Effect of Key Parameters on the Selective Acid Leach of Nickel from Mixed Nickel-Cobalt Hydroxide

Kelly Byrne, William Hawker, James Vaughan*

The University of Queensland, School of Chemical Engineering
Level 3 – Chemical Engineering Building (74), St Lucia QLD Australia 4072

*Corresponding author: james.vaughan@uq.edu.au, +61 7 3365 3850

Keywords: Selective acid leach, mixed hydroxide, nickel, oxidation

Abstract. Mixed nickel-cobalt hydroxide precipitate (MHP) is a relatively recent intermediate product in primary nickel production. The material is now being produced on a large scale (approximately 60,000 t/y Ni as MHP) at facilities in Australia (Ravensthorpe, First Quantum Minerals) and Papua New Guinea (Ramu, MCC/Highlands Pacific). The University of Queensland Hydrometallurgy research group developed a new processing technology to refine MHP based on a selective acid leach. This process provides a streamlined route to obtaining a high purity nickel product compared with conventional leaching / solvent extraction processes. The selective leaching of nickel from MHP involves stabilising manganese and cobalt into the solid phase using an oxidant. This paper describes a batch reactor study investigating the timing of acid and oxidant addition on the rate and extent of nickel, cobalt, manganese leached from industrial MHP. For the conditions studied, it is concluded that the simultaneous addition of acid and oxidant provide the best process outcomes.

Introduction

Nickel is a valuable commodity which is predominantly sourced from either sulfide or laterite mineral deposits. As large high grade sulfide deposits are increasingly rare, the processing of laterite ores is predicted to become the dominant source of the metal. In nickel laterites, cobalt and manganese are typically present. Cobalt has similar chemical properties to nickel and because of this, it is not possible to effectively separate the metals by selective sulfide or hydroxide precipitation.

A common method of treating nickel laterites is to leach the solids in acid. Acid leaching is generally followed by impurity precipitation by adding limestone. Following impurity precipitation, nickel and cobalt are usually recovered from the aqueous solution together by either mixed sulfide precipitation, or mixed hydroxide precipitation. Mixed hydroxide precipitation is a relatively recent large scale industrial technology achieved by pH adjustment using a basic chemical such as magnesia, lime, limestone or sodium hydroxide [1]. The mixed hydroxide precipitate (MHP) consists of mostly nickel hydroxide but also contains valuable cobalt hydroxides and various other impurities, the main one being manganese. MHP is a more value concentrated product, for example 1% nickel and 0.8% cobalt present in the original laterite ore are upgraded substantially to about 40% and 3.2% respectively in MHP. Since the MHP has such a high valuable metal content; the feasibility of transporting the material to a centralized nickel and cobalt refinery improves.

The UQ Hydrometallurgy group developed a novel method for treating MHP in a selective acid leaching (SAL) process [2-5]. The SAL process involves selective leaching of nickel from MHP, leaving cobalt and manganese in the solid residue (Fig. 1). The process yields a concentrated nickel sulfate solution suitable for direct recovery of a final nickel product and a cobalt concentrate which
can be processed further [5]. Selectivity in the leaching process is achieved by the tendency for manganese and cobalt to be preferentially oxidized. In the MHP, these metals are mainly present in the divalent oxidation state where they are all soluble below approximately pH 6, whereas their trivalent states are insoluble down to approximately pH 3. The SAL process involves contacting MHP with sufficient amount of strong oxidant to oxidize all of the cobalt and the manganese from their divalent to their trivalent states, while also contacting the MHP with a sufficient amount of acid to leach a portion of the divalent nickel. By controlling the oxidant addition dosage, the oxidation of nickel to its trivalent state can be largely prevented while oxidation of the cobalt and manganese proceeds quickly. By controlling the acid addition, the leaching of divalent nickel and other impurities can be controlled [5].

![Process flow diagram for the selective acid leach process to refine mixed Ni-Co hydroxide precipitate (MHP)](image)

The complex interactions of leaching and oxidation reactions means that the timing and order of oxidant addition may be critical to achieve the optimum process kinetics and separation efficiencies. In this paper, the outcomes of a series of batch reactor experiments are presented which describe the effect of varied order and timing of acid and oxidant addition on leaching kinetics and separation efficiencies. The three conditions tested were:

1. Leaching followed by oxidation (sulfuric acid addition followed by oxidant addition after 30 minutes)
2. Oxidation followed by leaching (oxidant addition followed by acid addition after 30 minutes)
   Simultaneous leaching and oxidation (simultaneous oxidant and sulfuric acid addition)

**Materials and Methods**

**Feed MHP sample and Reagents.** One industrial sample of MHP was used in all the experiments. The MHP was stored in a plastic bag within a sealed container to minimize drying and/or oxidation of the sample. The MHP sample moisture content was 43.5 wt. %, determined by air drying at 105 °C to constant mass. The composition of the moist MHP is shown in Table 1.
Table 1: Composition (wt. % wet) of feed MHP sample based on average back calculated values

<table>
<thead>
<tr>
<th>wt.%</th>
<th>Al</th>
<th>Ca</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mg</th>
<th>Mn</th>
<th>Ni</th>
<th>Si</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHP</td>
<td>0.02</td>
<td>0.04</td>
<td>0.71</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.67</td>
<td>1.40</td>
<td>22.4</td>
<td>0.19</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The reagents used in these experiments were sulfuric acid (98 wt. % pure), an oxidant (crystalline sodium peroxydisulfate, 98 wt. % pure) and deionized water. Nitric (70 wt. % pure) and hydrochloric (32 wt. % pure) acids were used for sample stabilisation prior to assaying the solution phase using inductively coupled plasma optical emission spectrometry (ICP-OES) at the University of Queensland Agriculture and Food Science analytical laboratory.

**Leaching Experiment Procedure.** To investigate how the timing of the acid and oxidant addition affected the selective leaching of nickel from MHP, a series of batch leaching experiments were performed in 1.2 L baffled glass reactors. Reactors were covered to minimize evaporation. Regardless, a small amount of water, approximately 50 mL over the course of the experiment, was added to the reactor to compensate for evaporation.

Firstly, the moist MHP was slurried with deionized water. Homogenous mixing of the slurry was provided by an overhead agitator with a two-bladed high-density plastic impeller stirred at 800 rpm. The solids loading for each condition was set to a target final leach solution of 55 g-Ni/L with a final volume of 1 L of solution. The water associated with the MHP and generated by the leaching reactions was taken into account.

The slurry was then heated to 60°C using a hot plate prior to addition of the concentrated sulfuric acid as the acid addition resulted in significant warming of the slurry due to the exothermic nature of the dissolution of concentrated H₂SO₄ in water. The slurry was then maintained at 85±2°C; by manual control of a hot plate heater. The experiments (time = 0) began upon complete addition of the first reagent (acid or oxidant). Due to the exothermic reaction of acid with water, acid addition to the reaction was carried out slowly over the course of a few minutes.

The feed MHP composition was estimated and the required oxidant and acid additions were calculated based on this estimate and the reaction stoichiometry. The target oxidant addition was 115% of the stoichiometric requirement to oxidize all manganese from the divalent to trivalent state and all the cobalt from divalent to trivalent as shown in Reactions 1 and 2; these reactions are kinetically favourable [5]. Manganese can be oxidized from divalent, to trivalent and further to quadrivalent or even heptavalent states. The heptavalent form of manganese, known as permanganate, is soluble in the mildly acidic conditions of this leaching process. Whereas, the trivalent and quadrivalent forms of manganese are insoluble. Reactions 1 and 2 are the preferred due to efficient utilisation of the oxidant.

The target acid addition was 95% of the stoichiometric requirement to dissolve all nickel and magnesium assuming all nickel was present as a nickel hydroxyl-sulfate and all magnesium was present as magnesium hydroxide as shown in Reactions 3 and 4. The generation of acid from the oxidation of cobalt and manganese was accounted for. Upon completion of the experiments, the initial assay of the MHP was back calculated and the reagent addition rates were recalculated. The concentrations of the cobalt and the manganese were lower than expected. Therefore, in all experiments the actual oxidant addition rate was calculated to be 187% of the stoichiometric requirement to oxidize all cobalt and manganese from divalent to trivalent states. The actual acid addition rate was calculated to be 82% of the stoichiometric acid required to dissolve all nickel and magnesium assuming all nickel was present as a nickel hydroxysulfate and all magnesium was
magnesium hydroxide. A summary of the experimental conditions and key outcomes of the test is provided in Table 2, at the end of the paper.

\[
\text{Reaction 1} \\
2\text{Mn(OH)}_2(s) + \text{Na}_2\text{S}_2\text{O}_5(aq) \rightarrow \text{MnO(OH)}(s) + \text{Na}_2\text{SO}_4(aq) + \text{H}_2\text{SO}_4(aq)
\]

\[
\text{Reaction 2} \\
2\text{Co(OH)}_2(s) + \text{Na}_2\text{S}_2\text{O}_5(aq) \rightarrow \text{CoO(OH)}(s) + \text{Na}_2\text{SO}_4(aq) + \text{H}_2\text{SO}_4(aq)
\]

\[
\text{Reaction 3} \\
\text{Ni}_7\text{(OH)}_{12}\text{SO}_4(s) + 6\text{H}_2\text{SO}_4(aq) \rightarrow 7\text{NiSO}_4(aq) + 12\text{H}_2\text{O}(l)
\]

\[
\text{Reaction 4} \\
\text{Mg(OH)}_2(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{MgSO}_4(aq) + 2\text{H}_2\text{O}(l)
\]

The leaching time was 165 minutes with slurry samples taken every 15 minutes for the first 75 minutes and every 30 minutes for the remaining 90 minutes. Temperature compensated pH measurements and oxidation-reduction potential (ORP) measurements were taken on the slurry samples once they had cooled to approximately 50 °C. The ORP was reported with respect to the SHE by subtracting 200 mV from the Ag-AgCl measured values. Solution samples were then isolated from the slurry sample by filtration through a 0.45μm nylon syringe filter. All solution samples were stabilized in 2 wt. % nitric acid for assay by ICP-OES.

At the end of the experiment, the final leach solution was sampled. The solid leach residues were separated from the leach solution by vacuum filtration, and dried at 60 °C to constant mass; between 24 to 48 hours. Dry leach residues were pulverized and redissolved in 5 wt. % hydrochloric acid to determine the elemental composition by ICP-OES. A small amount of sodium metabisulfite was added as a reducing agent to assist dissolution. The reaction extents were calculated based on the kinetic solution samples and the final solid assays.

**Result and Discussion**

Three scenarios for timing of acid and oxidant addition to the selective acid leaching of MHP were evaluated. The results provide insight into the rates, mechanisms and types of leaching and oxidation reactions occurring.

**Staged Acid – Oxidant Addition.** The first scenario is acid added at t=0 followed by the oxidant at t=30 minutes. This scenario is referred to as A-O. The deportment of the nickel, manganese, cobalt and magnesium for the A-O case is shown in Fig. 2.

The nickel leached very quickly with 65% dissolving within the first few minutes. The rate of nickel leaching then slowed down and crept up to 73% after 165 minutes. The nickel recovery was limited by the amount of acid present, as only 82% of the stoichiometric acid requirement to dissolve all of the nickel and magnesium was added to these experiments. Magnesium also leached quickly and to a greater extent than nickel. It should be noted that ~65% of the magnesium dissolved upon mixing the MHP with deionized water, ahead of the acid addition.
whereas nickel did not substantially dissolve upon mixing with water.

Significant amounts of cobalt and manganese also solubilized upon acid addition, 50% of the cobalt and 9% of the manganese. When the oxidant is added at 30 minutes, both the cobalt and the manganese oxidize and precipitated from solution. The oxidative precipitation of the manganese was effectively complete 15 minutes after addition of the oxidant while the oxidative precipitation of the cobalt was slower, taking approximately 30 minutes. This oxidative precipitation process was slow despite the excess of oxidant added to the experiment (187% of the stoichiometric requirement to oxidize all cobalt and manganese from divalent to trivalent states). Nickel appeared to be unaffected by the oxidant addition.

Figure 2. Nickel, cobalt, magnesium and manganese deportment over time – acid addition followed by oxidant addition after 30 minutes

Staged Oxidant – Acid Addition. In the second scenario, the oxidant was added first followed by the acid addition after 30 minutes. This scenario is referred to as the O-A case. The deportment of the nickel, manganese, cobalt and magnesium for the O-A case is shown in Fig. 3. Small amounts of nickel and magnesium were seen to dissolve in the first 30 minutes following oxidant addition. This is attributed to a small amount of acid being generated from the cobalt and manganese oxidation reactions (Reactions 1 and 2). Upon addition of the acid at 30 minutes, nickel and magnesium both dissolved significantly with nickel recovery to solution increasing to the final total recovery to solution of 73% within 15 minutes while the magnesium recovery to solution increased to 90%. The magnesium and nickel then slowly increased to a final extraction of 94% and 82% respectively, similar to the A-O case.

Cobalt did not dissolve to any appreciable extent (<0.1%) throughout the experiment. However, approximately 2% of the manganese dissolved upon addition of the acid. This dissolution of manganese is undesirable as the manganese is an impurity in the downstream processing of the nickel. To maintain separation of manganese, oxidation to the trivalent or tetravalent states are necessary to maintain the impurity as an insoluble solid. Manganese in the tetravalent states means that excess oxidant has been used. Further oxidation of the manganese will result in the formation of heptavalent permanganate; which carries a distinct purple colour in solution. The manganese dissolution may be attributed to the formation of heptavalent permanganate. Manganese near the
surface of the MHP particles would have been preferentially oxidized during the first 30 minutes as described in Reaction 5; and likely the formation of insoluble tetravalent manganese solids. The permanganate purple was observed in varying strengths in all samples after the addition of the acid, justifying the presence of permanganate. In the presence of excess oxidant, surface nickel hydroxide may also have been oxidized to trivalent nickel oxy-hydroxide, similar to manganese and cobalt in Reactions 1 and 2. The oxidation of nickel would therefore result in the stabilisation of nickel to the solid phase which is undesirable as this process aims to selectively dissolve the nickel. The slow reduction of manganese in solution with time may be attributed to the hydrolysis of permanganate as shown in Reaction 6.

\[
2\text{MnOOH}(s) + 4\text{Na}_2\text{S}_2\text{O}_8(aq) + 4\text{H}_2\text{O}(l) \rightarrow 2\text{NaMnO}_4(aq) + 3\text{Na}_2\text{SO}_4(aq) + 5\text{H}_2\text{SO}_4(aq)
\]

**Reaction 5**

\[
\text{NaMnO}_4(aq) + \text{H}_2\text{O}(l) \rightarrow \text{MnOOH}(s) + \text{NaOH}(aq) + \text{O}_2(g)
\]

**Reaction 6**

**Simultaneous Acid and Oxidant Addition.** The third scenario tested was simultaneous addition of both the acid and the oxidant and this condition was the best of the three scenarios in terms of achieving fast and efficient selective leaching of nickel. The deportment of the magnesium, nickel, cobalt and manganese for the case where reagents were added simultaneously is shown in Fig. 2 Nickel and manganese were readily solubilized as in the A-O scenario. Cobalt and manganese did not dissolve to any appreciable extent throughout the experiment (<0.1 % at all times).
Figure 4. Nickel, cobalt, magnesium and manganese deportment over time – simultaneous oxidant and acid addition

**pH and ORP.** The pH measured through this series of batch reactor experiments provides insight into the kinetics and mechanisms of the oxidation and leaching reactions taking place. The pH as a function of time for the three cases are shown in Fig. 5. At the beginning of the tests prior to any acid or oxidant addition, the pH was in the range of 7.0-7.2. For the case where both the acid and oxidant were added simultaneously (Sim) at t=0, the pH rapidly dropped to about 4. The pH then gradually increased over the first 30 minutes before stabilising; this means the majority of the oxidation and leaching are completed in this short time frame. For the A-O case, the pH initially dropped rapidly upon acid addition but only to pH 5.1 then increasing to 5.9 at 30 minutes. The pH then decreased further to 4.9 upon oxidant addition before increasing slightly and stabilising at 60 minutes. The oxidant generates considerably less acid than the acid dose. In the A-O case, most of the buffering basic solids had already been dissolved. This is highlighted in the O-A case where the oxidant addition only caused the pH to drop to 6.2 then when acid was added at 30 minutes, the lowest pH of 3.6 was recorded before stabilising after 80 minutes. This relatively slow acid reaction (compared with Sim) means that if the MHP is strongly oxidized first, the acid leaching reaction can become kinetically hindered. The terminal pH values were 5.6, 5.4 and 5.2 for the Sim, O-A and A-O conditions respectively. A higher terminal pH indicates that more of the basic material had in reacted with the acid added and generated from oxidation.
The oxidation-reduction potential (ORP) measurements as a function of time are shown in Fig. 6. Prior to any reagent additions, the initial ORP is around 25-50 mV. The experiment with simultaneous addition of oxidant and acid shows a rapid increase in potential which seems to stabilise which decreases slightly and stabilises between 400 and 500 mV. In O-A where the oxidant is added initially, surprisingly the ORP does not respond rapidly indicating that the oxidation-reduction is largely taking place at the surface of the particles and not at the ORP electrode surface which is indicative of aqueous phase reactions. Once the acid is added to O-A at 30 minutes, a very high solution potential is recorded that is likely due to aqueous permanganate. For the A-O case, the ORP remains low until the oxidant is added after 30 minutes. In this case there is significant oxidative precipitation of cobalt and manganese which may prohibit the formation of permanganate.
Summary of Experiment

Table 2: Summary of experimental conditions and key results

<table>
<thead>
<tr>
<th>Target</th>
<th>Units</th>
<th>Acid-Oxidant</th>
<th>Oxidant-Acid</th>
<th>Simultaneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>g/L</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>%</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Oxidant</td>
<td>%</td>
<td>115</td>
<td>115</td>
<td>115</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Added</th>
<th>Wet MHP</th>
<th>g</th>
<th>229.3</th>
<th>229.3</th>
<th>229.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulfuric acid</td>
<td>g</td>
<td>69.3</td>
<td>69.3</td>
<td>69.3</td>
</tr>
<tr>
<td></td>
<td>Oxidant (Na₂S₂O₅)</td>
<td>g</td>
<td>13.3</td>
<td>13.3</td>
<td>13.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Sulfuric acid</th>
<th>%*</th>
<th>83</th>
<th>83</th>
<th>83</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxidant</td>
<td>%*</td>
<td>187</td>
<td>187</td>
<td>187</td>
</tr>
</tbody>
</table>

*Based on average values of nickel, magnesium, manganese and cobalt back calculated as present in MHP.

Conclusion

The timing of acid and oxidant addition on the rate and extent of nickel, cobalt, manganese and magnesium leached from industrial MHP was evaluated. Three leaching scenarios, staged acid then oxidant, staged oxidant then acid, and simultaneous acid and oxidant, were tested. It is concluded that simultaneous addition of acid and oxidant is the best configuration to achieve the desired process outcomes in terms of reaction rate, extent and solution phase purity.

Acknowledgments.

The authors would like to acknowledge the financial assistance for this project provided by UniQuest. We acknowledge the support for this project from Scott Perry from BHP Billiton and Peter Jolly from Highlands Pacific Ltd. Furthermore, we acknowledge the many others who have contributed to the development of the selective acid leach process for refining mixed nickel-cobalt hydroxide precipitate in terms of laboratory research and development, engineering studies and commercialisation.

References


Queensland, patent ZL 201280010463.5, China (2012)

