ON-LINE ACID MEASUREMENTS VIA ELECTRODELESS CONDUCTIVITY AT HIGH TEMPERATURES

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
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ABSTRACT

On-line Acid Measurements via Electrodeless Conductivity at High Temperatures

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2009

This M.A.Sc. work focuses on the development of a sensor to operate at industrially relevant conditions, directly in autoclaves, to generate accurate online free acidity estimates. The main goal is to obtain accurate (within 5% from titrated) free acid estimates at leach temperature (up to 260 °C) while compensating for various metals in solution at high solid loadings. The electrodeless conductivity sensor and calibration technique that were developed in previous work have been improved upon for operation in slurry systems. The sensor operates at temperature on the basis of induction currents and is suitable for very concentrated solutions containing solid dispersions. Three systems have been investigated: limonitic feeds, limonite-saprolite blends, and a converter slag feed. Up to 40 wt.% solids were tested with investigation carried out from 25 °C to 260 °C. High quality estimates of acidity were produced for all systems studied, with the average difference between measured and titrated acidities being within 5%.
ACKNOWLEDGEMENTS

First and foremost, I would like to thank Professor Vladimiros G. Papangelakis for his guidance and support throughout this work. In addition to this, the motivation and encouragement he has provided always ensured I push myself to achieve the goals set out for this work. His mentorship is greatly appreciated.

Next, the members of the APEC group are acknowledged for their support. In particular, Ghazal Azimi, Ilya Perederiy, and Sammy Peters are acknowledged for the time spent discussing aspects of my work and helping with experimental setups and procedures.

Ming Huang is sincerely thanked for all of the support and guidance he has provided from day one of this project. He has been an integral part of my success; especially with the more subtle life lessons he has taught me over the last two years.

Kevin Quackenbush’s contribution to this work has been extensive and the relationship developed over time cannot be understated. He is thanked for his time, advice and of course for the hardware he and Foxboro Co. have provided.

Paul Jowlabar is also acknowledged, as he has been a constant source of information and support dealing with all mechanical aspects of this project. He is thanked for the time he has spent with me and the time he has allowed me to spend in the Unit Operations Laboratory working on various aspects of this work.

NSERC and the Centre for Chemical Process Metallurgy are thanked for their contribution to this work.

Lastly, I would like to, from the bottom of my heart, thank God and the family given to me for the strength and support provided throughout my life.

Ramanpal Singh Saini
September 2009
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### DEFINITIONS

The majority of definitions and nomenclature can be found directly in the text. Below is a list of terms that are not explicitly defined.

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electromotive Force</td>
<td>The external work expended per unit of charge to produce an electric potential difference across two open-circuited terminals; this electric potential difference is created by separating positive and negative charges, generating an electric field. Originally referred to the 'force' with which positive and negative charges could be separated. (<a href="http://www.wikipedia.org">www.wikipedia.org</a>)</td>
</tr>
<tr>
<td>Free Acid</td>
<td>For the systems of study it is the concentration of H$_2$SO$_4$. The total sulphate in solution, minus that stoichiometrically bound to metal sulphates.</td>
</tr>
<tr>
<td>HPAL</td>
<td>High pressure acid leaching. A process by which high pressures and temperatures are used in the presence of strong acids to leach metals from ore bodies. Generally carried out in high pressure reaction vessels called autoclaves.</td>
</tr>
<tr>
<td>HPOXAL</td>
<td>High pressure oxidative acid leaching. A process where high temperatures and pressures in the presence of strong acids and oxygen are used to dissolve oxides and oxidize sulphides to liberate metals.</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Motivation

The electrical conductivity of an aqueous solution offers considerable insights. The degree of dissociation of various species can be determined, precipitation and complex formation reactions can be explored, and direct quantitative analysis of acids, bases and salt solutions can be undertaken with great accuracy\(^1\).

In the chemical process industry, the presence of strongly concentrated acidic solutions is common and often necessary to attain desired products and process performance. For instance, in the hydrometallurgical industry, reaction vessels at high temperatures and pressures, and in the presence of strong acids, are used to manipulate solution chemistry resulting in a high recovery of base metals from ore bodies.

Laterite oxide ores are surface formations that are rich in iron and aluminum, but more importantly, contain significant amounts of nickel and cobalt that can be extracted through aqueous leaching routes. After reactions have taken place in the vessel (autoclave), the exiting leach liquor is low in iron and aluminum, but high in nickel and cobalt, allowing for a profitable recovery of metals.

Yet another example is high temperature pressure oxidative acid leaching, which is currently being explored as an option to recover valuable base metals from smelter slags\(^2\). Slag is a solid waste by-product of smelting and converting operations, which are carried out in pyrometallurgical plants worldwide. Base metals are found both as oxides and sulphides in slag bodies and thus require both acid and oxygen to dissolve into solution\(^2,3\).
The use of concentrated sulphuric acid in HPAL and HPOXAL processes is necessary to reach sufficient yields; reduce process times; and to ensure desired metals remain soluble for subsequent processing. On the other hand, excess acid dissolves more impurities, such as iron, into solution. In later purification stages, leach solutions are gradually neutralized with lime to produce gypsum tailings: a waste product that, although environmentally benign, should preferably be kept to a minimum, due to its requirement for large storage volumes. Therefore, it is essential to optimize sulphuric acid use during processing. Currently, no direct means of monitoring solution free acidity at temperature exists, where free acidity is defined as total sulphate minus that stoichiometrically bound to metal salts.

Measurement of a solution’s electrical conductivity has been shown to be more suitable for generating reproducible concentration estimates in strongly acidic solutions compared to pH measurements. Since the pH scale is logarithmic, significant acid concentration errors can be introduced if there is any uncertainty in the measurements; this is especially true for concentrated strong acids. Hydrometallurgical reactors at the industrial level operate under supersaturation, and contain various particles that can easily foul contact-type sensors, resulting in incorrect measurements and inaccurate estimates of acidity. Conductivity measurements are normally accurate within a few tenths of 1%, meaning they are trustworthy for online systems working in real time.

1.2 Objective

This work focuses on the suitability of a commercially available sensor to operate at industrially relevant conditions, directly in autoclaves, to generate accurate online and real-time free acidity estimates. The main goal is to obtain accurate (within 5% from titrated) free
acid estimates at leach temperature (up to 260 °C) and high pulp density, while also accounting for variations in feed composition. Three main systems have been investigated: HPAL of both limonitic laterite ores (low magnesium content) and limonite-saprolite ore blends (high magnesium content), as well as HPOXAL of converter slags (results from this study are presented in Appendix B).

1.3 Thesis Overview

The present document is structured as follows: Chapter 2 is a general review of relevant conductivity theory and parameters affecting acidity measurements. Chapter 3 outlines the experimental setup and procedures used to conduct HPAL tests. Design considerations and cell specifications are also given for the high temperature glass sensors used for this work. Chapter 4 deals with HPAL processes for Ni-Co extraction from lateritic ores. Two feeds are investigated, a low Mg limonite, and a high Mg limonite/saprolite blend. Correlations developed in this work are tested on systems under various conditions seen in industry and good estimates of acidity are produced. A sensitivity analysis is conducted to assess the impact of fluctuation of inputs to the correlation. Chapter 5 summarizes the major conclusions drawn from this work. Chapter 6 outlines recommendations for future work. Each chapter contains its own references.
References

CHAPTER 2

BACKGROUND

A great deal of knowledge about a system can be gained by studying its electrical conductivity. This is especially true for aqueous systems where conductivity can provide valuable quantitative chemical compositional information\(^1\). Let us first examine the theory behind conductivity measurements and then proceed to the importance of using electrodeless conductivity for high temperature industrial environments.

2.1 Electrical Conductivity Theory

There are many different instruments available to measure the electrical conductivity of a solution, generally all operate based on the same underlying principle. By imposing an electric field in an aqueous solution its electrical resistance can be measured. The specific conductivity, \(\sigma\) (S/m), is related to the reciprocal of the solution resistance, \(R\) (\(\Omega\)), an extensive property that can be directly measured, and the ratio of the distance between the electrodes, \(l\) (m), divided by their surface area (m\(^2\)). By definition, 1 Siemens equals 1 \(\Omega^{-1}\).

\[
\sigma = \frac{1}{R} \frac{l}{A} = \frac{1}{R} C_{cell}
\]  

(2.1)

Typically, this length to area ratio is a constant, and is referred to as the cell constant, \(C_{cell}\) (m\(^{-1}\)). For a strong electrolyte, the specific conductivity can be normalized to an equivalent conductivity, \(\Lambda\) (\(\Omega^{-1}\) m\(^2\) mol\(^{-1}\) of charge) through dividing by the product of the ionic charge, \(z\), and molar concentration, \(c_i\) (mol/m\(^3\)), of either the cation or anion.

\[
\Lambda = \frac{\sigma}{zc_i}
\]  

(2.2)
\( \Lambda \) is then the sum of the ionic equivalent conductivities of the anion and cation in solution, \( \lambda_+ \) and \( \lambda_- \):

\[
\Lambda = \lambda_+ + \lambda_-	ag{2.3}
\]

Since most solutions of interest are comprised of multiple electrolytes, the specific conductivity can then be related to the equivalent conductivities of all ions in solution by:

\[
\sigma = \sum_{i=1}^{n} z_i c_i \lambda_i \tag{2.4}
\]

where \( z_i \), \( c_i \), and \( \lambda_i \) are the ionic valence, molar concentration, and equivalent conductivity of ion, \( i \). The mobility of ions in a solution is an important factor influencing its conductivity. The ionic equivalent conductivity, \( \lambda_i \), is related to the mobility of an ion through Faraday’s constant (C/mol),

\[
\lambda_i = FU_i \tag{2.5}
\]

where \( U_i \) ([m/s]/[V/m]) is the mobility of ion \( i \). The value of \( \lambda \) depends upon the ionic strength of the solution. Typically, it drops with increasing ionic concentrations\(^{18}\). Its value at the limit of infinite dilution is known as the limiting equivalent conductivity.

From the above relationships we see that the electrical conductivity of a solution depends upon both the equivalent conductivities of ionic species and their respective concentrations. In the past, various techniques have been developed to examine the electrical conductivity of a solution. A concise review can be found elsewhere\(^2\). For this work electrodeless conductivity has been utilized over the more conventional contact type methods because there is less polarization error due to electrode fouling.
2.2 Electrodeless Conductivity

Historically, the first contactless method for measuring electrolyte conductivity was described by Piccard and Frivold\(^3\) in 1920. The purpose of the work was to show that induced currents are produced in an electrolyte in a similar manner to metallic conductors, and that it is possible to measure the resistance of a solution without electrodes, thus eliminating polarization. In 1926, Ruben\(^4\) described a setup composed of two coils where the conductance of an electrolyte contained in a test tube threading both coils was measured. Relis\(^5\), in 1947, was the first to illustrate the use of magnetic induction devices utilizing toroidal inductors for conductivity measurements in electrolyte solutions. After this time a number of patents emerged, further improving the technique of electrodeless conductivity to a point where it became commercially available in the 1950’s\(^6\). In 1979, Koski and Danielson\(^7\) designed a high temperature electrodeless probe, and in 1992 a three-toroid electrodeless sensor was developed by Reese\(^8\) to detect possible cell damage. The three toroids are arranged coaxially; two are used as drive toroids and one as the pick-up. Switching between sending a signal to both or one drive toroid allows for determination of whether the cell has been damaged externally, if the readings disagree\(^8\). This design is more sensitive, and suitable for low conductivity fluids compared to the two-toroid design\(^8\).

The electrodeless technique uses two toroidal inductors in close proximity to each other. A toroidal inductor is essentially a solenoid (a looping of wire wrapped around air or a metallic core) bent around in a circle and joined at its ends. Due to this shape, a toroid is self-shielding because the expanding and collapsing magnetic field from current oscillations is, for the most part, confined to the toroidal ring, and therefore the toroid is less liable to pickup extraneous signals. Please refer to Figure 2.1 for an illustration.
When two toroids are arranged coaxially, and an alternating current is applied to one toroid (called the primary or drive); an induced voltage will be detected on the other toroid (called the secondary or receiver) if there is a closed path linking them (a wire or an electrolyte solution). The reason for the previous phenomenon is that some stray flux exists in the center hole of a toroid (the magnetic field is stronger at the inner part of the toroid) and if a conducting medium, for example a closed loop of wire is present, a current will be induced in the wire that will in turn induce a current in the secondary toroid in a similar manner.
When magnetic lines of force from one coil “cut” another coil there is mutual inductance between the two. The resistance of the coupling loop and voltage applied to the drive toroid dictates the amount of mutual coupling between the two toroids. The cell constant (or cell factor) for an electrodeless conductivity probe is governed by the ratio of the current path-length to the cross-sectional area of the hole of the toroids\(^6\). Immersion of the cell into standard solutions of known conductivity and computation of the ratio of theoretical conductivity, \(\sigma \, (S/m)\), to measured conductance, \(G \, (S)\), is necessary to calculate the cell constant, \(C_{\text{cell}} \, (m^{-1})\): \[ C_{\text{cell}} = \frac{\sigma}{G} \] (2.6)

This is required because the end effects and geometrically complex current distribution outside the toroid makes it difficult to obtain cell constants in a conventional manner\(^6\). The toroids are covered with a non-conducting insulator that is chemically resistant to the surroundings. Coatings or precipitates that would corrode or scale conventional contact type cells have a minor to nonexistent effect on the measured conductance as long as they do not take up a considerable (roughly < 2 vol.% ) volume of solution\(^6\). In the cases where they do, many corrections are available to compensate for loss of solution in the bore\(^{13}\).
Industrial applications of electrodeless conductivity were originally for measuring ocean salinity. In more recent years, the technique has been used for monitoring acid concentrations in radioactive wastes, metallurgical and pulp and paper process streams$^{1,6}$. 

### 2.3 Conductivity to Acidity

The mobility of H$^+$ ions in water is very high. H$^+$ ions diffuse through aqueous solutions via the Grotthuss mechanism, where their movement can be thought of as hydrogen bond cleavage in front, and hydrogen bond formation behind the moving ion$^{10}$. The result is a high limiting equivalent conductivity compared to other ions in solution$^{11}$. As seen in Figure 2.4, throughout the temperature range of interest, the limiting equivalent conductivity of H$^+$ is much higher than that of other ions. This means that with proper calibration, conductivity measurements can translate to acid concentration values.
In order to obtain an acidity value from a conductivity measurement, a number of parameters must be known about the system. The conductivity changes significantly with temperature, where a change of anywhere from 2 to 7% per °C is not uncommon\(^6,12\).

The existence of a non-continuous phase (e.g. solid particles), tends to drop the overall conductivity measurement. There are a number of different corrections based on the volume fraction of the non-continuous phase available to compensate for dispersions present in solution\(^13\). In the present work, the Bruggeman model was chosen. It is based on particles with a wide size distribution and accounts for the effects of neighboring particles. As well, the model assumes that the field around large particles in dispersion with smaller particles is not disturbed. This makes it possible to evaluate the conductivity of a system considering the medium of small particles and the continuous phase as one. The overall correction takes the following form:

\[
\frac{\sigma}{\sigma_o} = (1 - \varepsilon)^{3/2}
\]  

(2.7)

**Figure 2.4** – Limiting equivalent conductivities of different ions up to 250 °C\(^11\)
where $\sigma$ is the measured conductivity (mS/cm), $\sigma_o$ is the corrected conductivity (mS/cm), and $\varepsilon$ is the volume fraction of the solid phase. The model produces accurate conductivity corrections for volume fractions of up to 20% solids\textsuperscript{13}. For the systems of interest in this work, the volume fraction of solids tends to remain below this limit.

Present work focuses on leaching processes where a significant concentration of metals is present in the leach liquors. The conductivity contribution of all these metals cannot be ignored. However, it has been found previously (Huang \textit{et al.}\textsuperscript{11}), that their contribution can be simplified to an equivalent concentration of overall divalent metals, MSO$_4$. The reason being that divalent metal ions have similar equivalent conductivities resulting in similar changes to the overall conductivity (e.g. Ni, Co, Mg)$^{11,14}$. Trivalent metal ions are insoluble at high temperatures and therefore are present to a much lesser extent in the leaching systems of interest. The main two are Al(III) and Fe(III), both of which tend to hydrolyze and form precipitates at 250 °C. It has been shown (Baghalha \textit{et al.}\textsuperscript{14}, Jankovic \textit{et al.}\textsuperscript{19}) that Al in sulphate solutions tends to exist predominately as a neutral species, Al$_2$(SO$_4$)$_3^0$, and to a lesser extent as the Al$^{3+}$ ion. Its concentration is generally much less than that of the divalent metal ions (roughly 10 to 20 times less), and in most cases can be ignored. It precipitates as hydronium alunite according to:

$$3\text{Al}_2(\text{SO}_4)_3 + 14\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{O}\text{Al}_3(\text{SO}_4)_2(\text{OH})_6(s)\downarrow + 5\text{H}_2\text{SO}_4 \quad (2.8)$$

There is very little Fe(III) present in these systems, typically less than 0.01 molal\textsuperscript{19}; most precipitates at 250 °C as solid hematite according to the following:

$$2\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3(s)\downarrow + 6\text{H}^+ \quad (2.9)$$

where acid is released in the process. Metal sulphates in solution with sulphuric acid tend to drop the overall solution conductivity as their concentration increases for a fixed acidity\textsuperscript{11}. 
The reasons being: (1) as the metals concentration increases, the equivalent conductivities of all species decrease. As more ions enter into solution, the structure of water changes and in most cases is enhanced, making the viscosity rise\textsuperscript{15}. Even in the case of neutral species, such as $\text{Al}_2(\text{SO}_4)_3^0$, an increase in viscosity can be seen, resulting in a greater drag force on moving ions, effectively lowering their mobility and thus their equivalent conductivities\textsuperscript{16,18}. (2) At high temperatures bi-sulphate ion ($\text{HSO}_4^-$) formation is favored, and effectively reduces the concentration of $\text{H}^+$.\textsuperscript{11,17} It has been shown by Huang \textit{et al.} that a rough estimate of the metals concentration is needed to generate an acidity value from a conductivity reading. A rough concentration value can readily be obtained for an industrial process as the overall range of concentrations of metals does not fluctuate drastically during continuous reactor operations.

Acidity becomes thus a function of the overall specific conductivity, metals concentration, temperature, and the volume fraction of solids in solution.
References

CHAPTER 3

EXPERIMENTAL

3.1 Setup

Batch experiments were conducted in a 2L Parr titanium autoclave equipped with an electric heating mantle and magnetic drive for agitation. For the electrical connections, Teflon coated copper wires were fed to the sensor via a Conax® pressure gland assembly. Temperature was controlled by a PID-controller which manipulated both the power output of the heating mantle and water flow in an internal cooling coil controlled with a J-type thermocouple with accuracy of ±1 °C. Please refer to Figure 3.1 for a schematic illustration of the setup.

Figure 3.1 – Experimental setup

1
3.2 Conductivity Cell

Originally, a high temperature conductivity cell was provided by Foxboro Co. (US). This cell was then modified to allow for operation at 250 °C. The commercial cell is rated at 200 °C; at higher temperatures the seal and certain housing components fail, making it necessary to modify the cell. The original cell was disassembled and the toroids placed in a new thicker, more compact borosilicate housing, which was filled with aluminum oxide (similar to the original cell) and partially sealed with Teflon to withstand highly corrosive environments. No pressure differential develops between the cell and the surrounding environment; the Teflon ‘seals’ are in place to produce layers of aluminum oxide that if in contact with the autoclave atmosphere, can sacrificially take in moisture, leaving the aluminum oxide in contact with the toroids dry. Please refer to Figure 3.2 for exact cell specifications. The reason glass is used for the cell housing as apposed to a polymer is that it has a very low coefficient of thermal expansion, about $3.25 \times 10^{-6}$ (length increase/initial length) per °C from 0 °C to 300 °C. This means that the toroids will not be deformed due to the expansion of the housing, resulting in a change of cell constant at temperature, causing inaccurate readings. The full-scale range of measurement for commercially available electrodeless conductivity devices is 0 to 2000 mS/cm. The typical range seen for our systems is from 100 to 300 mS/cm depending upon the ore type and acid-to-ore ratio chosen for leaching.

Two different cell arrangements were constructed. The first was a horizontal bore mimicking the commercial cell provided. This cell was used for laterite leach tests. The second bore was constructed vertically because in the converter slag systems the presence of magnetite resulted in a clogging of the horizontal design. When the cell is in operation the
toroids tend to attract particles which are magnetic. With laterite ores the particles are essentially magnetically inert; with converter slags, a significant amount of magnetite is present which quickly finds its way to rest in the horizontal bore. Foxboro Co. (US) provided high temperature toroids for these cells where the casings were constructed at the University of Toronto. The toroids are rated for 200 °C, but operate up to 260 °C as long as the housing does not deform their shape. Above this temperature, Teflon coating the wires sinters.

![Diagram of cell dimensions and sealing illustration.](image)

**Figure 3.2** – Cell dimensions and sealing illustration.

The sensor was calibrated using a two-point calibration at room temperature with conductivity standards from Fisher Scientific Inc. Considering equation 2.6; the cell constant is essentially the slope of the line for a plot of specific conductivity vs. conductance, where the specific conductivity values are entered manually during calibration. The first calibration point was for zero conductivity (using air as the medium); the second was usually a
conductivity standard at room temperature with nominal conductivity 100 000 μS/cm. Calculation of the cell constant was done internally in the analyzer. After calibration, the readings were checked by immersion of the cell into prepared reference solutions of known conductivity from literature data before mounting in the autoclave.

3.3 HPAL of Laterite Ore

During a typical experiment, a total of approximately 1 L of slurry was placed in the autoclave bomb. The autoclave bomb was then fixed to the head, where it was heated via the heating mantle to 250 °C. Once the temperature had stabilized, acid was injected through an injection system under N₂ pressure. The acid used for leaching tests was Reagent Grade ACS sulfuric acid (96–98%). Before injection, the pressure inside the autoclave was the equilibrium vapour pressure of the solution (approximately 4000 kPa at 250 °C). After injection, an overpressure of approximately 300 to 600 kPa was common. The slurry was agitated by two 4-blade impellers connected to the magnetic drive shaft rotating at 720 rpm (the maximum rate). Specific conductivity and temperature were measured continuously and sent to a computer via a RS-232 serial port for logging and estimation. The analyzer used for conductivity and temperature measurements was the Foxboro Model 875EC Electrochemical Analyzer, which was connected to the cell and an external resistance temperature detector (RTD) for temperature measurements. The J-type thermocouple and RTD agreed within ±1 °C.

Periodic samples were taken and titrated to compare with acid estimates. Samples were withdrawn via a water-cooled sampling line, where the solution was filtered by an in situ graphite filter of 45 μm. Once withdrawn, the samples were re-filtered immediately with a syringe filter of 0.22 μm before being analyzed for acid and metals content. Inductively
Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) was used to analyze for metals present in the samples. Titrations were performed by a Titro-Line 96 unit using certified 0.1 N NaOH as the titrant. To prevent hydrolysis during titration, the metal ions present in aliquots were chelated with a calcium cyclohexane-1, 2-diaminetetraacetate (Ca-CDTA) solution. It should be noted that at pulp densities greater than approximately 30 wt.% some pre-acidification was necessary; the reason being, at high pulp densities the feed slurry is very thick, and tends to accumulate in the bore of the sensor upon heating, preventing accurate reading when acid is injected. The previous condition would not be applicable to a continuous autoclave operation, as the sensor would constantly be exposed to slurry with sufficient acid at steady state.
References

CHAPTER 4

HPAL OF LATERITIC ORES

4.1 HPAL Processes

Hydrometallurgy is a well-established technology for the recovery of valuable metals from ore bodies. Direct sulphuric acid pressure leaching is the method of choice for recovering Ni and Co from limonitic laterite ores\textsuperscript{1,2}. Limonite is rich in Fe (>40 wt.%), and contains typically 1.1-1.4 wt.% Ni and 0.1-0.2 wt.% Co\textsuperscript{2}. Unlike Mg rich saprolite (10-20 wt.%), which is generally processed through pyrometallurgical routes, limonite contains relatively low magnesium (~1 wt.%), resulting in comparatively low acid requirements; making it well suited for HPAL processes\textsuperscript{1-4}. On the other hand, saprolite unlike limonite, contains much less Fe, usually in the range of 10-25 wt.%\textsuperscript{5}. Typically in industry, an optimal mix of limonite and saprolite is used to form a high-grade feed that results in acceptable acid consumption and excellent yields of Ni and Co\textsuperscript{5}.

HPAL is conducted in either titanium or brick and lead-lined steel continuously operating autoclaves, where temperatures are usually between 240 °C to 270 °C\textsuperscript{4}. Depending upon the purity of the feed (pure limonite or a blend of limonite/saprolite), acid-to-ore (a/o) ratios vary from 0.2 to 0.6 kg acid/kg dry ore\textsuperscript{4}. Pulp density normally ranges from 25 to 40 wt.% solids in the feed, with normal retention times of 1 to 3 hours\textsuperscript{4}. Under these conditions Fe, from goethite, and Al, from gibbsite (transformed to boehmite upon heating), dissolve and rapidly hydrolyze to precipitate as hematite and hydronium alunite, respectively\textsuperscript{1,2}. The result is a high selectivity for Ni and Co leaching. In lateritic ores these divalent metals are found as oxides that readily react with acid to form soluble sulphates according to:

\[
\text{MO(s)} + 2\text{H}^+ \rightarrow \text{M}^{2+} + \text{H}_2\text{O} \quad (4.1)
\]
were $M$ represents Ni or Co$^{1,3}$. In saprolite, the major phase of Mg is serpentine, which easily dissolves in sulphuric acid$^6$:

$$2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4(\text{s}) + 12\text{H}^+ \rightarrow 6\text{Mg}^{2+} + 4\text{SiO}_2(\text{s}) + 10\text{H}_2\text{O}$$  (4.2)

The exiting leach liquor is low in Fe, but high in Ni and Co, with ultimate recoveries of more than 95% and 90% respectively$^1$.

### 4.2 Limonite Feed

Indonesian limonite provided by Vale Inco Technical Services Ltd. (VITSL) was used for the first set of tests. Table 4.1 shows the average elemental compositions. The measured moisture content, bulk density, and solids density were 51 wt.%, 1.4g·cm$^{-3}$, and 2.3g·cm$^{-3}$, respectively. Pulp densities of roughly 22 to 40 wt% were tested to ensure the typical range seen in industry was considered. The limonite was weighed and mixed with the according amounts of de-ionized water to attain the final pulp densities of interest.

| Table 4.1 – Elemental composition of limonite in wt.% of dried solids |
|-------------------------|----------------|----------------|----------------|---------------|-------------|---------------|-------------|---------------|
| Fe     | Si     | Al  | Cr  | Ni  | Mg  | Mn  | S   | Co  |
| 47.7   | 3.87   | 1.9 | 1.56 | 1.22 | 1.03 | 0.97 | 0.26 | 0.14 |

#### 4.2.1 Low Pulp Densities

To verify how intimately the estimated acidity followed titrated values, laterite pressure leach tests were first conducted at low solid loadings. Two different solid loadings were tested, 22 wt.% and 27 wt.%, at acid-to-ore ratios of 0.3 and 0.2, respectively. Figures 4.1 and 4.2 show the respective acid profiles and Ni-Co kinetics for these tests. Upon injection, a sharp spike in the measured acidity for both tests is seen. As acid is injected, the solution’s specific conductivity suddenly increases, translating to an abrupt increase in the acidity value. The injection site is in close proximity to the sensor (see Figure 3.1), so a local
elevated concentration of acid is immediately seen. These profiles are consistent with previous work for laterite leach systems\textsuperscript{1,2}. After injection, in the first five minutes, a poor agreement between estimated and titrated acidities is seen. However, this is not surprising as a significant degree of change to the system occurs in this time: acid is consumed while metals are liberated into solution where simultaneous precipitation of Fe(III) to hematite occurs. The sensor readings gradually fall inline with the titrated acidity after this initial interval. The extraction curves show the kinetics for Ni and Co, and are identical to those seen for limonitic systems at similar conditions\textsuperscript{1}. As expected the concentration of divalent metals is fairly low (below 0.2 molal) due to the lower solids loading. The ultimate extractions for Ni and Co in Figures 4.1 and 4.2 are between 94-96%, and 92-95%, respectively. All extractions reported in this work are solution-based. For Figures 4.1 and 4.2, the absolute average difference between measured and titrated values is 4.8% with standard deviation 3.2% and 4.5% with standard deviation 3.0% after the first 5 minutes, respectively.

\textbf{Figure 4.1} – Online acid measurement and Ni/Co kinetics at 250 °C (22% solids, a/o = 0.3)
4.2.2 High Pulp Densities

Industrial autoclaves generally operate at high pulp densities to achieve high throughput of metals. Tests were conducted at 40 wt.% solids where conditions were modified to mimic changes that may occur in full-scale autoclaves. Figure 4.3 illustrates a near steady state system, where 100% of the acid was loaded and the autoclave heated to 250 °C. The profile for the entire temperature range is presented. It is seen that the acid quickly begins to be consumed upon heating as minerals begin to dissolve. The measured acidity was compared to titration values only after the system had stabilized at 250 °C. The divalent metals concentration does not vary greatly where samples were taken as the system has reached the latter stages of leaching; where the majority of metals have dissolved to their maximum extent. The measured acidity follows very closely to the titrated. The average absolute percent difference is approximately 1.1% with a standard deviation of 0.5%. The overall extraction is approximately 93% for both Ni and Co. This result shows that for high pulp densities at leach temperature, the technique works well for systems with slow acid dynamics, i.e. systems operating at near steady state conditions.
Next, in Figures 4.4 and 4.5, two systems are presented which show changes in acidity from an initial low to a final elevated concentration. The system in Figure 4.4 was pre-acidified by 50% (weight) with the remaining acid injected at temperature to give an overall acid-to-ore ratio of 0.2. After injection, the acid concentration is seen to increase in a similar manner as with lower pulp density systems. Initially, before acid injection, the system is in a state where insufficient acid for complete metal extraction is present. Once sufficient acid is injected, the total divalent metals concentration increases and extractions of Ni and Co proceed to their maximum extents. The overall extractions for Ni and Co are approximately 90% and 93%, respectively. The absolute average difference between measured and titrated acidity for Figure 4.4 is 2.6% with standard deviation 2.7%, after the first 5 minutes following acid injection.
Figure 4.4 – Acid measurement and Ni/Co kinetics, 50% pre-acidification at 250 °C (40% solids, a/o = 0.2)

For the system illustrated in Figure 4.5, an initial acid-to-ore ratio of 0.2 is present before injection, meaning there is enough acid present to fully leach out the Ni and Co. This can be seen when examining the total divalent metals concentration in Figure 4.5, there is very little change in the concentration of divalent metals before and after injection. Enough acid is injected to produce an acid-to-ore ratio of 0.3; a considerable surplus of acid. No significant deviation from titrated values is seen throughout the test. Before acid injection, in the time period where the first three samples were withdrawn, the acidity is seen to increase for both the measured (positive slope) and titrated values. During this period, as shown in Figure 4.5, the trivalent metals, Fe and Al, were seen to precipitate slightly, resulting in the observed moderate acid increase. The concentrations of Ni and Co remain relatively stable because they have been liberated to their maximum amounts. The final extractions for Ni and Co are 92% and 94%, respectively. After injection, the measured acid concentration is shown to gradually drop, reflecting perhaps the beginning stages of sensor clogging; the titrated values remain approximately constant. The absolute average difference between measured and titrated acidity for Figure 4.5 is 3.6% with standard deviation of 0.9%.
Next, systems are explored where there is a high Mg content present in the ore, resulting in greater acid requirements and higher concentrations of divalent metals in solution.

### 4.3 Limonite/Saprolite Blend

A limonite-saprolite blend was used for this series of tests, and was provided courtesy of VITSL. Table 4.2 shows the average elemental compositions. The measured moisture content, bulk density, and solids density were 57 wt.$\%$, 1.3 g·cm$^{-3}$, and 2.2 g·cm$^{-3}$, respectively. Once again, pulp densities of roughly 25 to 40 wt.$\%$ were tested to ensure the typical range seen in industry was considered.

| Table 4.2 – Elemental composition of limonite-saprolite blend in wt.$\%$ of dried solids |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fe   | Si   | Al   | Cr   | Ni   | Mg   | Mn   | S   | Co   |
| 26.75 | 15.38 | 0.82 | 0.68 | 4.06 | 4.17 | 0.46 | 0.13 | 0.07 |
Unlike the previous systems where the total divalent metals concentration in solution did not exceed 0.3 molal, all of the tests conducted on the limonite-saprolite blend resulted in a wide range of total metals concentrations, ranging from approximately 0.15 molal to 0.9 molal depending upon the conditions present in the autoclave. The result of this is that metals in solutions will have a much greater impact on the overall solution conductivity and their effects cannot be lumped over this much larger varying concentration range. Therefore, for the following tests, the approximate total divalent metals concentration was needed as an input to calculate the acidity of the solution at predefined stages of the leach; along with the conductivity, solids volume fraction, and temperature. The calculations are based on data for synthetic systems with varying acid and metals concentration, generated in this work and that previously published\textsuperscript{6,7}.

4.3.1 Low Pulp Density

A solids loading of 25 wt.\%, and acid-to-ore ratio of 0.3 was tested with no pre-acidification. Figure 4.6 shows the acid and total divalent metals profile. Again, the titrated acidity follows very closely to that of the measured acidity from conductivity. Compared to the previous systems at low pulp densities, the total divalent metals concentration is much higher, more than twice as high. Because there are more metals to dissolve, more acid is needed; this is especially true for Mg. The extractions of Ni and Co are seen to be relatively poor at approximately 60\% and 50\%, respectively. A greater concentration of acid is needed to facilitate further leaching and increase the solubility of the metals in solution. This is in agreement with previous work on the measurement of solution pH at 250 °C using ceramic electrodes\textsuperscript{12}. For Figure 4.6, the absolute average difference between measured and titrated
acidity is 1.4% with standard deviation 0.8%. This is an excellent agreement and allowed us to proceed onto systems with higher solid loadings.

![Graph](image)

**Figure 4.6** – Online acid measurement and divalent metals profile at 250 °C
(25% solids, a/o = 0.3)

### 4.3.2 High Pulp Densities

The following tests were conducted at 40 wt.% solids. Figure 4.7 illustrates a system that is initially deprived of acid, starting with an acid-to-ore ratio of 0.15. It is seen that the acid quickly begins to be consumed upon heating as metals begin to dissolve. As heating continues, it is clear that the acidity is too low to keep leaching metals in solution: the metals concentration decreases to a minimum when the system reaches 250 °C. Enough acid is injected to produce an overall acid-to-ore ratio of 0.3; the injection time is just slightly before the spike in acidity is witnessed in Figure 4.7. Once this acid enters the system we see that the metals concentration in solution begins to increase along with the acidity. The overall variation in total divalent metals is between approximately 0.15 molal to 0.7 molal.
Comparison with titrated values begins at about 220 °C. The average absolute percent difference between measured and titrated acidity is 3.6% with a standard deviation of 2.0%. Even with the acid injection, there is still insufficient acid present in the system to facilitate complete metal leaching. This is clearly seen by the extractions of Ni and Co that were measured to be approximately 56% and 40%, respectively.

**Figure 4.7** – Online acid measurement, injection from 0.15 to 0.3 a/o (40% solids)

For the next system, illustrated in Figure 4.8, an initial acid-to-ore ratio of 0.2 is present before injection. Enough acid is injected to produce an acid-to-ore ratio of 0.4; still an insufficient amount to fully leach out the Ni and Co. Because there is more acid in the system to begin with, the divalent metals concentration is greater at 250 °C. Once acid is injected (approximately the one hour mark), the divalent metals concentration increases to approximately 0.85 molal. Extractions of Ni and Co improve from the previous case: roughly 73% of the Ni, and 43% of the Co are extracted with this increased acid-to-ore ratio. Acidity
from conductivity is still in good agreement with that from titration; the average absolute percent difference is approximately 4.2% with a standard deviation of 1.8%.

**Figure 4.8** – Online acid measurement, injection from 0.2 to 0.4 a/o (40% solids)

The system shown in Figure 4.9 begins with an acid-to-ore ratio of 0.3, with injection to a final ratio of 0.4. The reason why a higher ratio was not chosen was because the higher concentration of acid in the system would be very detrimental to the autoclave internals. Ti is seen to corrode at acid concentrations above about 0.8 mol/L. When examining the autoclave after these runs, early signs of corrosion were present; therefore 0.4 was set as the maximum acid-to-ore ratio for this series of tests. Examining Figure 4.9, the metals concentration varies from about 0.55 molal to 0.9 molal. Injection of acid occurs just prior to the sudden jump in measured acidity at approximately 1 hour and 40 minutes into the test. As seen previously, the metals solubility follows the acidity in the system and increases upon injection of acid. There is improved extraction in this system compared to the previous, even
though the injected acid-to-ore ratio remains 0.4. The reason being, that this system was
given more time at temperature to leach (~1 hour 30 minutes versus ~40 minutes for Figure
4.8 at 250 °C), both before and after injection of acid; resulting in slightly improved
extractions of Ni and Co. The overall Ni and Co extractions are approximately 83% and 65%
respectively. The absolute average difference between measured and titrated acidity for
Figure 4.9 is 3.9% with standard deviation 2.0%.

**Figure 4.9** – Online acid measurement, injection from 0.3 to 0.4 a/o (40% solids)

Until now, only acid increases have been investigated, and good quality estimates
produced. To further validate the technique, a trial where acidity was decreased through the
addition of base is presented next.

**4.4 Further Validation**

The limonitic feed was used at a solids loading of 40 wt.%. A 5 molar NaOH solution
was prepared, and ~50 mL were injected to neutralize approximately one-eighth of the
stoichiometric amount of initial acid for a 0.2 acid-to-ore ratio. The system was heated to 250 °C and fully pre-acidified. It was allowed to remain at temperature for nearly 40 minutes before NaOH was injected under N₂ pressure. Figure 4.10 shows the acid and metals profiles during the experiment. Upon injection, the acidity is seen to abruptly drop and then increase gradually to a slightly lower value. The acid in the system gets partially neutralized according to:

\[
2\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}
\]  

(4.3)

where sodium sulphate is formed. Theoretically, a 45% (molar basis) decrease in total acid is expected from the average value before injection. However, the net decrease in acidity is approximately 2% (molar basis) based on samples taken at 30 minutes and 45 minutes in Figure 4.10. This reflects a nearly complete regeneration of acid. Due to the complexity of these systems, a number of different reactions are involved in this acid regeneration. Upon chemical analysis, very little change is seen to all metals (± 5 mol.%), except Al, Fe, and Mn. The Al concentration drops significantly upon NaOH addition, by almost 98%; Fe decreases by about 71%, and Mn by about 18% (all on a molar basis). Not all of the Na remains in solution, about 30% precipitates. At low pH and elevated temperatures Na₂SO₄ is known to react with Al₂(SO₄)₃ and Fe₂(SO₄)₃ in solution to precipitate as sodium alunite and jarosite compounds, NaM₃(SO₄)₂(OH)₆, where M is Al or Fe⁸,⁹. Acid is released upon this precipitation, explaining about 62% of the increase seen in Figure 4.10.

\[
\text{Na}_2\text{SO}_4 + 3\text{Al}_2(\text{SO}_4)_3 + 12\text{H}_2\text{O} \rightarrow 2\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6(\text{s}) + 6\text{H}_2\text{SO}_4
\]  

(4.4)

If all of the Al and Fe precipitation results in alunite and jarosite formation there is still about 82% Na remaining from the total precipitated. This Na is thought to react with Al in its solid phase, which is (H₃O)Al₃(SO₄)₂(OH)₆ at the conditions present¹²⁴. According to
Sobol (1969) and Das et al. (1996), Na, along with other ions, may substitute for hydronium ions present in hydronioalunite$^{4,10,11}$ as it is more soluble compared to Na-alunite. The following substitution occurs:

$$\text{Na}_2\text{SO}_4 + 2(\text{H}_2\text{O})\text{Al}_3(\text{SO}_4)_2(\text{OH})_{6(s)} \rightarrow 2\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_{6(s)} \downarrow + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$$

(4.5)

where the remaining 82% of the precipitated Na replaces hydronium ions, releasing acid into solution, giving the a total re-generation of roughly 81%.

The final metal that contributed to the acidity increase is Mn. In the current system it can exist as a divalent or tetravalent ion. The 18% that precipitated most probably followed one of the two following reactions:

$$\text{Mn}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{MnO}(s) \downarrow + \text{H}_2\text{SO}_4$$

(4.6)

$$\text{Mn}^{4+} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2(s) \downarrow + 2\text{H}_2\text{SO}_4$$

(4.7)

If only divalent Mn precipitates, the total acid regeneration adds up to approximately 88% of the total that was presumed to be neutralized. If the tetravalent Mn precipitation route was followed, the total acid regeneration becomes roughly 93% from the initial state. The result is a net acid consumption of 6% or 3% (respectively) from the pre-NaOH-injection state, compared to just 2% measured. An acceptable agreement exists as a number of other scenarios may have also taken place in the real system, and a more thorough analysis would require a detailed study of the phases in the solid residue, complemented by analysis of other soluble species.
Figure 4.10 – Online acid measurement and metals profiles at 250 °C (40% solids, initial a/o = 0.2)

The average absolute difference for the measurements in Figure 4.10 from titrated values is 1.5% with standard deviation of 0.9%.

4.5 Sensitivity to Inputs

We now assess the impact of three key inputs: specific conductivity, temperature, and total MSO\textsubscript{4} concentration (total divalent metals), on the accuracy of acidity estimates. It should be noted that variation in the solids volume fraction was not considered in this analysis, as it remains essentially constant during the process.

At 250 °C, there is a slight fluctuation around an average conductivity reading. The fluctuation is at most ±1 mS/cm, or usually less. To assess the significance of this fluctuation, Figure 4.11 compares a baseline with a fluctuation that is ±3 mS/cm. The baseline average absolute difference from the titrated values in this test (Figure 4.9) is 3.9%
with standard deviation 2.0%. With a fluctuation of ±3 mS/cm in the conductivity measurement, the average difference does not change noticeably, but the standard deviation increases to about 2.6%; which is relatively insignificant. Therefore, for the typical fluctuations present to specific conductivity at 250 °C, no significant impact is seen on the measured acidity.

![Figure 4.11](image)

**Figure 4.11** – Online acid measurement, conductivity fluctuation, from 0.3 to 0.4 a/o (40% solids, 250 °C)

Next we explore the typical uncertainty surrounding the temperature input. Usually the J-type thermo couple is accurate within ±1 °C. The RTD used to send temperature data to the computer normally agrees with the thermo-couple to within ±1 °C. Figure 4.12 shows a fluctuation of ± 5 °C; we can see that even with such a large variation in temperature, the accuracy of the estimated acidity is not greatly affected. The average absolute difference from titrated values actually decreases slightly to approximately 3.8%, and the standard deviation ranges from about 1.9% to 2.5%, meaning the estimated acidity still meets the targets set initially (see Introduction).
The last input to consider is the total MSO₄ concentration. We assume a 10 to 20% variation in total MSO₄ concentration (in molality units). Figure 4.13 shows a fluctuation of 10% to the total MSO₄ and Figure 4.14 shows a fluctuation of 20%. In Figure 4.13 the absolute average percent difference from titrated values increases to about 4.3% (from the baseline 3.9%) with standard deviations in the range of 2.9% (from the baseline 2.0%). As expected, a 20% fluctuation increases the percent difference from titrated values. The average becomes approximately 6.1% with standard deviation in the range of 3.5%. We can see from the previous that a fairly accurate value for total MSO₄ concentration is necessary to produce quality acid estimates, where an uncertainty of 20% in the concentration of MSO₄ would produce a larger error.
To conclude, the previous analysis of inputs has shown that the total divalent metals concentration is the most significant factor affecting the accuracy of estimated acidity when considering the typical range in variation of inputs.
References


CHAPTER 5

CONCLUSIONS

The objective of this work was to investigate the suitability of a modified commercially available sensor to operate at industrially relevant conditions, directly in autoclaves, to generate accurate online and real-time free acidity estimates. The main goal was to obtain accurate (within 5% from titrated) free acid estimates at leach temperature (up to 260 °C) and high pulp density, while also accounting for variations in feed composition. Two different feeds were investigated, a limonitic ore and a blend of limonite/saprolite. The metals content varied significantly between the two and allowed for a complete examination of industrial laterite feeds to be undertaken. Up to 40 wt.% solids were tested at 250-260 °C.

It was seen that an increase in pulp density decreased the conductivity measurement for fixed solution concentrations. The applied correction factor was able to accurately correct the conductivity readings for up to 20 vol.% solids (translating to slightly over 40 wt.% solids depending upon the feed).

The effects of the uncertainty in inputs were investigated. It was seen that fluctuations of up to ±3 mS/cm, ±5 °C, and ±10 mol.% in total MSO₄ still produced acceptable average free acidity estimates, meeting the target of 5% from titrated values.

The calibration technique produces accurate acidity estimates for a wide variety of process conditions. Measurements of acidity are possible for the full temperature range, from ambient temperature up to 260 °C. Its range of applicability for total MSO₄ concentration is between 0 and ~0.9 molal. Above this value, differences of greater than 5% from titrated values should be expected. Free acidities agreed with titration values as low as 0.02 molal at
250 °C. The maximum acidity accurately measured (within 5% of titrated) was roughly 1 molal for the systems investigated. Therefore, from current test work, the range of acidity that is accurately measurable is approximately 0.02 to 1 molal.

The converter slag system could not be fully examined due to time constraints. It was seen that the metal concentrations in solution were low compared to the limonite/saprolite blend, and similar to those from the limonite feed. Initial results from tests conducted with this feed showed that sensor clogging was the only hindering factor preventing acid measurements in this system. Thus, a new cell was designed. It currently requires additional testing before further conclusions can be drawn.

In conclusion, very high quality measurements were produced for free acidity at high temperatures under the conditions investigated.
CHAPTER 6

RECOMMENDATIONS FOR FUTURE WORK

Upon completion of this work a number of extensions to the project have arose:

1. **Water Salinity**

   Many industrial laterite leach processes are carried out with saline water as apposed to fresh. The influence of water salinity will be significant to the overall specific conductivity; thus, it is recommended that data be generated for quaternary systems of NaCl-H₂SO₄-MgSO₄-H₂O up to 250 °C. To complement this, OLI modeling can be carried out to obtain the NaCl contribution to the overall conductivity, where its contribution can be deducted from the total specific conductivity; resulting in an adjusted conductivity for a non-saline system (meaning current correlations can be applied). This adjustment should be validated via experimental data.

2. **Material Selection**

   It is recommended that some further material selection be carried out to obtain better coating for the lead wires as Teflon (PTFE) cannot withstand temperatures in excess of 260 °C. Possible alternatives to the glass cell housing should also be investigated to find a material that will perform just as well but will not be liable to shattering as easily.

3. **Vertical Cell**

   From APPENDIX B it is clear that more work needs to be done with the vertical sensor for use in slag leach systems. Repair to the current cell and extensive testing in slag systems is recommended.
4. **Industrial Tests**

Since the ultimate goal of this work is industrial use. It is recommended that the sensor be tested in a continuous autoclave setup, either pilot plant or full-scale if possible. If the system is large enough, it is advised that a larger toroid be used to form the cell (available from Foxboro Co.), as the likelihood of clogging would significantly be reduced.
APPENDIX A

INITIAL ANALYSIS

The majority of data utilized to produce correlations for acid estimations was previously published in work by Baghalha and Papangelakis\textsuperscript{1}, and Huang and Papangelakis\textsuperscript{2}. The same procedure employed previously was carried out in order to extend the correlation to higher concentration ranges and acidities for use in this work. All measurements made in previous work of solutions containing H\textsubscript{2}SO\textsubscript{4}, and/or MgSO\textsubscript{4}, and/or Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} at 250 °C are shown in Figure A.1. Similar plots were utilized from 25 °C to 250 °C in order to incorporate temperature variability into the generated correlation. Previous work dealt with systems where the total divalent metals concentration was relatively low (below 0.3 molal); where a direct linear relationship between acidity and conductivity was discovered. Estimates were produced with average accuracy of within 6% from titrated values for the leach solutions tested at 250 °C.
Figure A.1 – Linear relationship between free acidity and conductivity of $\text{H}_2\text{SO}_4$-$\text{Mg}_2\text{SO}_4$-$\text{Al}_2(\text{SO}_4)_3$-$\text{H}_2\text{O}$ system at 250 °C.

The previous correlation was enhanced to incorporate temperature effects and first tested on HPAL and HPOXAL leach solutions. Figures A.2 and A.3 show the acid measurements for a laterite leach solution and a converter slag leach solution, respectively. Tables A.1 and A.2 give the metals analysis for each test. For the laterite leach solution, the acidity remained constant throughout the temperature range because it was originally withdrawn through an *in situ* filter at temperature. The average absolute percent difference from titrated and measured acidities is 2.7% with standard deviation 1.0%.

For the converter slag test in Figure A.3, the sample was filtered at room temperature, upon heating, the solubility of ferric Fe decreased and a jump in the solution acidity was witnessed. The average absolute percent difference from titrated and measured acidities is 2.1% with standard deviation 1.4%.
Figure A.2 – Filtered laterite leach solution, originally retrieved at temperature. Original conditions: a/o = 0.3, solids = 30 wt.%, leach time = 3 h

Table A.1 – Metals analysis for laterite leach solution

<table>
<thead>
<tr>
<th>Metal Species</th>
<th>Concentration (molality)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$(SO$_4$)$_3$</td>
<td>0.006</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>0.221</td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>0.064</td>
</tr>
<tr>
<td>Total Divalent</td>
<td>0.285</td>
</tr>
</tbody>
</table>

Figure A.3 – Filtered converter slag leach solution, originally retrieved at room temperature. Leach conditions: solids = 25%, leach time = 1 h
Table A.2 – Metals analysis for converter slag leach solution

<table>
<thead>
<tr>
<th>Metal Species</th>
<th>Concentration (molality)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂(SO₄)₃</td>
<td>0.006</td>
</tr>
<tr>
<td>CoSO₄</td>
<td>0.065</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>0.052</td>
</tr>
<tr>
<td>Fe₂(SO₄)₃</td>
<td>0.12 – 0.02</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>0.021</td>
</tr>
<tr>
<td>NiSO₄</td>
<td>0.085</td>
</tr>
<tr>
<td>Total Divalent</td>
<td>0.223</td>
</tr>
</tbody>
</table>

It is seen from the previous that the sensor works well for solutions where the metals concentration was below 0.3 molal. For solutions with total metal concentration above 0.3 molal, similar plots to those seen in previous work were produced and effects of metals incorporated to form an extended correlation¹.²
References


APPENDIX B

HPOXAL OF CONVERTER SLAGS

1. HPOXAL Processing

Large quantities of slag, a solid waste by-product of pyrometallurgical operations, are produced continuously on a worldwide basis posing a potential environmental hazard as the base metals present have the potential of leaching into surrounding environments \(^1,2\). Smelting and converting operations are carried out in order to separate Fe from the base metals of interest, namely Ni, Co and Cu. The Fe sulphide present is oxidized in the molten form, where it is then fluxed with silica (and other oxide rock minerals) to produce a fayalite slag, \(2\text{FeO} \cdot \text{SiO}_2\) \(^1\). This slag has a lower density than the remaining melt, and is poured off the converter or smelter. Approximately 3-8\% of the original base metals are lost to waste slag dumps in form of either oxides or sulphides \(^3\). Mechanical entrapment of matte in the form of fine dispersions results in some base metal sulphides being present in slag \(^4\). The remaining appear as dissolved oxides chemically bound with silica in fayalite \(^5\). Most slags from smelters contain up to 1.2 wt\% Ni, 0.7 wt\% Co and 3.7 wt\% Cu \(^6\). Converter slags tend to contain more Ni and Co, but less Cu, with typical ranges of 2.87-4.8 wt\%, 0.77-1.59 wt\%, and 0.17-1.4 wt\% respectively \(^3\). High temperature pressure oxidative acid leaching is currently being explored as an option to recover valuable base metals from slag bodies \(^1\). Because the base metals are present as both oxides and sulphides, both acid and oxygen are necessary to facilitate leaching.
2. HPOX Acid Leaching of Converter Slag

A similar setup to one described in Chapter 3 was used to leach the converter slag. Details can be found in previous publications\(^1\). There was no need for pre-acidification in this system as the solids content never went above 30 wt.%. For a typical run, approximately 250 g of dry slag was mixed with 750mL of de-ionized water and placed in the autoclave. After heating to 250 °C, sulphuric acid was injected under O\(_2\) pressure to facilitate the leach. Samples were withdrawn and analyzed in a similar manner to that previously mentioned.

3. Slag Feed

Two different slag samples were investigated and their compositions presented in Tables B.1 and B.2. The dry slag feed had a solids density of roughly 3.7 g·cm\(^{-3}\) for both feeds. Unlike lateritic ores, slags contain a significant amount of magnetite, Fe\(_3\)O\(_4\), which quickly finds its way to the bore of the cell; resulting in partial or full clogging of the sensor. The consequence of this is that many test runs resulted in failure. The approximate ratio of magnetite to fayalite in slags CS7 and CS9 are 3:7 and 2:8, respectively.

| Table B.1 – Elemental composition of converter slag CS7 in wt.% of dried solids |
|-----------------|-------|-----|------|-----|-----|-----|-----|-----|-----|
| Fe  | Si   | Ni  | Cu   | Co  | S   | Al  | Ca  | Zn  |
| 52.36 | 10.59 | 1.09 | 1.01 | 0.60 | 1.05 | 0.15 | 0.14 | 0.14 |

| Table B.2 – Elemental composition of converter slag CS9 in wt.% of dried solids |
|-----------------|-------|-----|------|-----|-----|-----|-----|-----|-----|
| Fe  | Si   | Ni  | Cu   | Co  | S   | Al  | Ca  | Zn  |
| 52.29 | 12.74 | 1.69 | 0.70 | 0.68 | 0.61 | 0.21 | 0.08 | 0.16 |
4. HPOXAL with the Horizontal Sensor

A number of tests were carried out with the horizontal sensor used for laterite leach experiments with varying success. Only two of the 10 runs resulted in little or no clogging of the bore. In Figure B.1 an HPOXAL test of slag CS7 is presented, where acid is injected at about 30 minutes into the test. An acid-to-slag (a/s) ratio of 0.2 was chosen for this run where the solids loading was 25 wt.%. Similar to laterite systems, a sudden spike in acidity is initially seen; unlike laterite systems however, this spike is followed by relatively low acidity readings signifying rapid acid consumption and slower regeneration compared to systems previously examined. After this minimum in acidity, the readings slowing begin to increase until they reach a maximum, where they decease slightly and ultimately level off. Titration values follow closely to those from conductivity except when the maximum in measured acidity is considered. Titration shows a gradual leveling off in acidity without the maximum seen from conductivity. This gradual leveling off in acidity is consistent with previous work on similar systems\(^1\). Because the injection site and sensor were in close proximity inside the reactor (see Figure 3.1), it is thought that some residual acid may have been delayed from releasing upon injection, resulting in a localized acid increase seen by the sensor; but not by titration, as mixing rapidly consumed it. The sampling line is closer to the bottom of the autoclave, near the impellers, allowing for full mixing before sampling; where as the sensor is closer to the top and away from the impellers. The reason why acid is consumed quickly and regenerated more slowly compared to laterite systems is due to the following consecutive reactions:

\[
2\text{FeO} \cdot \text{SiO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{O} + \text{SiO}_2 \quad \text{(B.1)}
\]

\[
2\text{FeSO}_4 + (1/2)\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \quad \text{(B.2)}
\]
\[
\text{Fe}_2\!(\text{SO}_4)_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\!\text{O}_3\!(s)\downarrow + 3\text{H}_2\text{SO}_4 \quad (\text{B.3})
\]

Upon dissolution of fayalite acid is consumed and FeSO\(_4\) produced. FeSO\(_4\) oxidizes to Fe\(_2\)(SO\(_4\))\(_3\), consuming acid in the process. Due to the instability of Fe\(_2\)(SO\(_4\))\(_3\) at 250 °C, hydrolysis occurs, producing hematite and releasing acid. Compared to laterite systems where oxygen is not needed to regenerate acid, reaction B.2 is crucial to facilitate reaction B.3. The range of total divalent metals in solution is from 0.14 to 0.20 molal; meaning the simplified low metals correlation from Appendix A could be used to produce acidity estimates. Using this correlation, the average absolute difference between measured and titrated values is 5.0% (2.8% if the 40 minute sample in Figure B.1 is not considered) with standard deviation of 5.7% (2.3% respectively).

![Figure B.1 – Online acid profile for CS7, injected to a/s = 0.2 (25 wt.% solids)](image)

Next, slag CS9 was used. Two tests were run at 25 wt% solids and an acid-to-slag ratio of 0.1 kg/kg. In both cases very rapid acid consumption was seen. In Figure B.2, the test was cut short due to a broken wire terminating acidity readings after the 1 hour 20 minute mark. The sensor did not seem to be clogged for this run; when the autoclave was opened
after cooling, no buildup of solids was witnessed. For the first 20 minutes after injection (initial spike), the acid concentration from both conductivity and titration was very low, and continually increasing. Although the percent difference from titration appears to be high, 12.2% with standard deviation 3.0%, the values are very small in magnitude, meaning even small deviations from titration appear to be large. Table B.3 shows the exact measurements, where it is seen that the discrepancy might be acceptable. This run helps to show that very low acid measurements are possible with this technique.

<table>
<thead>
<tr>
<th>Time (hr:min:sec)</th>
<th>Acidity from Conductivity (molal)</th>
<th>Acidity from Titration (molal)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:09:30</td>
<td>0.018</td>
<td>0.020</td>
<td>10.7</td>
</tr>
<tr>
<td>1:15:30</td>
<td>0.028</td>
<td>0.025</td>
<td>10.3</td>
</tr>
<tr>
<td>1:18:30</td>
<td>0.035</td>
<td>0.030</td>
<td>15.7</td>
</tr>
</tbody>
</table>

Figure B.2 – Online acid profile for CS9, injected to a/s = 0.1 (25 wt.% solids)

Figure B.3 shows what readings from a partially clogged sensor look like. It is seen that the measured acidity follows the same trend as titrated values. It was impossible to physically check if the extent of clogging was constant throughout the test, but upon cooling
about 1/3 of the bore seemed to be clogged. A correction was applied to adjust the conductivity readings for a constant partially filled bore, but the resulting adjustment did not improve the measurement greatly for the entire test time, suggesting the bore was not clogged to the same extent throughout the test. Many tests resulted in similar outcomes when the sensor was partially clogged. When the sensor was completely blocked, very low readings were witnessed that did not vary with changing acidity. A gas line was used in laterite systems to inject high pressure N₂ directly into the bore of the sensor to clean it when blockage was suspected. It was installed towards the end of the limonite/saprolite campaign. However, this solution could not be applied to the slag systems as a different autoclave was used that did not have sufficient available ports to install such a system. The O₂ injection port present could not be used to unclog the sensor because O₂ was continuously being pumped into the autoclave, meaning bubbles would persistently fill the bore, unevenly distorting the readings.

![Figure B.3](image)

**Figure B.3** – Online acid profile for CS9, partially plugged sensor, injected to a/s = 0.1 (25 wt.% solids)
5. Vertical Cell Design

The vertical cell was designed for use in converter slag systems where magnetite persistently clogged the horizontal design. The sensor specifications can be found in Chapter 3. The cell was tested with synthetic solutions to ensure it was reliable at high temperatures. Not surprisingly, the measured conductivity was identical to that measured with previous designs; as the only difference between the sensors was orientation of the bore. As long as the cell was at least ~2 cm below the surface level of the liquid, accurate readings were produced. Upon testing with a converter slag, unexpected problems occurred with the autoclave setup and abortion of the test campaign was necessary due to Teflon sintering, exposing the lead wires to the sensor, causing a short in the circuit and resulting in incorrect readings sent to the analyzer. The initial readings with the sensor appeared to be correct and upon examination of the autoclave after the test run, no clogging of the bore was witnessed. Due to time constraints, no further testing was possible with this design. The sensor was however proven to work at temperature and did not seem to be prone to clogging. Further testing is recommended with this design in converter slag systems to validate the claims above.
References