sulfurated with H₂S to recover nickel and cobalt as sulfides. The leachate then underwent several stages of solid-liquid separation. Leachate containing magnesium and calcium was then concentrated to precipitate calcium sulfate. After removing calcium impurities from the solution, magnesium sulfate crystals were formed and roasted with a reductant at 950-1100 °C for 1 h to produce MgO.35

Ozaki et al. investigated an alkaline leaching process and the optimized sulfuric acid usage to reduce the sulfur content of HPAL residue to 1 wt.%. It was shown that by using 150-220 kg of sulfuric acid per ton of ore, a nickel extraction of 95 % could be achieved, while producing a HPAL residue with a sulfur content of 1 wt.%. It was also discovered that the addition of chloride salts at 4 times the molar ratio of sulfur present in the leach residue produced a residue with sulfur content less than 1 wt.%. 20 wt.% (7.5 M) of alkaline leachant at 60 °C with 2 h of residence time were determined to be the optimum conditions to suppress the sulfur content of the residue to 1 wt.%.36

Ohara et al. employed a three-step process to valorize HPAL residue to a feedstock ready for steelmaking industry. In the HPAL residue, iron existed in the form of hematite (Fe₂O₃), and the major sulfur-bearing compound in the residue was gypsum (CaSO₄·2H₂O). The average particle size of hematite particles was approximately 1 µm, and the average size of
gypsum was approximately 30 µm. The first step of the separation process used a hydrocyclone with the particle size of the overflow was set at ≤2µm. The purpose of using hydrocyclone is to separate larger gypsum particles from hematite particles. The majority of gypsum was removed from the residue in the underflow and the hematite particles were concentrated at the overflow. The hematite overflow was then subjected to magnetic separation to separate iron from chromite. Magnetic force was applied to hematite powder that passed through a mesh. Because of this unique set-up, a higher than usual magnetic force could be used in the process and this set-up also enabled the separation of hematite and chromite, which is not possible under conventional magnetic separation. A magnetic field strength of 5 to 20 kGauss was determined as optimum for the separation. After the two-step process, a final iron grade of 53 wt.% and sulfur content of 1 wt.% was achieved. Magnetically-separated hematite particles were then sintered to obtain a density of 4.0 g/cm³ to 5.0 g/cm³, and particle size greater than 3 µm. The optimum sintering temperature was selected to be 1150 °C to 1350 °C. After the calcination, the sulfur content of the hematite body was reduced to less than 0.1 wt.%, as a large amount of sulfur was removed as SO₂ gas.

Ohara et al. examined the possibility of introducing non-calcium based neutralizing agents in the neutralization process to reduce the formation of insoluble gypsum in HPAL residue. The neutralization process was divided into three stages: 1) preliminary neutralization, 2) first neutralization, and 3) second neutralization. In the preliminary neutralization step, the pregnant leach solution was neutralized using magnesium oxide-rich mineral to increase the pH to about 1-3 to increase the separation efficiency in the subsequent solid-liquid separation step. By using magnesium oxide-rich base rock to substitute conventional neutralizing agents, such as limestone or slaked lime, the precipitation of gypsum was avoided, reducing the sulfur content of the residue.

Valorizing HPAL residue has been receiving increasing attention over the past few years; however, the proposed processes so far pose a few disadvantages, namely high leachant concentration, long residence times, high operating temperatures, high capital and operating expenditures, and process complexity. Hence, in this work, we focused on developing a robust, efficient, and cost-effective process to valorize Vale’s Goro plant HPAL residue through sulfur removal.
CHAPTER 3  MATERIALS AND EXPERIMENTAL PROCEDURES

This chapter describes the materials characterization, experimental procedures, and analytical techniques used in this work.

3.1 MATERIALS

HPAL residue was acquired from Vale’s nickel plant located near the Goro mine in the south of New Caledonia, near the township of Yaté, Prony Bay, in the South Province. The residue existed in the form of wet slurry and was filtered, then washed three times with deionized water (>18 MΩ•cm, Millipore). The residue was dried for 24 h in an oven at 50 °C. Figure 3 shows a photo of the dried HPAL residue.

![Dried HPAL Residue](image)

Figure 3 – Dried HPAL Residue.

Sodium hydroxide (ACS reagent grade, 50.0% w/w) and potassium hydroxide (ACS reagent grade, 45.0% w/w), were purchased from VWR and diluted with deionized water to desired concentrations for the leaching experiments. Anhydrous sodium carbonate, Na₂CO₃ (ACS reagent grade, Bioshop Inc., Canada), anhydrous sodium bicarbonate, NaHCO₃ (ACS reagent grade, Sigma-Aldrich), and calcium hydroxide, Ca(OH)₂ (Certified grade, Fisher Scientific) were dissolved in deionized water and diluted to desired concentrations with deionized water for the leaching experiments.
3.2 CHARACTERIZATION OF HPAL RESIDUE

3.2.1 Aqua Regia Digestion and Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES)

To determine the elemental composition of the HPAL residue, aqua regia digestion was performed at 200 °C, using an Ethos EZ Microwave Digestion System. Digested samples were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (PerkinElmer Optima 8000). Samples of 0.5 g of dried HPAL residue were mixed with 20 mL of aqua regia (3:1, HCl: HNO₃) and digested for 2 h. The samples were then diluted to desired concentrations with 5 wt.% nitric acid.

Triplicate measurements were performed in ICP-OES analysis to ensure accuracy. The following wavelengths were employed for Fe (238.204 nm), Ni (221.648 nm), Cr (267.716 nm), Al (396.151 nm), Mg (279.077 nm), Mn (257.610 nm), Na (589.588 nm), Ca (317.933 nm), K (766.490 nm), and S (181.975 nm). To ensure better signal stability and precision, axial view and high purge gas flow (5 L/min) were selected for S (181.975 nm) measurements.

3.2.2 Scanning Electron Microscopy Energy Dispersive Spectroscopy

To gain insight on the elemental distribution and morphology of the HPAL residue, HPAL sample was characterized using scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS; Hitachi SU8230). To analyze the morphology of the particles, the samples were mounted on a specimen holder with carbon tape. To acquire cross section images of the particles, samples were mixed with self-curing resin, sectioned, and polished using standard metallographic procedures. To ensure the sample was electrically conductive, it was carbon-coated prior to characterization.

3.2.3 X-Ray Diffraction (XRD)

To obtain the crystal phases of the HPAL residue samples, XRD patterns were collected using Cu-Kα1 radiation (λ=0.15406 nm) in a MiniFlex X-Ray diffractometer, manufactured by Rigaku with a step size of 0.02° and a collection time of 0.8 s/step. The
XRD patterns were matched against the International Center for Diffraction Data files (JCPDF-ICDD Release 2005). Data processing was performed using PDXL software.

3.2.4 X-Ray Fluorescence (XRF)

To obtain the overall chemical composition of the HPAL residue, samples were analyzed by XRF (Bruker S2-Ranger). To ensure high accuracy, samples were pressed with a hydraulic press to form a pellet. The instrument was calibrated with a standard multi-element glass reference.

3.2.5 Particle Size Distribution

The average particle size distribution of the HPAL residue was determined using a Malvern Mastersizer S laser diffraction particle size analyzer. Particle size was analyzed using standard operating procedures. DI water was used as a dispersant.

3.2.6 Electron Probe Microanalyzer (EPMA)

To obtain quantitative analysis of chemical phases in the HPAL residue, electron probe microanalysis (EPMA) (JEOL JXA 8230) was utilized. Analyses were carried out in wavelength-dispersive detection mode, with an accelerating voltage of 15 kV and a beam current of 20 nA.

3.3 LEACHING EXPERIMENTS

For the leaching experiments, five different bases were utilized: NaOH, KOH, Na₂CO₃, NaHCO₃, and Ca(OH)₂. The effect of different solid-to-liquid ratio (S/L), temperature, and reaction stoichiometry were thoroughly investigated. The experimental matrix for the leaching experiments is summarized on Table 1.
Table 1 - Experimental matrix for sulfur leaching experiments from HPAL residue.

<table>
<thead>
<tr>
<th>Leaching agent</th>
<th>Concentration (mol/L)</th>
<th>Temperature (°C)</th>
<th>Solid/liquid ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>1</td>
<td>25, 45, 65, 80</td>
<td>1/1, 1/1.3, 1/2, 1/5, 1/10, 1/20</td>
</tr>
<tr>
<td>KOH</td>
<td>1</td>
<td>25, 45, 65, 80</td>
<td>1/2</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>1</td>
<td>65, 80</td>
<td>1/2</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>1</td>
<td>80</td>
<td>1/2</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>0.02</td>
<td>25, 80</td>
<td>1/22</td>
</tr>
</tbody>
</table>

All leaching experiments were conducted in a 500 mL glass reaction vessel. Most experiments were conducted at room temperature (25 °C), and for the ones at higher temperatures, heating was provided by a heating mantle. The system maintained the temperature with an accuracy of ±1 °C. A Teflon-coated stirring bar was used to create a homogenous system and the system was stirred at 500 rpm. Initial leaching experiments were conducted for 30 min and the results showed that the kinetics of the leaching process are fast and 10 min residence time was sufficient.

Sample solutions of 1 mL were withdrawn in pre-determined intervals through a 1/8” ID PVC sampling tubes and the liquid samples were filtered using 0.45 μm nylon syringe filters from VWR. The samples were diluted with 1.5 M HNO₃ to a pH of less than 3 by making up the solution volume to exactly 10 mL and the samples were stored in sealed plastic test tubes at room temperature.

The leach solid residue was filtered using vacuum filtration through grade 3 Whatman filter paper. The solid was washed three times with deionized water and dried in an oven at 50 °C for 12 h. Solid samples were digested with aqua regia and analyzed with ICP-OES or sometimes directly analyzed by XRF to determine the concentration of base elements and sulfur remaining in the leach residue.
CHAPTER 4 RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF HPAL RESIDUE

The elemental composition of the HPAL residue was determined by ICP-OES after aqua regia digestion. Table 2 presents the concentration of base elements in the HPAL residue. The iron and sulfur content of HPAL residue were 53.7 wt.% and 2.98 wt.%, respectively.

Table 2 - Elemental composition of HPAL residue.

<table>
<thead>
<tr>
<th>Element</th>
<th>wt.%</th>
<th>Element</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>53.7</td>
<td>Mn</td>
<td>0.061</td>
</tr>
<tr>
<td>Ni</td>
<td>0.038</td>
<td>Na</td>
<td>0.092</td>
</tr>
<tr>
<td>Cr</td>
<td>1.28</td>
<td>Ca</td>
<td>0.093</td>
</tr>
<tr>
<td>Al</td>
<td>1.68</td>
<td>K</td>
<td>0.003</td>
</tr>
<tr>
<td>Mg</td>
<td>0.205</td>
<td>S</td>
<td>2.98</td>
</tr>
<tr>
<td>Si</td>
<td>4.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The concentration of Si was determined by XRF, because of silicon’s insolubility in aqua regia.

The XRD diffraction pattern of the HPAL residue revealed three main solid phases: hematite (Fe₂O₃), natroalunite (NaAl(SO₄)₂(OH)₆), and silica (SiO₂). Minor phases in the residue were not detected by XRD, because of their low concentration. The XRD pattern is presented in Figure 4.

![X-ray diffraction pattern of HPAL residue.](image)

Figure 4 - X-ray diffraction pattern of HPAL residue.
SEM analysis was performed to observe the overall morphology of the HPAL residue. Cross-sectional compositional analysis of HPAL residue was also performed to gain insight into the elemental distribution within the sample. Figure 5 (a) to (e) presents the topographical contrast of different phases in the residue. As can be seen from Figure 5 (a) to (e), hematite particles were mostly in the nanometer size range and spherical in shape. Natroalunite and silica were larger in size and mostly existed in planar shape.

Figure 5 - Secondary electron images of HPAL residue. (a) and (b) SEM images of agglomerated silica and hematite, (c) and (d) nanosized hematite particles, (e) natroalunite particle in agglomerated hematite particles.
Figure 6 (a) presents the cross-sectional backscattered SEM image of HPAL residue particles, and Figure 6 (b) to (f) present the elemental maps of the agglomerated particles. The co-occurrence of aluminum, sulfur, and sodium confirmed the presence of natroalunite, which was finely disseminated throughout the particle. The SEM images indicate that the HPAL residue was an agglomeration of various phases and most of Si was not associated with hematite and that natroalunite was rich in Al.

![Figure 6](image)

Figure 6 – (a) SEM Backscattered image of HPAL residue; elemental maps for (b) iron, (c) silicon, (d) aluminum, (e) sulfur, and (f) sodium.

Figure 7 presents the particle size distribution (PSD) of the HPAL residue. The average particle size of HPAL residue was 1.88 µm. The span (d90-d10) was 25.8 µm; the quartile ratio (d75/d25) was 7.3 µm, and the median diameter (d50) was 2.7 µm. The particle size distribution is due to the different phases in the residue, such as quartz and natroalunite that were larger in size, and hematite particles that were smaller, as shown in SEM images of Figures 4 and 5.
Figure 7 - Particle size distribution of the HPAL residue on a logarithmic scale.

Electron probe microanalysis (EPMA) characterization of the HPAL residue was performed to determine the mineral composition. Minor phases that were not detected with XRD were determined here. The EPMA results indicated the presence of hematite (78.7%), natroalunite (NaAl(SO$_4$)$_2$(OH)$_6$) (9.42%), silica (2.74%), magnesium silicate (3.87%), iron magnesium silicate (2.16%), sulfur-rich iron oxide (2.16%), and minor amount of other phases as shown in Figure 8.

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur-rich iron</td>
<td>2.16</td>
</tr>
<tr>
<td>Natroalunite</td>
<td>9.42</td>
</tr>
<tr>
<td>Hematite</td>
<td>78.67</td>
</tr>
<tr>
<td>Silica</td>
<td>2.74</td>
</tr>
<tr>
<td>Aluminosilicate</td>
<td>0.01</td>
</tr>
<tr>
<td>Chromite</td>
<td>0.52</td>
</tr>
<tr>
<td>Magnesium silicate</td>
<td>3.87</td>
</tr>
<tr>
<td>Iron silicate</td>
<td>0.45</td>
</tr>
<tr>
<td>Fe-Mg silicate</td>
<td>2.16</td>
</tr>
</tbody>
</table>

Figure 8 - Color-coded electron probe microanalyzer (EPMA) compositional results.
4.2 LEACHING OF HPAL RESIDUE

4.2.1 Reaction Stoichiometry

The reaction stoichiometry of natroalunite and sodium hydroxide was studied prior to the experiment. The reaction of natroalunite with sodium hydroxide produces sodium aluminate (NaAlO₂) and sodium sulfate, as shown below:

\[
\text{NaAl}_3\text{(SO}_4\text{)}_2\text{(OH)}_6(s) + 6\text{NaOH}(aq) \rightarrow 3\text{NaAlO}_2(aq) + 2\text{Na}_2\text{SO}_4(aq) + 6\text{H}_2\text{O}(l) \tag{11}
\]

Using the natroalunite content of the HPAL residue detected by EPMA, the relationship between base molarity (M), volume of NaOH required, and theoretical S/L ratio was determined.

To obtain theoretical S/L ratio, we considered \(m_{\text{solid}}\) in grams of solid residue, and mass of natroalunite was 0.0942 \(m_{\text{solid}}\). The volume of NaOH required is presented below (equations 1-3).

\[
mole_{\text{solid}} = \frac{0.0942m_{\text{solid}}}{397.93} = 2.34 \times 10^{-4}(m_{\text{solid}}) \text{ mol} \tag{1}
\]

\[
mole_{\text{NaOH}} = 6 \times mole_{\text{solid}} = 1.42 \times 10^{-3}(m_{\text{solid}}) \text{ mol} \tag{2}
\]

\[
M_{\text{NaOH}}V_{\text{NaOH}} = mole_{\text{NaOH}} \tag{3}
\]

where \(M_{\text{NaOH}}\) is the molarity of NaOH and \(V_{\text{NaOH}}\) is the volume in L. Therefore, the relationship between S/L ratio and \(M_{\text{NaOH}}\) is as follows:

\[
\frac{S}{L} = \frac{m_{\text{solid}}}{mole_{\text{NaOH}} \times 1000} = \frac{1.424 \times 10^{-3}m_{\text{solid}}}{M_{\text{NaOH}} \times 1000} \tag{4}
\]

\[
\frac{S}{L} = 0.70M_{\text{NaOH}} \tag{5}
\]

The relationship between theoretical S/L ratio and molarity of NaOH leachant is presented in Figure 9.
4.2.2 Investigation of Optimum S/L Ratio

NaOH was selected as the leaching agent in the first set of experiments and the operating conditions were fixed at 25 °C and 30 min residence time. The effect of residence time, temperature, and other leaching agents were subsequently investigated and the results are presented in the later parts of this work. For all experiments, a pre-determined mass of original HPAL residue was leached by alkaline solution with known concentration and the leach solution and solid residue were analyzed to determine the concentration of sulfur.

Figure 10 shows the sulfur content remaining in the leached HPAL residue at various S/L ratio using 1 M NaOH at 25 °C for 30 min residence time. A plateau is reached for S/L≤1/2; hence, a S/L ratio of 1/2 was chosen as the optimum value, since higher S/L ratio requires a smaller reactor size; hence reducing the capital expenditure and enhancing the feasibility of the developed process. The results obtained are in agreement with the theoretical values. Under these conditions, the concentration of sulfur was reduced to 0.989 wt.%, corresponding 67% reduction from pre-leached sulfur level, and is below the 1 wt.% threshold for sulfur level in steelmaking.
Figure 10 - The content of the remaining sulfur in the leached HPAL residue at various S/L ratios using 1 M NaOH at 25 °C and 30 min residence time. Error bars represent the standard error of the mean for three replicates.

4.2.3 Leaching using NaOH

Figure 11 presents the concentration of sulfur in the leach solution at 25, 45, 65, and 80 °C. 1 M NaOH was utilized as the leachant with a S/L of 1/2. As shown in Figure 11, the reaction is rapid and equilibrium is achieved after 10 min, which was chosen as the optimum residence time for the current process.

Leaching efficiency increased by 9% at 80 °C in comparison to leaching efficiency at 25 °C, which might be related to a more complete dissolution of natroalunite in the system. However, considering the energy and operating expenditure required to run the process at 80 °C, and that the gain in extraction is below 10%, 25 °C was selected as the optimum operating temperature going forward.
4.2.4 Leaching using KOH

Figure 12 presents the concentration of sulfur in the leached solution at 25, 45, 65, and 80 °C when 1 M KOH was utilized as the leachant with a S/L of 1/2. As shown in Figure 12, the reaction kinetics at 25 °C and 45 °C were significantly slower with KOH than with NaOH. The final leaching efficiency with KOH was 64%, which is 6% less than that of NaOH. Reaction 12 illustrates the leaching process with KOH. Considering the leaching efficiency at low temperatures, kinetics, and significant difference in cost between NaOH and KOH, NaOH was chosen as the leaching agent in this study. A kinetic model was developed to explain the difference in leaching efficiencies between NaOH and KOH, which is presented in the section 4.5 of the thesis.

\[
\text{NaAl}_3\text{(SO}_4\text{)}_2(\text{OH})_6 + 6\text{KOH} \rightarrow 3\text{KAlO}_2 + 0.5\text{Na}_2\text{SO}_4 + 1.5\text{K}_2\text{SO}_4 + 6\text{H}_2\text{O} \tag{12}
\]
Figure 12 - Concentration of extracted sulfur as a function of time at various temperatures using 1 M KOH at S/L of 1/2 as the leaching agent. Error bars represent the standard error of the mean for three replicates.

4.2.5 Leaching using Na$_2$CO$_3$ and NaHCO$_3$

Figure 13 compares the leaching effects of Na$_2$CO$_3$, NaHCO$_3$, KOH and NaOH. As can be seen in Figure 13, the leaching efficiency using Na$_2$CO$_3$ and NaHCO$_3$ was significantly lower than that of NaOH. After two hours of leaching with a S/L of 1/2 at 80 °C, the leaching efficiency of sulfur using 1 M Na$_2$CO$_3$ and 1 M NaHCO$_3$ were 41.4% and 29.8%, respectively. The leaching efficiencies of sulfur extraction using NaOH and KOH under similar operating conditions were 67% and 64%, respectively. The reason behind the difference in leaching efficiencies was most likely due to the difference in base strength. While the pH of 1 M NaOH and 1 M KOH were between 13.5 and 13.8 at 80 °C, the pH of 1 M Na$_2$CO$_3$ and 1 M NaHCO$_3$ were only 11.0 and 8.3, respectively. Reactions 13 and 14 illustrate the leaching process for NaHCO$_3$ and Na$_2$CO$_3$, respectively.

\[
\text{NaAl(SO$_4$)$_2$(OH)$_6$ (s) + 6NaHCO$_3$} \rightarrow 3\text{NaAlO$_2$ + 2Na$_2$SO$_4$ + 6H$_2$CO$_3$} \quad (13)
\]
\[
\text{NaAl(SO$_4$)$_2$(OH)$_6$ (s) + 3Na$_2$CO$_3$} \rightarrow 3\text{NaAlO$_2$ + 2Na$_2$SO$_4$ + 3H$_2$CO$_3$} \quad (14)
\]
4.2.6 Leaching using Ca(OH)$_2$

Because of its abundance and low cost, Ca(OH)$_2$ is an attractive choice of leachant. However, because of its limited solubility (0.02 mol/L at 25 °C), it was not possible to make a 1 M solution in this study. Reaction 15 presents the reaction between Ca(OH)$_2$ and natroalunite.

$$2\text{NaAl}_2\text{(SO}_4\text{)}_3\text{(OH)}_{3\text{aq}} + 6\text{Ca(OH)}_2 \rightarrow 3\text{Ca(AlO}_2\text{)}_2 + \text{Na}_2\text{SO}_4 + 3\text{CaSO}_4.2\text{H}_2\text{O} + 6\text{H}_2\text{O} \quad (15)$$

On the basis of the reaction mechanism, and the reaction stoichiometry illustrated in section 4.2.1, the theoretical S/L ratio is 1/22, which implies that to use Ca(OH)$_2$ as leaching agent, the tankage requirement is 11 times larger than the case where NaOH is utilized. This will increase the capital expenditure significantly, which is undesirable. To further investigate the feasibility of employing Ca(OH)$_2$ as the leaching agent, leaching experiments were conducted at 25 °C and 80 °C at S/L of 1/22. The leaching efficiencies at 25 °C and 80 °C after 2 h residence time were 9.7% and 17.3%, respectively. Because of the low leaching efficiency and larger tankage requirement, Ca(OH)$_2$ was not chosen as a leaching agent in this
study. Figure 14 presents the concentration of the extracted sulfur in the leached solution using all five bases as the leaching agent.

Figure 14 - The concentration of the extracted sulfur in the leached solution using Ca(OH)$_2$ (0.02 M, S/L=1/22, 25 °C and 80 °C), NaHCO$_3$ (1 M, S/L=1/2, 80 °C), Na$_2$CO$_3$ (1 M, S/L=1/2, 65 °C, 80 °C), and NaOH (1 M. S/L=1/2, 80 °C) as the leaching agent. Error bars represent the standard error of the mean for three replicates.

4.3 EXTRACTION OF ALUMINUM

Most of aluminum present in the sample was associated with natroalunite (NaAl(SO$_4$)$_2$(OH)$_6$); thus we also recorded aluminum concentration in the leach solution, and the results are presented below.

4.3.1 Extraction of Aluminum Using NaOH as Leachant

Figure 15 presents the extraction of aluminum in 1 M NaOH at temperatures of 25, 45, 65, 80 °C with S/L of 1/2. As can be seen, at 25 °C and 45 °C, the extraction of aluminum follows the same trend as sulfur extraction, where a plateau is reached after 10 min. This phenomenon was expected, because most aluminum in HPAL residues is associated with
natroalunite. However, at reaction temperatures of 65 and 80 °C, a gradual decrease in the concentration of aluminum in the leach solution was observed. This phenomenon can be explained by the reaction of silica/silicate minerals with sodium hydroxide at high reaction temperatures producing silicate ions, which could react with aluminum and aluminate ions, producing sodium aluminosilicate, thus reducing aluminum concentration in the system.

Figure 15 - Concentration of extracted aluminum as a function of time at various temperatures using 1 M NaOH as leaching agent at 25, 45, 65, and 80 °C. Error bars represent the standard error of the mean for three replicates.

4.3.2 Extraction of Aluminum Using KOH as Leachant

Figure 16 presents the extraction of aluminum in 1 M KOH leach solution at various temperatures with S/L of 1/2. Similar to the NaOH case, the extraction of aluminum increased in the beginning of the reaction and plateaued at lower reaction temperatures. However, at high reaction temperatures (65, 80 °C), the extraction of aluminum decreased with time. The reason behind this decrease could also be related to the dissolution of silica/silicate minerals in KOH at high reaction temperatures producing silicate ions, which could react with aluminum and aluminate ions, producing aluminosilicate.
Figure 16 – Concentration of extracted aluminum as a function of time at various temperatures using 1 M KOH as leaching agent at 25, 45, 65, and 80 °C. Error bars represent the standard error of the mean for three replicates.

4.4 EXTRACTION OF SILICON

As discussed in section 4.3, at higher temperatures (65 °C, 80 °C), the extraction of aluminium decreased with increasing residence time. It was hypothesized that aluminosilicate precipitated during the process. Therefore, the concentration of silicon at various temperatures as a function of time was investigated. Figure 17 presents the concentration of silicon, measured by ICP-OES, in the NaOH leach solution (1 M, S/L of 1/2). Similar to aluminium, the concentration of silicon decreased with increasing time at higher temperatures (65, 80 °C). However, the difference between the concentration drop of aluminium and silicon did not match their molar ratio in aluminosilicate. This phenomenon will be investigated in a future study to elucidate the mechanism.
Figure 17 - Concentration of extracted silicon as a function of time at various temperatures using 1 M NaOH as leaching agent at 25, 45, 65, and 80 °C. Error bars represent the standard error of the mean for three replicates.

4.5 CHARACTERIZATION OF LEACHED HPAL RESIDUE

To further confirm the dissolution of natroalunite present in the HPAL residue, the leached HPAL residue was characterized by X-ray diffraction, SEM-EDS, and aqua regia digestion followed by ICP-OES. Figure 18 shows the comparison between X-ray diffraction pattern of the leached and original HPAL residue. As can be seen, the peaks associated with natroalunite were eliminated after leaching with 1 M NaOH at 25 °C with S/L of 1/2 and 10 min residence time, confirming that the most of natroalunite has been dissolved in the reaction.
Figure 18 - XRD pattern of the leached vs. original HPAL residue. Leaching conditions: 1 M NaOH, 25 °C, S/L=1/2, 10 min residence time.

Table 3 presents the elemental composition of original and leached HPAL residue. On the basis of the measured concentration for sulfur and aluminum in the leach liquor, 67% of sulfur and 64% of aluminum present in the original HPAL residue were leached out with NaOH. The remaining aluminum can be attributed to aluminum associated with hematite and chromite or aluminosilicate minerals in the residue. Most of the remaining sulfur was associated with iron. Sulfur associated with iron was most likely due to the entrapment of sulfate in the hematite structure during the formation of hematite particles. Hematite formed in sulfate-based systems has a certain degree of sulfur impurities, typically in the range of 0.5-1 wt.%.\(^2\)

Table 3 - Chemical compositions of the original HPAL residue and leached HPAL using 1 M NaOH at 25 °C for 10 min with S/L of 1/2 measured by ICP-OES.

<table>
<thead>
<tr>
<th>Element / wt.%</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Mg</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Before leaching</strong></td>
<td>53.7</td>
<td>0.038</td>
<td>1.28</td>
<td>1.68</td>
<td>0.205</td>
<td>0.061</td>
</tr>
<tr>
<td><strong>After leaching</strong></td>
<td>56.1</td>
<td>0.043</td>
<td>0.132</td>
<td>0.608</td>
<td>0.249</td>
<td>0.067</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element / wt.%</th>
<th>Na</th>
<th>Ca</th>
<th>K</th>
<th>S</th>
<th>Si*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Before leaching</strong></td>
<td>0.092</td>
<td>0.093</td>
<td>0.003</td>
<td>2.98</td>
<td>4.20</td>
</tr>
<tr>
<td><strong>After leaching</strong></td>
<td>0.135</td>
<td>0.073</td>
<td>0.003</td>
<td>0.99</td>
<td>4.20</td>
</tr>
</tbody>
</table>

\(^*\)Si composition was measured by XRF.
To further support the claim that most of natroalunite compound has been dissolved under the stated operating conditions, SEM-EDS was employed. Figure 18 presents the SEM-EDS elemental maps of sulfur and aluminum in the original and leached HPAL residue. As can be seen, most of the sulfur and aluminum associated to natroalunite have been dissolved; hence confirming the removal of natroalunite during the leaching process.

![SEM-EDS elemental maps of sulfur and aluminum in the original and leached HPAL residue.](image)

Figure 19 - SEM-EDS elemental maps of sulfur and aluminum in the original and leached HPAL.
4.6 INVESTIGATION OF THE KINETICS OF THE LEACHING PROCESS

The leaching results in this study suggested that in the case of NaOH, the leaching efficiency first increases rapidly with time and then slows down as it reaches reaction equilibrium. The leaching efficiency of sulfur is mostly limited by the presence of free OH\(^-\) in the system. If the amount of OH\(^-\) is not sufficient for the complete dissolution of natroalunite in the system, no additional natroalunite can be leached.

To investigate and to explain the differences in kinetics when using NaOH and KOH as leachants, kinetic models for the leaching of sulfur from HPAL residue using NaOH and KOH were developed. The concentration vs. time curves were fitted by polynomials (as shown in Figure 20 (a) and Figure 21 (a)). Using the differential method and the equations of (6) and (7), the plot of \(\log(\frac{dc}{dt})\) vs. \(\log(c)\) resulted in straight lines with the adjusted coefficient of determination (\(R^2\)) more than 0.99, for which the intercept is \(\log k\), where \(k\) is the apparent reaction rate constant (Figure 20 (b) and Figure 21 (b)).

\[
\frac{dc}{dt} = k c^n
\]  \(\text{(6)}\)

\[
\log(\frac{dc}{dt}) = \log k + n \log(c)
\]  \(\text{(7)}\)

Using the apparent reaction rate constant (\(k\)) from Figure 20 (b) and Figure 21 (b), the Arrhenius equation (Equation 8) was used to determine the activation energy of the reaction, where \(A\) is the frequency factor, \(E\) is the apparent activation energy (J.mol\(^-1\)), \(R\) is the universal gas constant (8.314 J. mol\(^-1\).K\(^-1\)), and \(T\) (K) is absolute temperature.

\[
k = A\text{Exp}\left(-\frac{E_a}{RT}\right)
\]  \(\text{(8)}\)

Plotting \(\ln k\) as a function of \(1/T\) resulted a straight line with \(R^2\) of 0.83 (Figure 20 (c)). Using the slope of the line, the apparent activation energy for leaching of sulfur from HPAL residue using 1 M NaOH was calculated to be 88.5 kJ/mol. It should be mentioned that variations in the plots are due to the convolution of errors and that the mechanism does not change over the temperature range of interest. According to the literature, the apparent
activation energy of the diffusion-controlled leaching is ~20 kJ/mol; whereas it is greater than 40 kJ/mol for a chemical reaction-controlled leaching. Thus, on the basis of the $E_a$ value, the sulfur leaching process from HPAL residue is controlled by chemical reaction in NaOH system.

![Graphs showing leaching kinetics](image)

Figure 20 - a) Concentration of sulfur as a function of time at various temperatures using 1 M NaOH, S/L=1/2 as the leaching agent. (b) Plot of $dc/dt$ (i.e., reaction rate) as a function of log $c$, where the intercept is log $k$. (c) Arrhenius equation plot to determine the apparent activation energy ($E_a$) of the leaching reaction using 1 M NaOH, S/L=1/2. Error bars represent the standard error of the mean for three replicates.

To understand the slow leaching kinetics in the KOH system, similar calculations were performed to elucidate the mechanism. Figure 21 (a) shows the concentration of the extracted sulfur as a function of time at various temperatures using KOH as the leaching agent. Figure 21 (b) shows reaction rate as a function of log $c$ and Figure 21 (c) shows the
Arrhenius plot to determine the apparent activation energy of \( E \) of the leaching reaction using 1 M KOH as leaching agent, which was calculated to be 97.9 kJ/mol. This result is consistent with the result of a previous study using KOH as the leaching agent for the extraction of aluminium and sulfur from alunite, which showed an activation energy of 94.18 kJ/mol. The calculation also explained the slow kinetics of sulfur extraction in KOH compared with NaOH. This result is encouraging as NaOH is a more economical choice of leaching agent compared with KOH.

Figure 21 - a) Concentration of sulfur as a function of time at various temperatures using 1 M KOH at S/L=1/2 as the leaching agent. (b) Plot of \( dc/dt \) (i.e., reaction rate) as a function of \( \log c \), where the intercept is \( \log k \). (c) Arrhenius equation plot to determine the apparent activation energy \( E \) of the leaching reaction using 1 M KOH with S/L=1/2. Error bars represent the standard error of the mean for three replicates.
To assess the economic feasibility of the developed process, a preliminary economic analysis on the operating expenditure of the developed process was performed. The cost of electricity was not included because of the feasibility of the developed process at room temperature. A preliminary economic analysis of operating costs is presented in Table 4. A summary of average reported prices of the bases used in this study is provided in Table 5.

Table 4 – Preliminary cost analysis for processing 1 tonne of HPAL residue.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Unit Price</th>
<th>Cost per tonne of HPAL residue (USD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPAL Residue</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>375 USD/tonne</td>
<td>60</td>
</tr>
<tr>
<td>Water</td>
<td>1.08 USD/m^3</td>
<td>2.07</td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>62.07</td>
</tr>
</tbody>
</table>

Table 5 – Average reported price for the bases used in this study.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Unit Price, USD/tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slaked Lime (Ca(OH)_2)</td>
<td>100-142</td>
</tr>
<tr>
<td>Caustic soda (NaOH)</td>
<td>375</td>
</tr>
<tr>
<td>Caustic potash (KOH)</td>
<td>888</td>
</tr>
<tr>
<td>Soda ash (Na₂CO₃)</td>
<td>155</td>
</tr>
<tr>
<td>Baking soda (NaHCO₃)</td>
<td>100-180</td>
</tr>
</tbody>
</table>

As of August 2017, the price of 62% iron ore is 74.14 United States dollars (USD). Although, the grade of the valorized HPAL residue is not comparable to the industrial standard at this point, it is worth noting that the economic benefits of the current study are not limited to the sale of the leach residue, it is also beneficial in terms of extending the lifespan of tailing ponds, reducing the operating expenditure of the HPAL process at the Goro plant.
CHAPTER 6    CONCLUSIONS

In the present work, the process of the sulfur removal and recovery of hematite from HPAL residue was investigated. HPAL residue is the byproduct of nickel production from laterite ore, which can be utilized as a secondary resource of iron for steelmaking. The HPAL residue was obtained from Vale’s Goro plant, located in Yaté, Prony Bay, New Caledonia. The current study was focused on three main aspects: 1) thorough characterization of HPAL residue, using various spectroscopy and microscopy techniques; 2) performing systematic leaching experiments to establish the best leachant and optimal operating conditions for the sulfur removal process; and 3) investigating the kinetics of the leaching process. The following points were concluded on the basis of the results obtained from this study.

1) The major source of sulfur in the HPAL residue is derived from natroalunite. The sulfur content in the residue was 2.98 wt.%. HPAL residue particles were fine (average size: 1.88 µm).

2) The leaching results indicated that 1 M NaOH at 25 °C, S/L of 1/2 and 10 min residence time were the optimum operating conditions.

3) It was found that natroalunite dissolution is chemical reaction-controlled, and the activation energy using NaOH and KOH as the leaching agents were 88.5 kJ/mol and 97.9 kJ/mol, respectively.

The results of this study provide a fundamental understanding of the leaching process and an insight into the feasibility of the process on an industrial scale. The characterization results showed that natroalunite, a major source of sulfur-bearing compound in the residue, is finely distributed throughout the residue. The leaching experiments using five different bases provided an in-depth understanding of the process and operating conditions, which could potentially lead to the development of an industrially viable process to recover hematite from HPAL residue as a source of iron for the steelmaking industry.
CHAPTER 7  RECOMMENDATIONS FOR FUTURE WORK

Upon completion of this study, a number of prospective investigations have been identified:

1) Future research needs to be conducted to investigate the recycling of NaOH. Although NaOH has been chosen as the most efficient leachant in this process, utilizing NaOH as a leachant remains a challenge from an economic perspective. Therefore, a future study on the recycling of NaOH would be extremely valuable.

2) The particle size of hematite in HPAL residue remains a significant challenge to recover hematite as a feedstock for steelmaking industry. Future investigations could be performed on the aspect of adding hematite seed during the HPAL process to encourage heterogeneous nucleation, increasing hematite particle size.

3) The moisture level of HPAL residue remains a significant challenge for the process, as the moisture of the residue needs to be reduced for leaching and transportation. A novel and cost-effective study on drying HPAL residue needs to be performed to make the process feasible in an industrial scale. The effect of microwave drying can be explored in the future.

4) The feasibility of using end-of-life NaOH leachant from the desulfurization process as a neutralizing agent for HPAL process could be studied. Such a study would increase the value of the developed process, because utilizing NaOH as neutralizing agent will not produce insoluble sulfur-bearing compounds, such as gypsum.

5) Performing an in-depth techno-economic analysis to explore the feasibility of the developed process at Vale New Caledonia.
REFERENCES

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34. Ma, B. *et al.* Pilot-scale plant study on the innovative nitric acid pressure leaching


APPENDIX A: Effect of Base Concentration on the Extraction of Sulfur

The development of the leaching process started with investigating the effect of NaOH concentration on the leaching efficiency of sulfur and aluminum. Experiments were performed at 80 °C for 4 h at S/L of 1/20. Figure 22 presents the leaching results based on the solid characterization using XRF. On the basis of the results, it was concluded that 1 M is the best concentration among those studied here.

Figure 22 - The effect of NaOH concentration on the extraction of sulfur, aluminum, iron.
APPENDIX B: Effect of Residence Time on the Extraction of Sulfur

The effect of residence time on the extraction of sulfur was investigated. The effect of residence time is a crucial factor in determining the feasibility of the developed process, because of higher capital expenditures when the residence time is long. Figure 23 presents sulfur, aluminum, and iron concentration based on the solid characterization using XRF as a function of time when 1 M NaOH at 80 °C with S/L of 1/20 was used. As can be seen, the dissolution of alunite was very fast and the reaction was completed before 30 min.

![Figure 23 - The effect of residence time on the extraction of sulfur, aluminum and iron](image)

Figure 23 - The effect of residence time on the extraction of sulfur, aluminum and iron
APPENDIX C: Effect of Reaction Temperature on the Extraction of Sulfur

The energy consumption of the proposed process is an important factor and because of the lack of literature data on this topic, various temperatures were investigated in this study. Figure 24 presents sulfur, aluminum, and iron concentration based on the solid characterization using XRF as a function of temperature when 1 M NaOH with S/L of 1/20 and 4 h residence time was used. The results showed that the effect of temperature was not too significant; thus, 25 °C was chosen as the most effective leaching temperature. This result was a key aspect of the economic feasibility of the developed process, as the steelmaking industry operates with a thin profit margin.

Figure 24 - The effect of reaction temperature on the extraction of sulfur, aluminum and iron.
APPENDIX D: Effect of Utilizing Recycled Sodium Hydroxide as Leachant

The effect of utilizing recycled sodium hydroxide as leachant was briefly studied in this work. The process investigated was with 0.2 M NaOH, at 80 °C, 2 h residence time, and S/L of 1/20. At dilute S/L ratio, the recycled agent is as effective as fresh sodium hydroxide. A future study will be conducted to develop a recycling process at the optimum S/L of 1/2. Figure 25 presents the effect of utilizing recycled sodium hydroxide as leachant analyzed with XRF characterization of the solids.

![Figure 25 - The effect of utilizing recycled sodium hydroxide as leachant.](image-url)
APPENDIX E: Magnetic Separation of Hematite from Impurities

Physical separation of impurities, such as magnetic separation, is often desirable to improve the quality of the ore before hydrometallurgical treatment. Considering the importance of physical separation, a simple magnetic separation study was performed using NdFeB (N35SH) magnet with 12 kGauss. The XRD patterns of the magnetically separated and original HPAL sample were compared and presented in Figure 26. The XRD pattern showed that magnetic separation did not separate hematite from the HPAL residue. The fine particle size of hematite and relatively fine natroalunite particle probably affected the selectivity of magnetic separation.

Figure 26 - The comparison of X-Ray Diffraction (XRD) pattern between magnetically separated HPAL residue and original HPAL residue.
APPENDIX F: Additional SEM-EDS Images of the HPAL Residue

The following figures illustrate additional SEM-EDS images taken from the HPAL residue.

Figure 27 - SEM image and EDS elemental mapping of HPAL residue.

Figure 28 - SEM image of HPAL residue indicating (a) hematite, natroalunite, and (b) magnesium silicate particles morphology.
Figure 29 - Low magnification SEM image of HPAL residue and EDS elemental mapping.