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FACTORS AFFECTING THE LEACHING STAGE
OF THE AMMONIA LEACHING PROCESS AS
APPLIED TO NICKEL SULFIDE ORES
AND CONCENTRATES

by

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INTRODUCTION

The principle underlying the process for nickel recovery by ammonia leaching, is the high solubility of finely divided metallic nickel in an oxygenated ammonia solution. Caron\(^{(1)}\) recognized the industrial possibilities of such a process and obtained a patent in 1924 covering this principle for commercial purposes. Application of this process was primarily directed towards nickel ores of an oxidized nature, such as limonite and serpentine, in which the nickel is present as a hydrated nickel-magnesium silicate known as garnierite. Due to various difficulties encountered, very little commercial development followed until World War II, when the Freeport Sulphur Company constructed a plant\(^{(2)}\) to treat lateritic nickel ores occurring in Cuba, utilizing ammonia leaching. The basic operations were as follows:

1. Decompose the hydrated silicate ore at elevated temperatures.
2. Selectively reduce the nickel oxide to metal leaving most of the iron in the oxidized form.
3. Leach out the reduced nickel with an oxygenated solution of ammonium hydroxide and ammonium carbonate.
4. Filter off the residue and precipitate the nickel as a basic carbonate by boiling off the free ammonia.
5. Calcine the basic nickel carbonate to produce nickel oxide.
6. Recover \(\text{NH}_3\) and \(\text{CO}_2\), to regenerate the leaching solution.
Copper, copper oxide and metallic cobalt behave similarly when subjected to an ammonia solution, so if present they will be leached out along with the nickel.

In 1946, F.A. Forward and C.S. Samis of the Department of Mining and Metallurgy investigated the possibilities of applying an ammonia leaching process to a nickel sulfide ore, in particular to a 16% nickel concentrate from the Sherritt Gordon Lynn Lake properties in Northern Manitoba. Results appeared to be promising, but recoveries were too low for an economic process, therefore a comprehensive investigation was undertaken the following year, to evolve a process that would produce high recoveries and would be economical for large scale operation. The results from this investigation indicated a possibility of obtaining a 96% nickel and an 85% copper recovery. Generally, it is difficult to predict accurately the economics of a process from results on a laboratory scale, however, there was good indication of an economically feasible process.

A tentative flow sheet resulting from this investigation is reproduced in Figure 1, and following is a summary of the proposed process.
Fig. 1 - Proposed Flowsheet for Ammonia Leaching of Nickel Sulfide Concentrates

CONCENTRATE

Air → ROASTING

H₂ → REDUCTION

O₂ → DIGESTION

O₂ → LEACHING

FILTER

Residue (Tails) Filtrate

Nickel Powder → CEMENTATION

Filtrate Solids (Ni,Cu)

NICKEL RECOVERY

Nickel Leach Solution
SUMMARY OF PROPOSED PROCESS

Roasting

No particular difficulty was encountered in roasting the ore, however a finishing temperature around 800°C is required to decompose sulfates that tend to form at lower temperatures. The sulfates are soluble and thus the sulfate concentrations would tend to build up in the leaching solution, if a cyclic process were used. Higher temperature increases ferrate formation and since copper ferrate is not readily reducible and is insoluble in the ammoniacal solution, copper recovery will decrease with increased finishing temperature.

Reduction

The nickel, which appears as NiO in the calcine, must be converted to the metallic form before dissolution can occur. H$_2$ was used as the reducing agent, however CO or water gas are possible substitutes. Optimum reduction temperature was found to be in the range of 480 - 500°C when H$_2$ was used for reduction.

Digestion

It was found necessary to introduce this stage to reoxidize the small quantity of metallic iron formed during the reduction stage, which otherwise, would seriously effect the leachability of the nickel. This reoxidation was carried out in the leach solution prior
to leaching. The optimum conditions for digestion were found to be a temperature of $35^\circ - 40^\circ C$ with mild agitation of the mixture.

**Leaching**

A maximum solubility of 14-16 gm. of nickel per liter was obtained using an 8% NH$_4$OH + 8%(NH$_4$)$_2$ CO$_3$ (by weight) aqueous solution. The nickel must be present in the metallic state before dissolution can occur, as NiO is insoluble. Copper behaves differently as both the metal and oxide (CuO) are soluble. Oxygen is a prime requirement for the leaching process, and the rate of leaching depends upon the concentration of oxygen in solution.

**Solution Purification**

Copper is present with the nickel in solution and must be removed. Copper can be cemented out completely by nickel powder, providing free ammonia is present and the temperature is maintained at $68^\circ - 75^\circ C$.

**Nickel Recovery From Solution**

The relatively pure nickel ammonia solution resulting from the foregoing operation is heated to boil off NH$_3$, CO$_2$ and water vapor. As the ammonia concentration is depleted, the nickel precipitates as a basic nickel carbonate. The latter is readily calcined to NiO and may be marketed in this form.
OBJECT OF INVESTIGATION

The investigation as carried out in the laboratories of the Department of Mining and Metallurgy was primarily concerned with the feasibility of applying ammonia leaching to a nickel sulfide ore, however the importance of the theoretical aspects of the various stages evolved were realized, therefore further studies were undertaken with this point in view. This paper includes the results of an investigation of the factors that affect the leaching stage of the proposed process.

As the description of most of the equipment used and mode of operation were described in the published paper, they will be deleted here, as well as results that have no bearing on this paper.
DISCUSSION

Reduction

The temperature at which the calcines were reduced, had a very important effect on the nickel recovery from the leaching stage. This effect is quite evident in Figure 2, where results of leaching tests, using calcines reduced at various temperatures, are plotted. As can be seen from this curve, the optimum reduction temperature appears to be in the neighborhood of 480-500°C.

![Fig. 2 - Effect of Reduction Temperature on Nickel Leachability.](image)

Using hydrogen, NiO begins to reduce to metallic nickel around 230°C (5), but the rate of reduction is quite slow. This rate increases with rising temperature, but is not rapid enough until 480°C is reached, to get complete reduction of the NiO in the allowed reaction time. Therefore, below 480°C, complete reduction does not occur and indicates the reason for the decreased nickel recovery.
On the other hand, apparently magnetite begins to reduce to iron around 475°C and the quantity of reduced iron formed, increases rapidly as the temperature is raised above 500°C. As indicated earlier, this reduced iron seriously interferes with the nickel leachability and explains the sharp decrease in nickel recovery when temperatures above 500°C are used in reduction.

R. Johnson\(^{6}\), applying a similar scheme to a Cobalt sulfide ore, obtained similar results. Results of the reduction temperature on Cobalt recovery are reproduced in Figure 3, with Mr. Johnson's kind permission.

Various reducing gases, such as H\(_2\), CO, or mixtures such as water gas, can be used for this reduction, however H\(_2\) is probably the best suited for low temperature reduction as it apparently produces the most active form\(^5\) of nickel.
Hydrogen being a highly penetrating gas would also tend to give a more rapid and complete reduction.

**Digestion**

With the introduction of digestion preceding the leaching stage, recoveries of 96% of the nickel were realized and consistent results were obtained, providing proper conditions were maintained during the roasting and reduction stages. Upon first considerations, no apparent reason was evident that could satisfactorily explain the necessity for this preliminary treatment, therefore a study of the digestion stage was undertaken in an attempt to determine the cause of the inhibition of the nickel leaching without digestion and how this inhibition was overcome when digestion was employed.

The original method utilized for digestion was simply to add 10 grams of the reduced calcine to 500 ml. of oxygenated ammonia leach solution in a 2 liter winchester bottle and allow the mixture to stand 24 hours without agitation. If the mixture was stirred at room temperature during this period, no benefit was derived from the digestion. However, at temperatures above 35°C, agitation had no adverse effect on the digestion reaction.

In observing the appearance of the mixture as the digestion reaction proceeded, red Fe(OH)₃ could be seen to form in the solution above the reduced calcine and would settle as a reddish-brown layer on the black pulp. The
residues from the leach solutions that had been subjected to digestion and produced high nickel recoveries, were reddish-brown, while those that were not digested and consequently produced low recoveries, remained black in color as the original reduced calcine.

From the foregoing, there was strong indication that the iron present was responsible for preventing the nickel from being leached. During the reduction of the calcine, temperatures (480 - 500°C) are maintained to selectively reduce the NiO to metallic nickel and the Fe₂O₃ to Fe₃O₄, however, some metallic iron is formed which apparently must be converted to Fe(OH)₃ during the digestion, before satisfactory leaching can be attained.

The first series of tests were carried out to obtain evidence that the iron did inhibit the nickel leaching and to determine whether the manner in which the iron and nickel were associated had any effect on the leaching reaction.

In these tests, pure nickel powder, mechanical mixtures of iron and nickel powder, and synthetic iron-nickel mattes that had been roasted and reduced, were subjected to ammonia leaching with and without digestion and the resulting nickel recoveries compared.

Typical results for these tests appear in Table I.
Table I - Effect of Iron-Nickel Association on Nickel Leachability.

<table>
<thead>
<tr>
<th>No.</th>
<th>Material</th>
<th>Digested</th>
<th>Leach Time</th>
<th>% Ni Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-1</td>
<td>Ni Powder</td>
<td>No</td>
<td>20 hrs.</td>
<td>99.8</td>
</tr>
<tr>
<td>T-2</td>
<td>Ni &amp; Fe Powder</td>
<td>No</td>
<td>&quot;</td>
<td>100.0</td>
</tr>
<tr>
<td>T-3</td>
<td>Syn. Matte</td>
<td>No</td>
<td>&quot;c&quot;</td>
<td>53.0</td>
</tr>
<tr>
<td>T-4</td>
<td>&quot;</td>
<td>Yes</td>
<td>&quot;</td>
<td>99.5</td>
</tr>
</tbody>
</table>

The results indicate that nickel is readily soluble if present alone and is not affected by the iron, providing the latter is present as a mechanical mixture. In considering the material resulting from the roasted and reduced matte, it is highly probable that the nickel and iron are associated as an alloy or are in direct contact with one another. Therefore, it is apparent that if the iron is associated in this manner it must be reoxidized, that is, it must be subjected to digestion before the nickel can be leached successfully.

From the foregoing it can be concluded that the iron present in the reduced calcine is mutually associated with the nickel, necessitating the preliminary treatment termed digestion, if high nickel recoveries are to be attained. Evidently the digestion stage provides the necessary mechanism for the iron removal to occur, therefore attention was directed to determining how this mechanism takes place and the conditions necessary for it to occur.
The leach solution was saturated with oxygen before digestion, therefore it was necessary to determine whether the oxygen was utilized in the reaction. Digestion was carried out using solutions saturated with $N_2$, air and $O_2$.

Use of nitrogen resulted in very low recoveries, but improved when air was used, particularly if sufficient time was allowed for digestion. High nickel recoveries resulted when oxygen was employed with a digestion time of 4-6 hours at $23^\circ C$, and $\frac{1}{2}$ - 1 hour at a temperature of $35^\circ C$ or higher.

Consideration of the mechanism of digestion can now be undertaken. With the preceding points in mind, it becomes apparent that in the digestion reaction, a system exists involving two contacting metals present in an electrolyte and requiring oxygen for the reaction to proceed. This all points to the possibility that a short circuited galvanic cell is set up and that the iron is removed by a process similar to electrochemical corrosion. The iron must act as the anode, as it goes into solution and therefore the nickel must become the cathode. The reactions occurring at each electrode can be represented as follows:

Anode:
$$Fe \rightarrow Fe^+ + \nabla + 3 e$$

Cathode:
$$O_2 + 2H_2O + 4e \rightarrow 4 OH^-$$

the overall reaction being represented by the following equation:
$$4 Fe + 3O_2 + 6H_2O \rightarrow 4 Fe(OH)_3$$
Investigation of the finely reduced calcine by microscopic methods revealed very little to substantiate this theory, therefore a macroscopic method was used.

Since it was believed that the reaction was similar to electrochemical corrosion, the method adopted for studying this reaction was similar to those frequently used for galvanic corrosion tests in the laboratory. The corrosion cell used in the study of the digestion, consisted of an iron electrode and a nickel electrode, immersed in the ammonia leach solution and shorted through a milliammeter. A millivoltmeter measured the difference in potential existing between the two electrodes. An indication of the rate of corrosion and the polarity could thus be obtained from the current and voltage measurements.

In the first corrosion test, an attempt was made to determine the reason why the iron inhibited nickel leaching if digestion was not used. A nickel and an iron electrode were immersed in an oxygen saturated solution, and the solution agitated vigorously to simulate conditions encountered in leaching. Upon immersion of the electrodes, the iron became anodic with a potential difference of 60 millivolts and a current of 3 milliamps. Within a half hour, a thin, lustrous, brown film formed on the iron electrode and the current decreased to 0.4 milliamps, indicating that the corrosion had practically ceased. When the iron electrode was removed, the film was observed to be very tough and
continuous as illustrated on the left electrode of Figure 4. The light area surrounding the film, was the portion of the electrode covered with wax to prevent attack and thus have some method for comparison. The nickel electrode appeared to be unattacked, however upon re-immersing the electrode for 24 hours, without the presence of the iron electrode, some of the nickel dissolved as indicated on the right electrode of Figure 4. This would be expected, as it was indicated earlier that if no iron was present in contact with the nickel, the nickel was readily soluble.

Fig. 4-Corrosion Effects on Iron and Nickel Electrodes when Leaching solution is Agitated.

V.R. Evans\(^{(8)}\) states that, "In general, where anodic reaction leads to the formation of a soluble salt of the anode metal, nothing will occur which can interfere seriously with
the corrosion of the anode. When, however, cases are consid­
ered in which the discharge of the anion can lead to the
production of an insoluble salt at or near the anode surface,
other effects may come in. In considering the protective
effect of the anodic corrosion product, we have to determine
whether that corrosion product is adherent and continuous or
whether loose and porous. Further attack will be prevented
if the corrosion product is or becomes closely adherent to
the metal".

Apparently a case where a tightly adherent, continuous-
film on the iron surface results when the reduced calcine is
leached without digestion, as indicated by the results from
the corrosion cell test. The iron becomes anodic preventing
dissolution of the nickel, but due to the tightly adhering
film that forms on the iron, further removal of the iron is
prevented. However, the potential still exists, therefore
the nickel does not dissolve.

In actual practice some nickel dissolution does occur,
even though no digestion is carried out. This may be explained
by the fact that at the reduction temperature employed, only
small quantities of metallic iron are produced, therefore
there probably is some nickel not mutually associated with
the iron and thus would be soluble without digestion.

To determine the effect of the digestion stage,
electrodes of nickel and iron were immersed in an oxygen
saturated leach solution but no agitation was employed and
the temperature maintained at 23°C. When the electrodes were first immersed the nickel was anodic, but in a few minutes the polarity was reversed and the iron became anodic. The potential difference increased to 60 millivolts and the current increased to 3 milliamps and both remained constant for the duration of the test, indicating that in this case no interference with the corrosion rate was encountered.

As the test progressed, a flocculent coating of Fe(OH)₃ was observed forming on the iron electrode. This corrosion product did not adhere tightly, tending to fall off, exposing a fresh surface for corrosion. After 48 hours, the iron electrode was considerably corroded as can be seen on the left electrode of Figure 5.

Fig. 5-Corrosion Effects on Iron and Nickel Electrodes when Leaching solution is not agitated.
During this period no attack of the nickel occurred; however, upon removing the iron electrode and agitating the solution considerable dissolution occurred, as indicated on the right electrode of Figure 5.

Evidently, due to the quiescent state existing in the digestion stage, the oxygen concentration in the immediate vicinity of the iron electrode is less than when vigorous agitation is employed and under these conditions a porous corrosion product is formed. Without agitation, the oxygen must reach the surface by slow diffusional processes, resulting in the decrease oxygen concentration.

The effect of temperature on the digestion was studied by use of the corrosion cell maintained at 35°C. At the higher temperature, the electrodes were effected in a similar manner as the corrosion cell maintained at 23°C without agitation. However, when gentle agitation was employed a porous film was formed whereas the use of agitation at 23°C resulted in a continuous film. Here again the reason may be to the decrease in oxygen solubility at higher temperature.

The current flowing through the milliammeter from the cell maintained at 35°C increased to 30 milliamps, thus indicating that the corrosion was proceeding about 10 times as fast as at 23°C, which explains the shorter time required for digestion when carried out at 35°C or higher.
LEACHING

The nickel must be present in the metallic state before dissolution can occur, as NiO is insoluble. Copper behaves differently, as both the metal and the oxide CuO are soluble in the leach solution. The reason for this may be tied in with the relative strengths of the bonding between the oxygen and metal. The copper oxide is relatively easier to reduce than NiO, therefore the oxygen is not held as tenaciously as in the case of NiO.

In the reduced calcine the nickel is present in the metallic form but is soluble in the leach solution only if oxygen is available. The oxygen is necessary for oxidation of the nickel from metallic to the ionic form that appears in solution. Oxygen is quite satisfactory for this necessary oxidation; however if stronger oxidizing agents such as $\text{H}_2\text{O}_2$ are used no leaching occurs. This may be due to the possibility of forming NiO, which is insoluble.

Tests indicated that not only is oxygen necessary for the leaching reaction, but that the rate of leaching is dependent upon the oxygen concentration in the leach solution. Results of leaching time, when various oxygen pressures are used, appear in Figure 6. The decrease in leaching time as oxygen pressure is increased is quite evident.
The curves of Figure 7 were obtained from results in Figure 6, thus giving a direct relationship between leaching rate and oxygen pressure. The logarithmic plot of the curves of Figure 7 are illustrated in Figure 8.
The leaching tank was not designed to operate below atmosphere pressure, therefore air at various pressures was substituted for the oxygen atmosphere, to attain oxygen partial pressures of less than one atmosphere. However, as can be seen from Figure 7 and Figure 8, a distinct change occurs when oxygen is replaced by air, therefore the air atmosphere can not be used to represent the leaching rate of an oxygen atmosphere if pressure equal to the corresponding partial pressure of the $O_2$ in the air atmosphere.

From the curves of Figure 7 and Figure 8, an equation approximating the curve of Figure 7 was determined

$$r = 0.85 P^3$$

where $r$ = % nickel leached per minute

$P = O_2$ pressure in atmospheres.

For the air atmosphere, the following equation was
obtained,
\[ r = 0.8 \, P \]
indicating the rate was directly proportional to the partial pressure of the \( O_2 \) in the air atmosphere.

It should be emphasized that these equations do not represent rigorous mathematical derivations, but are simply empirical relationships that appear to satisfy the data over the very limited range of pressures investigated.

In considering the system that exists in the leaching reaction, it is apparent that three phases are involved - gaseous, liquid and solid, which gives rise to a very complex situation when reaction kinetics are considered. In a case of this nature, generally several mechanisms are involved and all must be considered if a mathematical derivation, or even a qualitative explanation of the reaction rate is to be attempted. In general, where these reaction mechanisms are consecutive, if one step is slow in comparison to the others, it will actually be the controlling mechanism and the overall rate is a measure of this particular mechanism. However, if the rates of all steps are about equal, complexity increases as it is difficult to assign the measured rate to any particular mechanism. Difficulty may also arise if the controlling step is not evident and attempts of assigning the measured rate to the obvious mechanisms will prove fruitless, therefore in a complex case of this type it is very difficult to make a complete analysis of the system without a very
detailed investigation.

However, we may consider some of the obvious mechanisms that occur in the system and if any one of them have general reaction rates similar to the measured rate, then it is quite probable that it is the controlling mechanism. The obvious mechanisms that do occur are as follows:

(1) Mass transfer of $O_2$ from the gaseous phase into the liquid phase.

(2) Transfer of $O_2$ from solution to the surface of the nickel with the possibility of the $O_2$ being adsorbed on the nickel surface.

(3) Reaction on the surface to form the complex.

(4) Removal of products from the nickel surface.

The measured rate was found to follow the equation $r = b \cdot p^x$ therefore (1) and (4) can probably be excluded as they are diffusional processes and generally are directly proportional to the concentration or pressure. However, if air is used as the leaching atmosphere, the rate is directly proportional to the pressure. In this case (1) may be controlling due to the presence of the $N_2$. The layer of air in immediate contact with the solution becomes depleted in $O_2$ forming a blanket of $N_2$ through which the $O_2$ must diffuse from the bulk of the gas. Thus the measured rate becomes the rate of $O_2$ diffusion through this $N_2$ layer.

In considering the possibility of oxygen adsorption, it can be seen that the measured rate using an oxygen atmos-
phere is similar to Freundlich's adsorption isotherm

\[ m = a P^n \]

therefore, there is some indication that adsorption of oxygen on the nickel surface does occur and that this mechanism is the controlling process.

The foregoing has been presented to stimulate interest in the theoretical aspects of reaction kinetics of this and similar leaching processes rather than an absolute explanation of what occurs and further work is contemplated to obtain more conclusive data to uphold or discard this theory of adsorption.
SUMMARY

The significant factors affecting the leaching stage were found to be: (1) temperature at which the calcine was reduced, (2) presence of metallic iron in the reduced calcine, (3) necessity for oxygen during leaching.

The optimum temperature range for reduction was found to be 480 – 500°C. In this range a minimum quantity of reduced iron is formed, while the nickel oxide is practically completely reduced within a three hour period required for reduction.

Reduced iron formed during reduction alloys with the nickel and prevents the latter from dissolving in the leach solution, therefore the iron must first be reoxidized. The digestion stage was introduced for this purpose and under controlled conditions the small quantity of reduced iron is reoxidized in the leach solution, leaving the nickel free to dissolve during the leaching stage. If the digestion, which is merely a soaking operation, is carried out at room temperature, no agitation can be tolerated; however if the temperature is raised above 35°C, mild agitation can be used and reaction rate increases about five fold. If higher reduction temperatures are used, reoxidation cannot be carried out completely during the digestion, resulting in lower nickel recoveries.
Dissolved oxygen in the leach solution is necessary for the leaching reaction to occur and the rate of leaching is dependent upon the oxygen concentration. If pure oxygen is used for leaching, the leaching rate is proportioned to the oxygen pressure cubed, indicating the considerable increase in rate when leaching is carried out under pressure.

Leaching at room temperature produced the best results, higher temperatures were favorable for the ferrous complex formation which would remain in the solution along with the nickel.
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ABSTRACT

An investigation of the factors affecting the leaching stage of the ammonia leaching of nickel sulfide concentrates that were first dead roasted and then subjected to reduction with hydrogen at elevated temperatures, revealed that:

(a) The temperature at which the calcine was reduced, was critical and had to be maintained within a fairly narrow temperature range of 430 - 500°C, if satisfactory nickel recoveries were to be realized.

(b) The presence of reduced iron produced during the reduction stage, seriously hampered the leaching of the nickel, but could be overcome by a preliminary treatment termed "digestion". During this stage the mixture of reduced calcine and leach solution were gently agitated at slightly higher than room temperature in the presence of an oxygen atmosphere. Under these conditions the iron was preferentially attacked and oxidized to ferric hydroxide, thus preventing any interference during the leaching stage.

(c) Oxidizing conditions were necessary during the leaching stage, which could be satisfied by air or an atmosphere of oxygen. The leaching rate increased five fold when the air was replaced with a pure oxygen atmosphere at normal pressure. Pressure had a pronounced effect on the leaching rate; the rate being directly proportional to the partial pressure of the oxygen when air was used and a cubical function of the pressure when pure oxygen was used. Strong oxidizing agents such as H2O2 were unsatisfactory due to their vigorous oxidizing nature resulting in very low recoveries.