Flash smelting versus aqueous oxidation

Habashi, F. (1)

Smelters have been operating for hundreds of years emitting millions of tons of SO₂ in the environment every year. In the middle of 1960’s environmental groups started pressing for cleaner air. The industry responded by building taller stacks, collecting some of the SO₂ to make H₂SO₄, improving flotation process to reject as much as possible pyrite or pyrrhotite, shifting from reverberatory to flash smelting, etc. These measures are, however, futile. The solution is treating sulfide concentrates to get elemental sulfur - a product that can be stockpiled safely, used as needed to make SO₂ or H₂SO₄, or even thrown away at no detriment to the environment.

During the recovery of copper, nickel, lead, and zinc from their sulfide ores, SO₂ is formed in large quantities [1]. For a long time, the problem was of little concern to metallurgists as can be attested from an important metallurgy book published in 1945 in which the fate of SO₂ was not even mentioned. The problem associated with this gas is twofold:

- About 30% of this gas is actually utilized to make H₂SO₄ and the rest is emitted in the atmosphere. Sulfur dioxide is emitted because its concentration in the exit gases is only 1-2% which is too low to be utilized directly for making acid. Millions of tons of SO₂ from this source are emitted annually in the environment. There have been numerous attempts to solve these problems and much research is being done for this purpose. However, processes aimed at solving the problem of SO₂ in smelter gases by obtaining highly concentrated SO₂ suitable for liquefaction, or exit gases rich in SO₂ that are suitable for H₂SO₄ manufacture, must assume the existence of a nearby market for either the liquid SO₂ or the acid [2].

- Sulfide ores normally contain small amounts of mercury, arsenic, selenium, and tellurium. These impurities either go to the process gases used to make H₂SO₄ or are emitted in the atmosphere. In both cases, there is the possibility of their entering in the nutrition cycle. Hence, processes have to be developed to cope with this hazard since these metals are highly poisonous. While arsenic, selenium and tellurium are collected in the dust recovery system, mercury is not removed by such system because of its much lower concentration. To condense mercury, the gases have to be cooled to at least -10 °C which is economically out of question. Processes have been developed to cope with this problem and they are now widely adopted [3]. If there is no market for H₂SO₄ near a smelter, then the tendency is to emit SO₂ in the atmosphere. As a result of recent legislation this is no longer tolerated. To get around this situation, tall stacks have been constructed. The tallest stack in the world has been constructed in Sudbury, Canada. It is 381 m high - as high as the Empire State Building (Figure 1). Its diameter at the bottom is 36 m and at the top about 16 m; it is made of reinforced concrete 1 m thick at the bottom and 1/4 m at the top, containing 1,050 tons of steel and 13,000 tons of concrete. A slightly shorter stack of similar design was also constructed at the Bingham Canyon, Utah where the largest copper smelter in the world is in operation. The cost of constructing such stacks was about $75,000/meter of height in 1982.

The case of copper

The roast reaction

Copper was produced over the centuries by pyrometallurgical route. The technology has undergone many changes. When high grade massive sulfide ores were available, they were broken down into small lumps and charged in a vertical furnace whereby the unwanted rock was removed as a slag and the copper-containing minerals were collected as a matte. When solidified, the matte was crushed and finely ground; half of it was oxidized then mixed thoroughly with the other half and the mixture was melted in a horizontal furnace with fluxes so that the roast-reaction between copper oxide and copper sulfide may take place to produce metallic copper, and at the same time iron is eliminated as a slag:

\[ 2CuO + Cu₂S \rightarrow 4Cu + SO₂ \]

The Welsh metallurgists were skilled in conducting this process, which became known as the Welsh Process.

Fig. 1: A smelter stack 381 meters high (photo: INCO)
Matte from as far as Butte, Montana and Chuquicamata in Chile was shipped to Swansea in Wales for transformation to copper.

Conversion reaction

Not far from Swansea, Henry Bessemer invented his revolutionary process in 1856 to produce steel from pig iron by blowing air through the molten material. The process became known as conversion. In this process, the time to produce a batch of steel was reduced from days to few minutes and at the same time the need to use fuel for making the transformation was eliminated. The copper industry adapted the same principle few years later and as a result, the roast reaction was displaced by what became known as the conversion reaction:

\[ \text{Cu}^+ + e^- \rightarrow \text{Cu} \]

\[ \text{S}^2- + \text{O}_2 \rightarrow \text{SO}_2 + 2^- \]

Overall reaction:

\[ \text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2 \text{ Cu} + \text{SO}_2 \]

When rich massive copper sulfide deposits became scarce, mining engineers turned to low grade ores for exploitation. This coincided with the invention of the flotation process at the beginning of the twentieth century. Hence it became possible to obtain rich pulverized concentrates from low-grade ores. These concentrates, however, were not suitable for charging to the vertical furnace, since the charge would be blown out of the furnace when air is introduced at the lower part of the shaft. As a result, copper metallurgists turned their attention to adapt the same horizontal furnace that was used for the roast-reaction to melt the concentrates. This was the beginning of the era of the reverberatory furnace which dominated the copper industry worldwide during a major portion of this century. While the vertical furnace is an excellent reactor: it is a heat exchanger as well as counter-current mass transfer reactor, the horizontal furnace suffers from the following:

- Excessive dust formation since the powdered concentrate is charged at right angles to the gas flow thus necessitating installing large dust recovery system.
- Gases leaving the furnace are at high temperature necessitating installing bulky and expensive heat recovery system.

Modern smelting routes

New smelting routes were directed mainly towards energy economy. The most successful are the flash melting (Outokumpu Process), the bath smelting (Noranda and INCO) and the continuous Mitsubishi Process. All these routes make use of oxygen or oxygen-enriched air instead of air and have several advantages:

- All the steps leading to the production of the raw metal are exothermic: flash smelting to produce a matte, purification of the matte to produce the white metal, and conversion of the white metal to blister copper. In bath smelting all these processes take place in one reactor (Noranda’s original version).
- Sulfur dioxide is produced in high concentrations and can be economically captured for sulfuric acid manufacture.
- The electrolytic refining of blister copper is a low energy process.
- The precious metals are collected as solid residue in a single step during the electrolytic refining.
- However, there are some disadvantages:
  - Large amounts of dust are produced which are usually recycled creating impurity problems.
  - Slag requires special treatment, e.g., slow cooling, grinding, and flotation or treatment in an electric furnace to recover its high copper content which represents a heavy recycling load.

Gases leaving the furnace are at high temperature necessitating installing bulky and expensive heat recovery system.

Fig. 2: Comparison between flash converting and anodic dissolution of copper sulfide

- The presence of certain impurities, e.g., antimony and bismuth in the feed material renders the single reactor process (the Noranda Process) incapable of producing a high quality copper because these metalloids will contaminate the refined copper.
- Although SO_{2} can be economically captured and transformed to H_{2}SO_{4}, the operation of the acid plant is dependent on the SO_{2} flow which is intermitted by the nature of the processes.

The problems mentioned above are not impossible to solve. For example:

- Dust collected from these furnaces can be treated in a special hydrometallurgical circuit instead of recycling to avoid the accumulation of impurities.
- Antimony and bismuth impurities may be removed from the concentrates by a selective leaching process, e.g., sodium sulfide leaching. They may also be removed from the refined copper by vacuum melting.
- The intermittent SO_{2} flow to the sulfuric acid plant is said to be solved by adopting a new technology – flash converting.

Flash converting

With the introduction of flash smelting it became possible to decrease the cost of operation because of the favorable economics of this technology. However, in copper smelters, the
generation of SO₂ in the converter is intermittent because the conversion reaction is a batch process. As a result, it is difficult to have a constant flow of SO₂ to feed the sulfuric acid plant. To solve this problem, a major smelter in the USA abandoned the Peirce-Smith converters and replaced them by flash converters. Flash converting has been used by INCO in Canada for many years to treat copper sulfide concentrates, mainly Cu₃S, obtained in powder form during metallurgical separation from nickel sulfide. This is a logical route since the feed material is already in powder form. In the recent adoption of this technology, however, the matte is cooled, crushed, and ground then fed to another flash smelting furnace to produce blister copper. The ground matte must be stock-piled in absence of air and moisture to prevent formation of sulfates which would otherwise result in impure copper. In this way a constant supply of SO₂ can be assured from the flash converting furnace [4]. Although crushing and grinding are known to be a high capital and operating costs operation, the designers of this new technology claim that the overall process is most economical.

If the copper industry is willing to adopt this technology one would wonder why then not consider the anodic dissolution of white metal to get elemental sulfur and by-pass the converting step? In such process a high grade matte approaching the composition of white metal would be produced in a flash smelting or a Noranda reactor, for example, then cast in form of anodes. These anodes are then dissolved by passing electric current to get copper cathodes and slimes containing elemental sulfur. The advantages of this procedure would be the following:

- There will be only one continuous flow of SO₂ that can be used to make acid.
- Fugitive emissions at the converting step will be eliminated because the converting step is already eliminated.
- The amount of acid produced would be reduced by about 25% (assuming a chalcopyrite concentrate feed).

- By-passing the fire-refining step.
- No new equipment would be needed because the blister casting wheel may be used for casting the white metal.

The expected disadvantages, however, could be:

- Conducting the anodic dissolution in bags.
- Increased potential during anodic dissolution as compared to electrolyzing of fire-refined blister copper.
- Processing of the slimes in this case may be more complicated as compared to the anodic slimes of traditional copper refining.

Anodic dissolution of sulfides has been practiced for many years for nickel and has been studied by a number of researchers for copper. Anodic dissolution of copper matte has also been studied but cannot be recommended because of the dissolution of iron. Fig. 1 shows a comparison between the present technology, flash converting, and anodic dissolution.

The case of nickel

The metallurgist produces nickel sulfide concentrates from the following sources [5]:

- Natural deposits composed mainly of the mineral pentlandite.
- Industrial pyrometallurgical operations producing Ni₃S₂-FeS matte.
- Leach solutions by precipitation with H₂S producing NiS.

In all these cases, nickel sulfide is accompanied by a small amount of cobalt and in some cases by an appreciable amount of copper.

Pentlandite

The major nickel sulfide mineral is pentlandite, (Ni,Fe)₉S₈. It occurs associated with other sulfide minerals as follows:

- Pyrrhotite, e.g., as in Thompson, Manitoba.
- Pyrrhotite and chalcopyrite, e.g., as in Sudbury, Ontario and Norilsk, Russia.
- Pyrrhotite, pyrite, and chalcopyrite, e.g., as in Lynn Lake, Manitoba.

A typical analysis of concentrates from these sources is given in Table 1. The first two concentrates in Table 1 represent the major tonnage treated. It should be noted that nickel is not only present in the mineral pentlandite, but also in solid solution with the pyrrhotite. As a result, in addition to these concentrates, a low-grade pentlandite - pyrrhotite fraction is usually obtained during the beneficiation process. A typical analysis of such concentrates is given in Table 2. This concentrate is considered as a source of iron after the recovery of its nickel content.

**Hydrometallurgy of high-grade pentlandite concentrates**

Sherritt Gordon developed the first hydrometallurgical route for the treatment of pentlandite concentrates. The process is based on aqueous oxidation in ammoniacal solution. Nickel, cobalt, and copper are solubilized as ammine complexes.

<table>
<thead>
<tr>
<th></th>
<th>Sudbury Ontario</th>
<th>Norilsk Russia</th>
<th>Thompson, Manitoba</th>
<th>Lynn Lake, Manitoba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>5.6</td>
<td>3.8</td>
<td>7.5</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>1.2</td>
<td>2.2</td>
<td>0.25</td>
<td>2</td>
</tr>
<tr>
<td>Fe</td>
<td>47.7</td>
<td>25</td>
<td>41</td>
<td>38</td>
</tr>
<tr>
<td>S</td>
<td>31.8</td>
<td>6</td>
<td>28</td>
<td>31</td>
</tr>
</tbody>
</table>

Table 1: Typical analysis of some high-grade nickel sulfide concentrates in per cent; balance gangue
Table 2: Typical analysis of low-grade nickel sulfide concentrates in percent; balance gangue

<table>
<thead>
<tr>
<th></th>
<th>INCO Ontario</th>
<th>Falconbridge</th>
<th>Stillwater</th>
<th>Montana</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.75</td>
<td>1.1</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.05</td>
<td>0.1</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>58</td>
<td>57</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>35</td>
<td>36</td>
<td>31.5</td>
<td></td>
</tr>
</tbody>
</table>

with formation of sulfate ion which is later recovered in form of ammonium sulfate fertilizer. The process has the advantage of not emitting SO₂ but is bound to form ammonium sulfate as a co-product [6].

Treatment of low-grade pentlandite concentrates

Pentlandite is always associated with large amounts of pyrrhotite. It is mandatory to remove as much as possible of this pyrrhotite when a pentlandite concentrate is prepared for the smelter to decrease SO₂ generation. The pyrrhotite fraction obtained contains small amounts of nickel, partly in solid solution and partly in form of pentlandite. It is considered a low-grade pentlandite concentrate but represents a large tonnage of nickel. Because of its fine particle size and the ease of its oxidation when stored in the open air, it represents an environmental problem. Therefore, many attempts have been made to treat this material:

Pyro – hydrometallurgical route

INCO Process

In the late 1950’s INCO built a semi-commercial plant for treating its low-grade pentlandite concentrate (Table 2) by the following method which was later abandoned because of unfavorable economics (Fig. 3):

- Oxidation to eliminate the sulfur content as SO₂ with the formation of nickel and iron oxides.

- Controlled reduction of the oxides to form metallic nickel and transform Fe₃O₄ into FeO.

- Cooling of the reduced material in absence of air.

- Leaching metallic nickel selectively with ammonia in presence of air.

- Boiling the solution to precipitate NiO and recover NH₃.

- Sintering FeO₂ to form agglomerated Fe₂O₃ suitable for the blast furnace.

Falconbridge Process

During the same period, Falconbridge developed a process for treating its concentrate (Table 2), based on sulfation roasting, water leaching of the sulfates, precipitation of the nickel values by H₂S generated as a result of the addition of pyrrhotite concentrate. The precipitated sulfide is then sent to smelting.

Hydrometallurgical route

Work conducted in 1960’s at Anaconda in Arizona showed that it was possible to solubilize nickel and copper from Stillwater concentrates (Table 2) while all the iron and most of the sulfur remain in the residue, by boiling with dilute nitric acid under a reflux condenser:

\[ \text{MS} \rightarrow \text{M}^{2+} + \text{S} + 2 \text{e}^- + 4 \text{H}^+ + \text{NO}_3^- + 3 \text{e}^- \rightarrow \text{NO} + 2 \text{H}_2\text{O} \]

where M represents Ni or Cu. For FeS, the overall reaction is:

\[ 2 \text{FeS} + 2 \text{HNO}_3 \rightarrow \text{Fe}_2\text{O}_3 + 2 \text{S} + 2 \text{NO} + \text{H}_2\text{O} \]

The advantage of this system is operating at ambient pressure, but the disadvantage is the necessity of recovering nitric oxide for recycle:

\[ 2 \text{NO} + 3/2 \text{O}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 \]

Nickel matte

Nickel sulfides in form of a matte, i.e., a solidified Ni₃S₄-FeS or Ni₃S₄-Cu₃S-FeS mixtures is obtained from:

- High-grade pentlandite concentrates by melting with fluxes to separate the gangue minerals as a slag.

- Oxide ores by melting with a sulfur-containing raw material such as pyrite, gypsum, or elemental sulfur.

The last mentioned concentrates are usually produced in remote locations and are shipped to nickel smelters in industrial countries. The oxide ore may be:

- Garnierite, a magnesium silicate containing nickel, e.g., New Caledonia

- Laterite, an iron oxide containing nickel, e.g., Indonesia.

There are a variety of methods used for treating nickel mattes. The first operation is the removal of iron to get either a binary sulfide, Ni₃S₄-Cu₃S or the monosulfide, Ni₃S₄:

Treatment of the binary sulfide Ni₃S₄-Cu₃S

Separation of Ni₃S₄ from Cu₃S is done by the following methods:

Segregation by slow cooling

At INCO refinery in Sudbury, the molten binary sulfide Ni₃S₄-Cu₃S is cast in molds and allowed to cool slowly, then crushed, ground, and separated by flotation. The Ni₃S₄ concentrate is then treated in a variety of ways to get the nickel while the Cu₃S...
concentrate is converted to blister copper in a flash converting furnace. During these operations large amounts of SO₂ are also formed.

**Hydrochloric acid leaching**

A process was developed by Falconbridge based on the separation of Ni₃S₂ from Cu₂S by leaching with concentrated hydrochloric acid, Ni₃S₂ is solubilized while Cu₂S is not:

\[ \text{Ni}_3\text{S}_2 + 6 \text{HCl} \rightarrow 3 \text{NiCl}_2 + 2 \text{H}_2\text{S} + \text{H}_2 \]

Cu₂S is separated by filtration for copper recovery, while NiCl₂ solution is first purified from dissolved H₂S, then crystallized as NiCl₂·2H₂O. Since it is technically difficult to reduce NiCl₂ by hydrogen to nickel, the chloride is first calcined to NiO then reduced:

\[ \text{NiCl}_2·2\text{H}_2\text{O} \rightarrow \text{NiO} + 2 \text{HCl} \]

\[ \text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O} \]

The process was later modified by dissolving both sulfides in aqueous chlorine, then separation is effected by adding fresh white metal to solubilize more nickel and precipitate the copper:

\[ \text{Ni}_3\text{S}_2 + 3 \text{Cu}^{2+} \rightarrow 3 \text{Ni}^{2+} + \text{CuS} + \text{Cu}_2\text{S} \]

When nickel chloride solutions are electrolyzed to recover metallic nickel, chlorine is generated at the anode which is collected and recycled to the leaching step.

**Sulfuric acid leaching**

This process is used in South Africa and Finland (Outokumpu). Both sulfides are solubilized by sulfuric acid in presence of oxygen at moderate temperature and pressure in autoclaves. Copper in solution is then precipitated by adding fresh white metal whereby more nickel sulfide is solubilized in the same way as in the previous process.

**Treatment of the monosulfide Ni₃S₂**

A variety of methods are also used for processing nickel sulfide:

**Anodic dissolution**

A relatively pure Ni₃S₂ is obtained at INCO refinery in Manitoba. This is cast in form of anodes and dissolved anodically to get pure nickel cathodes and elemental sulfur at the anode:

Anodic reactions:

\[ \text{Ni}_3\text{S}_2 \rightarrow 2 \text{Ni}^{2+} + 2 \text{NiS} + 2 \text{e}^- \]

\[ \text{NiS} \rightarrow \text{Ni}^{2+} + \text{S} + 2 \text{e}^- \]

Cathodic reaction:

\[ \text{Ni}^{2+} + 2 \text{e}^- \rightarrow \text{Ni} \]

**Thermal oxidation**

In some plants, Ni₃S₂ is oxidized to NiO and SO₂ which must be captured; the NiO can either be:

- Reduced by carbon to metallic nickel which is then refined electrolytically or by the carbonyl process.
- Dissolved in H₂SO₄ to from nickel sulfate solution from which pure nickel is obtained by electrowinning.

**Conversion**

Nickel sulfide undergoes conversion with oxygen in a top blown rotary converter (TBRC):

\[ \text{Ni}_3\text{S}_2 + 2 \text{O}_3 \rightarrow 3 \text{Ni} + 2 \text{SO}_2 \]

This route is more efficient than the oxidation-reduction route described above, because the process is not only exothermic but also does not require a reducing agent. Like the oxidation-reduction route, sulfur dioxide must be captured. Pure nickel is then obtained by the carbonyl process.

**Precipitated nickel sulfide**

Nickel sulfide, NiS, is obtained from leaching operations of laterites by precipitation with H₂S. The precipitate which contains CoS is shipped either to smelters or hydrometallurgical refineries for further processing. Two types of leach solutions are treated:

- **Sulfuric acid leach solutions.**
  In this case precipitation is conducted at high temperature and pressure, e.g., at Moa plant in Cuba.
- **Ammoniacal leach solutions.**
  In this case precipitation is conducted at ambient conditions e.g., at Nicaro plant in Cuba.

When the precipitated sulfide is flash-smelted, SO₂ is emitted. This technology which was adopted in the 1940's does not make sense today for the following reasons:

- Sulfur is added in form of H₂S to be removed later as SO₂. Hydrogen sulfide is a hazardous gas - it is toxic and may cause explosions. The emission of SO₂ creates an additional concern about its capture or rejection.
- Today, processes based on solvent extraction - electrowinning are now available for obtaining the pure metal instead of a sulfide. This technology was not available in the 1940's.
- Refining NiS by the ammonia leaching process such as Sherritt's process, recovers the sulfur in form of ammonium sulfate. While this is a credit for the process, the technology may not be economically viable in certain locations.

**Aqueous oxidation**

In most countries, smelters are plagued with the necessity to produce sulfuric acid as by-product. In the case of copper smelters, for example, one ton of copper is associated with 3 tons of acid. With modern smelting technology, the hot SO₂-rich gases can be reduced to elemental sulfur by injecting a reducing agent such as coal or natural gas in the gas stream. This would be an ideal solution since in this case 1 ton of copper will be associated with 1 ton of sulfur which is easy to store or transport.
technology is adopted in only one plant at Norilsk in Russia. Copper smelters could produce ammonium sulfate by reacting $SO_3$-containing gases with $NH_3$ thus by-passing constructing an acid plant. In this case 1 ton of copper will be associated with 4 tons of ammonium sulfate. The amount of ammonium sulfate produced annually will, however, be tremendous.

Formation of elemental sulfur

The pyrometallurgical route for treating such concentrates was the logical way because, historically this was the only way known. When, however, hydrometallurgical knowledge became well established, it became evident recently that other routes are possible based on the formation of elemental sulfur, thus avoiding the $SO_3$ problem. Under certain leaching conditions (temperatures about 150 °C, in an acid medium, and under oxidizing atmosphere) elemental sulfur can be produced directly in one step (Fig. 4) [7]. The zinc industry was the first and the only one so far to adopt such technology.

Before World War I zinc was produced exclusively by the retort processes which were highly polluting and energy intensive. This was replaced by the roasting-leaching-electrowinning route. This new technology, however, introduced serious disposal problems. Finally the pressure leaching technology was introduced in the 1980’s whereby elemental sulfur was produced, instead of $SO_2$, according to the reaction [8]:

$$ZnS + 2 H^+ + 1/2 O_2 \rightarrow Zn^{2+} + S + H_2O$$

The process is self sufficient with respect to acid consumption since the zinc-containing solution can be electrolyzed by the standard technology to generate the acid needed for leaching (Fig. 5):

$$Zn^{2+} + 2 e^- \rightarrow Zn$$  $$H_2O \rightarrow 2 H^+ + 1/2 O_2 + 2 e^-$$

Overall reaction:

$$ZnS + H_2O \rightarrow Zn + 2 H^+ + 1/2 O_2$$

Elemental sulfur can be stock piled to be used when needed to make $H_2SO_4$ or shipped long distances to the market. Oxygen is preferred to other oxidizing agents, e.g., $Fe^{3+}$ ion, $HNO_3$, etc., because it does not need to be regenerated. Further, large autoclaves 5 meter diameter and 30 meters long are now used [9]. The same technology can be applied to other sulfide concentrates.

Treatment of chalcopyrite

In case of chalcopyrite the reaction is:

$$2 CuFeS_2 + 4 H^+ + 5/2 O_2 \rightarrow 2 Cu^{2+} + 2 FeOOH + 4 S + H_2O$$

The process is also self sufficient with respect to the acid used when the copper-containing solution is electrolyzed [10-13]:

$$Cu^{2+} + H_2O \rightarrow Cu + 2 H^+ + 1/2 O_2$$

Treatment of pentlandite

In case of pentlandite the reactions are approximately:

$$NiS + 1/2 O_2 + 2 H^+ \rightarrow Ni^{2+} + S + H_2O$$

$$2 FeS + 3/2 O_2 \rightarrow Fe_3O_4 + 2 S$$

Overall reaction:

$$2(NiS + FeS) + 5/2 O_2 + 4 H^+ \rightarrow 2 Ni^{2+} + Fe_3O_4 + 4 S + 2 H_2O$$

In these reactions, pentlandite is represented as $NiS + FeS$ and not $(NiFe)_2S_2$ for the sake of balancing the equation in a simplified way. In this process also the acid needed for the reaction is generated during the electrowinning of nickel from the solution. The following points are worth noting:

- The behavior of $FeS$ is different from $NiS$: the first forms iron oxide while the latter forms $Ni^{2+}$ ions. This is because of the ease with which $Fe^{3+}$ ion first formed is oxidized, then precipitated according to:

$$2 Fe^{2+} + 2 H^+ + 1/2 O_2 \rightarrow 2 Fe^{3+} + H_2O$$

$$2 Fe^{3+} + 3H_2O \rightarrow Fe_3O_4 + 6 H^+$$

Overall reaction:

$$2 Fe^{3+} + 1/2 O_2 + 2 H_2O \rightarrow Fe_3O_4 + 4 H^+$$

The presence of acid is essential for the liberation of elemental sulfur from $FeS$ although it does not appear in the equation:

$$2 FeS + 3/2 O_2 \rightarrow Fe_3O_4 + 2 S$$

In the absence of acid, the ferrous ion is not capable of oxidation to ferric, and the product will be ferrous sulfate:

$$FeS + 2 O_2 \rightarrow FeSO_4$$

Acid added at the start is regenerated during the course of reaction in an amount equivalent to the iron in the feed, but will be consumed for the aqueous oxidation of nickel sulfide. However, this consumed acid will be regenerated during the electrowinning of nickel from the solution.

- Precious metals will remain in the residue and can be recovered by gravity methods after floating elemental sulfur (Fig. 6).

Fig. 6: Aqueous oxidation of pentlandite concentrates.
Ni^{2+} + 2 e^- → Ni
H₂O → 2 H⁺ + 1/2 O₂ + 2 e⁻

It is remarkable, that such a process was never tested on pilot scale although similar operation is now conducted successfully for treating zinc sulfide concentrates on industrial scale.

**Pressure hydrometallurgy**

Initially autoclaves were used for leaching bauxites more than 100 years ago, but the technology has progressed extensively since the mid 1980’s when applied for zinc sulfide concentrates and refractory sulfide gold bearing ores [14]. There are presently four plants treating zinc sulfide concentrates with elemental sulfur recovery and 23 autoclaves operating world wide for refractory gold ores. Some of these are 5.6 meters inside diameter and about 30 meters long, lined with acid resisting bricks (Figure 7).

Operational experience in autoclave technology has made rapid progress and the result is much smoother and safer operation. New special alloys have been introduced to reduce maintenance time. Sophisticated instrumentation allow for many safety features. The advanced design has allowed for greater availability and as a result, operating and maintenance costs have decreased. Many of these autoclaves operate up to 9 months continuously without shutdown. Large and efficient membrane piston pumps that can feed autoclaves continuously are now available. Flash tanks for heat recovery from the discharged slurry are widely used for efficient operation.

**Conclusions**

Constructing a new smelter or modernizing an old one can only be justified if all the SO₂ generated can be transformed to H₂SO₄ and a need exists for the acid. A more flexible route, however, is to treat the sulfide concentrate by hydrometallurgical route to get elemental sulfur which can be transformed to SO₂ or H₂SO₄ when needed.

**References**


(Fathi Habashi, Department of Mining, Metallurgical, and Materials Engineering, Laval University, Quebec City, Canada G1K 7P4, Fathi.Habashi@gnn.ulaval.ca)