LEACHING BEHAVIOR OF THE ROASTED NICKEL CALCINE

*D. Yu, T.A. Utigard, M. Barati

University of Toronto
Department of Materials Science and Engineering
184 College Street
Toronto, Canada M5S3E4
(*Corresponding author: dawet.yu@mail.utoronto.ca)

ABSTRACT

Sulfation roasting of nickel concentrate to generate water-soluble metal sulfates was investigated as an alternative process to smelting for the recovery of valuable metals. The kinetics of dissolution of various species of the calcine in three leachants was studied; hot water, dilute HCl, and concentrated HCl. The results indicated that dissolution of sulfates by hot water at 90 °C is achieved within 30 minutes. In order to increase the recovery of the valuable metals, acid leaching is necessary due to the existence of ferrite in the calcine.
INTRODUCTION

Investigations on the sulfation roasting of nickeliferous sulfide ores or concentrates were mainly carried out in 1950’s to 1990’s to generate water soluble non-ferrous metal sulfates followed by metal recovery by leaching (Stephens, 1953; Thornhill, 1954, 1961; Fletcher and Shelef, 1964a, 1964b; Fletcher and Hester, 1964; Frankiewicz, 1977; Norrgran, 1983). Commercialization of the sulfation roasting process was only performed by Falconbridge Ltd. (Thornhill, 1961; Boldt, 1967), which employed a sulfation roast process on nickeliferous pyrrhotite at 680 °C where Ni, Cu, and Co were leached and Fe₂O₃ was produced for the iron industry. In 1965, 118,342 tons of pyrrhotite was processed, however because of the huge SO₂ emissions (no acid plant) relative to the nickel production and the poor economics, this plant was shut down.

Nickel production from sulfide ores via pyrometallurgical means, especially the electric furnace smelting process, is a major emitter of SO₂ to the environment and a big energy consumer (Warner, Diaz, Dalvi, Mackey, Taranov and Jones, 2007). Nowadays, due to the more stringent environmental regulations as well as the need to reduce energy consumption, metal production by sulfation roasting is gaining more attention as an alternative process to smelting. The main focus of this paper is to investigate the extent and rate of leaching of valuable metals from the sulfation roasted nickel calcine, aiming to maximize the metal recovery and minimize the dissolution of iron species.

The main minerals in the nickel sulfide concentrate are: pentlandite (Fe₉Ni₅)S₈, pyrrhotite Fe₁₋₅S, chalcopyrite CuFeS₂, and siliceous gangue materials. The main species that the roasted calcine may contain are: hematite (Fe₂O₃), magnetite (Fe₃O₄), nickel oxide (NiO), nickel ferrite (NiFe₂O₄), cupric oxide (Cu₂O), pyrrhotite (hexagonal type Fe₉S₈, monoclinic type Fe₈S₉), hazelwoodite (Ni₅S₈), iron nickel monosulfide solid solutions [(Fe,Ni)₁₋₅S], NiS, bornite (Cu₃FeS₄), and chalcocite (Cu₂S), as well as the water soluble sulfates (Zamalloa, 1995; Zamalloa and Utigard, 1996; Yu and Utigard, 2012). The leaching of water soluble sulfates is rather straightforward without the involvement of chemical transformations. The major focus of this paper is, as a result, to study the leaching behavior of the other minerals in the calcine and the possible interactions among the species present in the leaching system.

EXPERIMENTAL

Nickel concentrate as received is Raglan concentrate from Xstrata Nickel’s smelter in Sudbury, Ontario, Canada. It is mainly composed of pentlandite (Fe₉Ni₅)S₈, chalcopyrite CuFeS₂, pyrrhotite Fe₁₋₅S and small amount of siliceous flux and gangue materials. Its chemical composition is shown in Table 1. Roasting of the nickel concentrate was conducted in the experimental setup illustrated in Figure 1. In each roasting test, Raglan concentrate of 5 grams was put in a porcelain boat. In order to maximize the heat and mass transfer rate between the sample and its local surroundings, the concentrate was spread evenly in the boat to cover an area of 28 cm² with a thickness of 1.5 mm. The boat was then placed in a sealed tube inside a resistance heating furnace. The samples were heated under flowing argon and were subsequently subjected to the roasting gas (dried air and/or SO₂ mixed with N₂). The offgas was analyzed for its SO₂ content before it was scrubbed to eliminate the SO₂ and SO₃ for purging to the atmosphere. The SO₂ concentration of the off-gas was measured using a gas analyzer (ABB EL3200) and was recorded using a computer controlled data acquisition system (FLUKE Hydra Series II). After roasting, the tube was withdrawn from the electric furnace to ensure a fast cooling rate.

In order to investigate the leaching behaviors of calcines under different leaching conditions and the influence of roasting conditions on the leaching behavior of calcines, three types of leaching tests were conducted: Dilute Acid Leaching (DAL), Hot Water Leaching (HWL), and Concentrated Acid Leaching (CAL). Conditions of the leaching experiments are summarized in Table 2. Leaching took place in a 250 mL flask equipped with a water condenser on exhaust to minimize the vaporization losses of the solution. For precise temperature control within ±1°C, the flask was placed in a water bath heated by a hot plate. 1mL aliquot samples of leach liquor were drawn from the flask after predetermined time intervals. After leaching, the pulp was filtrated and the residue was dried. Roughly 0.079 g residue was taken and digested.
in aqua regia. Both the leach liquor samples and the solutions from residue digestion were analyzed by ICP-OES after appropriate dilution. Calcines and leaching residues were analyzed by optical microscopy, SEM/EDS and XRD.

Table 1 – Chemical composition of the Raglan concentrate

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>17.9</td>
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<tr>
<td>Fe</td>
<td>30.8</td>
</tr>
<tr>
<td>Cu</td>
<td>4.54</td>
</tr>
<tr>
<td>Co</td>
<td>0.36</td>
</tr>
<tr>
<td>S</td>
<td>27.6</td>
</tr>
<tr>
<td>MgO</td>
<td>5.43</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.76</td>
</tr>
<tr>
<td>SiO₂</td>
<td>8.69</td>
</tr>
<tr>
<td>Total</td>
<td>96.1</td>
</tr>
</tbody>
</table>

Figure 1 – Experimental setup for the roasting of nickel concentrate

Table 2 – Leaching conditions of three types of leaching tests

<table>
<thead>
<tr>
<th></th>
<th>DAL</th>
<th>HWL</th>
<th>CAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcine mass (g)</td>
<td>1.5</td>
<td>1.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Leaching temperature (°C)</td>
<td>90</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Leachant</td>
<td>HCl</td>
<td>H₂O</td>
<td>HCl</td>
</tr>
<tr>
<td>Normality</td>
<td>0.57</td>
<td>N/A</td>
<td>5.00</td>
</tr>
<tr>
<td>Volume (mL)</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Leaching time (hours)</td>
<td>48.00</td>
<td>5.00</td>
<td>12.75</td>
</tr>
<tr>
<td>Stirring rate (rpm)</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Calcine Preparation

Three calcines were prepared for leaching by roasting the Raglan concentrate under various conditions. The first calcine (named Calcine650) was prepared by roasting 5 grams of Raglan concentrate at 650 °C with 500 mL/min air stream until the SO₂ concentration in the offgas dropped to near zero. The temperature and SO₂ profiles and the switch of the feeding gas are shown in Figure 2. This calcine was examined using SEM/EDS. Figure 3 illustrates a backscattered electron (BSE) image of this calcine and the elemental maps of Fe, Ni, and S of the same area. It shows that even the largest pyrrhotite particles were completely oxidized, indicating the complete oxidation of pyrrhotite in the sample, forming iron oxides by Reaction 1 (Yu et al., 2012). Relatively large pentlandite particles have a characteristic microstructure of a nickel sulfide core and iron oxide rim, indicating the preferential oxidation of iron sulfide from the pentlandite via Reaction 2 (Yu et al., 2012). The degree of sulfur elimination of this calcine is 69.9% by chemical analysis.

\[2\text{Fe}_{1-x}\text{S} + (3.5-1.5x)\text{O}_2 \rightarrow (1-x)\text{Fe}_3\text{O}_4 + 2\text{SO}_2\]  \hspace{1cm} (1)

\[(\text{Ni},\text{Fe})\text{S}_8 + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{Ni}_x\text{S} + \text{SO}_2\]  \hspace{1cm} (2)

![Figure 2 - Temperature and SO₂ concentration in the offgas during roasting of sample Calcine650](image)

One partially roasted calcine (named Calcine650S) was prepared by roasting the Raglan concentrate at 650 °C with the feeding gas of a mixture of 500 mL/min air and 500 mL/min 10% SO₂ (balance N₂) until no apparent SO₂ was emitted from the sample. The last calcine (named Calcine750) was produced by roasting the concentrate at 750 °C with air, aiming to investigate how the roasting temperature would affect the leaching behavior of the calcine. The degree of sulfur elimination for Calcine750 is 91.8%. The temperature and the SO₂ concentration in the offgas are plotted against roasting time in Figures 4 and 5 for Calcine650S and Calcine750, individually.
Figure 3 — BSE image and elemental maps of Fe, Ni, and S of the sample Calcine650
Leaching Tests

Leaching Test 1: DAL of Calcine650

Dilute HCl acid leaching of sample Calcine650 was conducted in this test for 48 hours. The progression of leaching for various elements is shown in Figure 6. The degree of sulfur elimination is 69.9% during roasting. The sulfur curve levels off immediately after 0.5 hour leaching and remains constant at 63%. This 63% sulfur that leached out within very short time most likely existed as sulfates, as sulfates have fast leaching rate due to their direct dissolution into the leachate without chemical transformations involved. In order to further prove that the 63% sulfur is from sulfates, a thermogravimetric analysis (TGA) test was conducted on the sample Calcine650. The calcine was heated up to 950 °C at 15 °C/min in argon. After the temperature was held at 950 °C for 10 min, it started to drop to room temperature at 15 °C/min. The SO₂ concentration in the offgas was analyzed by the gas analyzer. The result is illustrated in Figure 7. The weight loss and the emission of SO₂ are due to the decomposition of sulfates, which can be generally described as Reaction 3. The weight change is ~7.6 mg for 50.5 mg sample. Based on the weight change, the weight fraction of the sulfur as sulfates in the calcine can then be calculated to be 6.00%. While in the leaching test, the weight of the sulfur that was leached into the
solution is calculated to be 5.26% of the calcine sample. These two values are in good agreement with each other, indicating the initially removed 63% sulfur has been presented in the form of sulfates.

Figure 6 – Progression of leaching for DAL of Calcine650

Based on the EDS analysis of the Raglan concentrate and the calcines, all the Mg and Al are in the siliceous gangue materials. As is shown in Figure 6, almost all Mg was leached in 4 hours. A large proportion of Al was also leached although it only weighs 0.40% in the concentrate. However, only around 50% Si was dissolved. This shows that the Mg and Al in the siliceous gangue materials were preferentially attacked by the acid. The percentage of Cu that was leached was also very high, and the dissolution took place primarily in the first 30 minutes, corresponding to sulfate leaching period. This points to the formation of a large amount of copper sulfate during roasting. The major portion of the Ni
was still in the sulfide cores in the calcine based on the EDS analysis. After 48 hours leaching, over 90% of Ni was leached out, indicating that the nickel sulfide cores were gradually attacked by HCl acid. Apart from nickel sulfide, NiO and NiFe₂O₄ could also be leached, contributing to the high percentage of Ni extraction. However, the leached percentage of sulfur remains constant although the nickel sulfide core was gradually attacked.

The possible reason is the formation of elemental sulfur during the acid leaching of the nickel sulfide cores, which can be represented by Reactions 4 and 5. These two reactions require the presence of oxidants in the leaching solution (e.g., Fe³⁺, Cu²⁺). The leaching profile of Cu is similar to that of Ni because of the similarity of these two elements as well as the co-presence of Cu as inclusions with Ni in the pentlandite. Of all the elements of interest, Fe has the least extent of leaching, which can be seen in Figure 6. In sample Calcine650, most of iron is in the form of Fe₂O₃ and NiFe₂O₄, accounting for its low dissolution rate. The formation of iron sulfates is limited under the examined conditions due to their relatively low decomposition temperature. Figure 8 shows the BSE and optical images of the leach residue. The remains are mainly nickel ferrous ferrite (Ni₄Fe₄O₁₂) and silicious gangue materials. Most of the oxide rims in the partly oxidized pentlandite particles were broken down into fragments as can be seen in the BSE image. In the optical image, the oxide rim was seen to be relatively intact, in which the sulfide core is mostly leached with very little remains (shown as the while yellow part).

\[
\begin{align*}
\text{Ni}_2\text{S}_2 & \rightarrow \text{Ni}^{2+} + \text{NiS} + 2e^- \\
\text{NiS} & \rightarrow \text{Ni}^{2+} + \text{S} + 2e^-
\end{align*}
\]

Figure 8 – BSE and optical images of the leaching residue from the DAL of Calcine650

Leaching Test 2: HWL of Calcine650

Sample Calcine650 was leached in water at 90 °C for 5 hours, with the leaching results shown in Figure 9. The only water-soluble species in the calcine should be sulfates. The results show that 30 min is long enough to leach all the sulfates into water. After 30 min, the content of most of the species, except Cu and Si, stay relatively constant. Around 63% sulfite was leached after 30 min water leaching, which is consistent with the results from the CAL of Calcine650. No sulfates of Fe and Al were formed in the calcine since these two elements were not found in the leaching solution. The content of Cu²⁺ in the leaching solution decreased after 30 min, indicating the Cu²⁺ started to precipitate out. Cu²⁺ precipitation has also been reported in the heap leaching of copper–nickel sulfide ore. Maley, Bronswijk, and Watling (2009a, 2009b) studied the interactions of Cu with selected sulfide minerals and the effect of aeration and pH on the Cu recovery. It is claimed that the copper deposition is partly caused by the reaction Cu²⁺+H₂S→CuS+2H²⁺, in which the hydrogen sulfide is the product of the dissolution of pyrrhotite. This copper deposition can occur in the solution with a pH range 1 to 5, preferentially with pH higher than 2.3.
pH plays an important role in the Cu precipitation. When pH is higher than 2.3, \( \text{Cu}^{2+} \) is precipitated by absorption on or reaction with the sulfide minerals. In the present study, the precipitation of \( \text{Cu}^{2+} \) is believed to be caused by its reaction with the sulfide in the calcine, which is represented by Reaction 6. Nickel sulfide (NiS\(_2\)) in the calcine acts as a source of electrons and sulfur for the reduction of \( \text{Cu}^{2+} \) and formation of \( \text{CuS} \). The slight increase in the content of \( \text{Ni}^{2+} \) in the leaching solution after 30 min in Figure 9 coincides with the assignment of Reaction 6, which produces \( \text{Ni}^{2+} \) as one product.

\[
2\text{Cu}^{2+} + \text{NiS}_2 \rightarrow \text{NiS} + 2\text{Ni}^{2+} + \text{CuS}
\]

(6)

![Graph showing percentage of leached elements over leaching time](image)

Figure 9 – Hot water leaching results of sample Calcine650

**Leaching Test 3: CAL of Calcine650**

Sample Calcine650 was leached with concentrated HCl acid (5N) at boiling temperature for 12.75 hours, the results being shown in Figure 10. As can be seen, the leaching by concentrated HCl acid is less selective but much faster compared with the DAL results. Most of the species, except Ni and S, were leached into solution after 2 hours. It is known that the iron compounds in the calcine are mainly hematite \( \text{Fe}_2\text{O}_3 \), magnetite \( \text{Fe}_3\text{O}_4 \), and nickel ferrite \( \text{Ni}_x\text{Fe}_{2-x}\text{O}_4 \). The complete dissolution of iron species shown in Figure 10 demonstrates that these three iron-containing compounds are readily attacked by concentrated HCl solution. The leaching rate of Ni is relatively slow due to the protective elemental sulfur layer formed on the sulfide surface, which diminished further dissolution of the nickel sulfide cores. As can be seen in Figure 11, the main minerals in the leaching residue are siliceous gangue materials, nickel sulfide and elemental sulfur. Small particles of nickel sulfide cores were completely leached forming elemental sulfur particles. For larger sulfide particles in which the leaching was incomplete, an elemental sulfur layer can be clearly observed on the surface of the sulfide.
Figure 10 – Concentrated HCl acid leaching behavior of sample Calcine650

XRD analysis was used to determine the mineralogical composition of the leach residue, with the spectrum shown in Figure 12. The formation of elemental sulfur is confirmed by the dominant peaks of S₇ in the XRD pattern. It also shows the presence of another phase Ni₇S₈ as a by-product. Based on its stoichiometry, this phase should be an intermediate product during the oxidative transformation of nickel sulfide Ni₅S₂ to Ni³⁺ and elemental sulfur S₇. The dissolution of Ni₅S₂ forming Ni³⁺ and S₇ requires oxidant. It is clear that the main oxidant in the leaching solution should be Fe⁴⁺ from the dissolution of iron oxides.

In this scenario, Reactions 7 and 8 are tentatively suggested as the mechanism of the dissolution of nickel sulfide in the present study; nickel sulfide core (Ni₅S₂) is first oxidized by Fe⁴⁺ in the highly acidic solution with the preferential dissolution of metallic ions into the solution, forming solid Ni₅S₈ on the surface of the sulfide; the Ni₅S₈ is then further oxidized by the Fe⁴⁺ forming elemental sulfur. Figure 13 schematically illustrates the dissolution of a Ni₅S₂ particle with the presence of the oxidant Fe³⁺ in the HCl solution. Ni₅S₈ should be found as a layer beneath the elemental sulfur rim. The non-stoichiometry of Ni₅S₈, as well as the rate controlling step which should be ionic diffusion through the solid product, suggests a decreasing content of Ni in Ni₅S₈ away from the sulfide core, which is exhibited in Figure 13. The morphological feature of the incompletely leached nickel sulfide with elemental sulfur rim is shown in Figure 14. The Ni₅S₈ layer could not be clearly differentiated from elemental sulfur using EDS due to its low content of Ni.
Figure 11 – BSE image and elemental maps of Fe, Ni, and S of the leaching residue from the CAL of Calcine650

Figure 12 – XRD pattern for the residue from the CAL of Calcine650
3Ni\textsubscript{3}S\textsubscript{2} + (18-2x)Fe\textsuperscript{3+} \rightarrow Ni_{3}S_{6} + (9-x)Ni\textsuperscript{2+} + (18-2x)Fe\textsuperscript{2+} \quad (7)

Ni_{3}S_{6} + 2xFe\textsuperscript{2+} \rightarrow 3/4S\textsubscript{8} + xNi\textsuperscript{2+} + 2xFe\textsuperscript{3+} \quad (8)

Figure 13 – Schematic representation of the oxidative dissolution of Ni\textsubscript{3}S\textsubscript{2} in HCl solution with the presence of Fe\textsuperscript{3+}

Figure 14 – Optical and elemental mapping images showing the morphological features of the nickel sulfide core coated with elemental sulfur rim

Leaching Test 4: DAL of Calcine650S

Partly sulfation roasted sample Calcine650S was leached with dilute HCl solution, the results being shown in Figure 15. The profiles of the leaching curves are similar to those of the DAL of Calcine650. The sulfur dissolution is approximately 72%, which is 9% higher than that of the DAL of Calcine650, indicating the higher amount of sulfate formation. The amount of sulfate formation of Ni, Co, and Cu, which could be estimated based on the 30 min data in Figure 15, are all higher than in Figure 6. The formation of NiSO\textsubscript{4} is still very low (34%) after the sulfation roasting for 56 min, due to the protective layer of NiSO\textsubscript{4} formed which inhibited further sulfation (Yu et al., 2012). It can also be observed that the dissolution of Si increased from 52% (in Figure 6) to 87% (in Figure 15) after reaching plateau, showing higher susceptibility of Si in the form of silicate to acid leaching after sulfation roasting. Elemental sulfur must also have formed from the dissolution of the nickel sulfide, indicated by the constant percentage of sulfur dissolution after 30 min in Figure 15.
Leaching Test 5: DAL of Calcite750

In order to investigate the leaching behavior of calcite roasted at higher temperature, the calcine, generated by roasting the Raglan concentrate at 750 °C, was leached with dilute HCl acid. The degree of sulfur elimination of this calcine is 91.8%, much higher than that of the Calcite650. As is shown in Figure 16, 98% of sulfur in the calcine was leached as sulfates within 0.5 hour, and the balance is sulfides, which indicates that the weight ratio of sulfates to sulfides in the calcine increases with the increase of roasting temperature. Compared with the results of the Leaching test 1, much lower percentages of elements of interest, i.e., Ni, Cu, and Co, were leached at the beginning of the leaching process, because of the lower percentages of these elements existing as sulfates in the Calcite750.

The iron profile in Figure 16 is lower than that in Figure 6, especially at the beginning. Apparently, this has nothing to do with the formation of sulfates, since no iron sulfates formed in both calcines. But the higher the degree of roast, the higher amount of the iron species in the concentrate would be oxidized to Fe₂O₃ than to Fe₃O₄. Previous study by other researchers demonstrated the relative reactivity of hematite, magnetite, and nickel ferrite in HCl solution is in the order Fe₂O₃ > Fe₃O₄ > NiFe₂O₄ (Lu and Muir, 1988), in other words, the leaching rates of these three compounds would be in the same order. Less fraction of magnetite in the Calcite750 than in the Calcite650 is partially responsible for the lower leaching rate of iron in Figure 16 than that in Figure 6. Similarly, more nickel ferrite forms when the concentrate is roasted at higher temperature, especially above 700 °C. The leaching rate of nickel ferrite is rather slow, which is another factor that contributes to the slower leaching rate of nickel in this leaching test, apart from the factor that less fraction of nickel sulfate exists in the Calcite750.
CONCLUSIONS

Water leaching and non-oxidative HCl leaching tests were performed on the calcines produced by roasting the nickel concentrate under various conditions. Results show that all sulfates could be leached by water within 30 min. Longer leaching time results in the slow precipitation of Cu⁺⁺ possibly due to its reaction with the nickel sulfide in the calcine. In acid leaching of calcine, the formation of elemental sulfur would inhibit the dissolution of the nickel sulfide in the calcine. Substantial amount of iron species was also leached along with the dissolution of non-ferrous metal species in the non-oxidative acid leaching of the calcine. Leaching the calcine with stronger HCl solution is much faster but less selective. Calcine produced at higher temperature was less susceptible to acid leaching due to the formation of more acid-resistant compounds, such as NiFe₂O₄ and Fe₂O₃.

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REFERENCES


