ABSTRACT

Smelting of ores for metal extraction is an ancient art in our civilization. New technology is being introduced, but forces of resistance are sometimes so strong to permit a radical change. While the iron and steel, zinc, aluminum, and gold industries are responding to change, the copper and nickel industries seem to be more conservative.

Key words: iron, steel, copper, pressure hydrometallurgy, gold, aluminum, zinc, nickel, sulfur dioxide, elemental sulfur, sulfuric acid, pyrite, arsenopyrite.
INTRODUCTION

Extractive metallurgy today is usually divided into two sectors: ferrous and nonferrous because of the large scale operations in the ferrous [1]. Steel production in one year exceeds that of all other metals combined in ten years. As a result, metallurgists in the nonferrous sector usually do not participate in the activities of iron and steel makers and vice versa. This is a pity because for sure one can learn from the other. In fact, the copper industry adopted many technologies used first in iron and steel production. For example, when Bessemer invented the convertor in 1856 it was adopted in the copper industry ten years later, and when high grade massive copper sulfide ores were exhausted and metallurgists were obliged to treat low-grade ores, the puddling furnace was adapted in form of a reverberatory furnace to treat the flotation concentrates. Continuous casting started first in steel plants and was adopted later in the nonferrous industry. In general, the copper industry was in the footsteps of the iron industry although the two chemistries are far apart.

Pyrometallurgy is an ancient art and is most suitable for treating high grade oxide ores [2]. It is beyond doubt that iron will always be produced by pyrometallurgical route since iron occurs in nature mainly as an oxide. The case of copper is, however, different. But, before discussing the copper situation it will be interesting to review the changing technology in iron and steel production.

IRON

The reduction of iron ore to produce metallic iron took place in ancient times in a small furnace 2 to 3 meters high, charged with lumps of iron ore mixed with pieces of charcoal prepared from timber. Air required for burning of charcoal to supply the necessary heat for reduction was supplied by small bellows. The ore lumps were reduced to iron but not melted because the air draft was not strong enough to generate the high temperature needed for melting. When the furnace was cooled, the lump of metallic iron mixed with partially melted gangue minerals and slag, is then removed from the furnace, heated and hammered to get a consolidated metallic product. A furnace of this type would produce 1 or 2 kilograms of malleable iron per day which was enough to supply the need of that time(Figure 1).

The large charcoal furnace

To increase productivity, large furnaces were built with large air bellows mechanically operated by large water wheels. As a result, the temperature increased, and the iron produced melted in the furnace. Some iron was tapped directly into moulds in the casting house and the remaining was collected by allowing it to drain into sand moulds (called "pigs") prepared in the immediate vicinity. The product contained much dissolved carbon and was suitable for casting many items. A furnace of this period would be 5 to 10 meters high and would produce 10 or 20 tons of iron per day. The maximum size of the furnace was limited by the mechanical strength of the charcoal. To produce a high quality iron for tools and knives, it was necessary to refine this cast iron in what was known as a "finery". Small pieces of the cast iron were remelted in an oxidizing atmosphere to remove as much as possible of the carbon (Figure 2).
Figure 1 - Production of wrought iron in a short charcoal furnace with small air bellows.

Figure 2 - Production of cast iron in a short charcoal furnace with large air bellows.

The coke furnace

The industrial revolution started in England in 1709 when charcoal was substituted by coke. Coke is produced from coal - it is porous and can withstand high mechanical pressures. Hence larger furnaces could be built which resulted in a further increase in production. Coal cannot be used because it softens during heating and renders the charge impermeable. Coal mining was also unsafe because of the natural gas explosions until Humphry Davy introduced the miner's safety lamp and a great effort was needed to pump out the water flooding the mines. Using coal also solved the problem of cutting trees from the forests which were needed to build ships.

Pig iron containing 3-5% carbon is hard and brittle. It was used for making pots and pans, firegrates, some machine parts especially for steam engines, anchors, cannons and cannon balls. This was particularly important in warfare, because before the arrival of pig iron, cannons were made of bronze or brass which were more expensive. A small amount of pig iron was made into wrought iron (Figure 3). Wrought iron contains less than 1% carbon is soft and malleable. It was used for the production of nails, small arms, agricultural implements, horseshoes, wire, locks, and bolts.
Once the blast furnace technology using coke was established, efforts were made to economize its consumption and to cope with increased productivity.

- In 1828, the Scots engineer James B. Neilson (1792-1865) proposed preheating the air blast to about 95°C by passing the cold blast in a stove heated by burning coal. This decreased coke consumption by half and doubled pig iron production.

- In 1845, Edward Cowper burned blast furnace gas in the stoves to supply the heat instead of burning coal. However, to collect the gas it was necessary first to design a device to close the top of the furnace. Thus came the single-bell top into existence followed by the double-bell to eliminate completely the escape of gases.

- In some plants the blast furnace gas was first used to generate steam in a boiler before being burned in the stoves. Steam was used in the steam engine to blow air in the tuyeres (Figure 3).

- In 1900 the casting machine was introduced to replace the sand moulds in the ground. This became necessary due to increased furnace production. The molten iron was poured into the moulds from a ladle and cooled by water sprays as the chain travel to the head sprocket, falling from the mould into wagons.

- Many improvements were later introduced to economize fuel, e.g., sizing of the charge, air preheating to 1000°C, etc.
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Today a modern blast furnace produces 10,000 tons of pig iron daily and the molten iron is transferred in special refractory-lined wagons to steelmaking plant for making steel.

STEEL

A good quality metal was produced from wrought iron at high expense and on a small scale. It contained 1 to 3% carbon and was hard and tough, and was used for making knives and tools. The following methods were used (Figure 3).

- **Blister steel.** Pieces of wrought iron were surrounded with finely divided charcoal and heated for 10 days in pots at high temperature to permit diffusion of carbon at the surface layer of the iron thus rendering it strong. It became known as blister steel.

- **Cast steel.** Blister steel pieces produced by the previous method were remelted in crucibles to get a product of much higher quality containing homogenously dispersed carbon. The process was invented by Benjamin Huntsman (1704-1776) and the product was known as cast steel.

- **Puddle steel.** Another product of nearly equal quality was also developed in England by Henry Cort (1740-1800) in 1783 who improved the "finery furnace" by adjusting the amount of air to control the carbon content of the product. The method was tedious and must be carefully controlled but was more economical although nearly 30% of the iron was lost as a slag. It became known as the "puddling process".

- **Bessemer steel.** In the 1856, Henry Bessemer, (1813-1898) in England invented the pneumatic process for steelmaking. Not only the new process reduced the time of transforming iron into steel from a few days to a few minutes but also it eliminated the large amount of fuel needed for the puddling furnace since the process was exothermic (Figure 4). After solving the problem of dissolved oxygen by Robert Mushet in 1858 and that of phosphorus by Sydney Thomas and Percy Gilchrist in 1880, the process became well established. Cheap steel became now available to built ships and manufacture rails for the newly established railroad industry.

- **Open hearth steel.** Simultaneously, another process was developed in France by Pierre Martin using the horizontal furnace originally conceived by Wilhelm Siemens in England; the process became known as the Siemens-Martins open hearth furnace. The process used fuel for heating and iron oxide for removing the carbon (Figure 4). It produced steel of high quality, had the advantage of recycling a large amount of scrap, but was slow and environmentally unacceptable. The stack gases contained traces of hydrogen fluoride generated from the fluorspar added as flux.

- **Electric furnace steel.** The electric furnace process was introduced in 1900 to melt scrap by Paul Heroult when the cost of electricity became resonable, and been adopted on a large scale ever since.

- **LD steel.** The top-blown converter invented in 1955 in Linz, Austria in which oxygen was introduced at the top of the reactor thus decreasing the blowing time and at the same time increasing the amount of scrap that can be melted because of increased temperature.
• **Bottom-blown converter.** The bottom-blown converter invented in Canada and Germany in 1970's in which oxygen was introduced at the bottom of the reactor. It was evident for a long time that bottom-blowing is more efficient than top-blowing (better agitation, less dust formation, less noise, etc.), but no material of construction was available that can withstand the high temperature generated at the tuyeres when oxygen was used. The solution was found when the tuyeres were enveloped by a small stream of natural gas. The cracking of the hydrocarbons cooled the tips of the tuyeres and prevented their melting.

• **Top-blown bottom-blown steel.** Today, all primary steel is produced by a simultaneous top-blowing and bottom-blowing using oxygen, which results in higher productivity in a shorter time. In addition continuous casting of steel started in 1960's became today the major technology (Figure 5).
COKE

While organic chemistry is the chemistry of carbon, ferrous metallurgy is the technology of carbon. The carbon first used was charcoal produced from timber. When coal mining became safe, attempts were made to replace charcoal by coal, until the solution was found by first transforming coal into coke. Coke was first produced by piling coal in mounds and partially burning it in the open air in the same way charcoal was made.

- *The beehive process.* Beehive ovens replaced the open air method in 1763. The volatile matter was burned to supply heat for carbonization.

- *The horizontal retorts process.* The first attempt to recover the volatile matter was in the horizontal retorts system. The gas collected was known as coal-gas and was first used for illumination and later as a fuel.

- *The vertical retorts process.* Now large batteries of vertical retorts are used. Volatile matter collected proved to be an important source of chemicals such as tar, ammonia, H₂S, and hydrogen. The distillation of the tar and the separation of its different components became the basis of the organic chemical industry in the nineteenth century. Today, a coke manufacturing plant is a battery of hundreds of vertical retorts assembled together.

ROLE OF THE STEAM ENGINE

The growth of the iron industry suffered from the following:

- Water power was neither abundant nor reliable. Power was needed for operating the following equipment:
  - Pumps to drain water from coal mines
  - Bellows to blow air in the blast furnace
  - Hammers for forging
  - Rolling mills

- The use of coke necessitated a more powerful blast than that obtained from water-driven bellows because of its higher ignition temperature.

- A cheap way to transport coal in bulk to the coke making plant which is located near the blast furnace.

The steam engine was invented to fulfil these needs.

- Newcomen’s machine invented in 1712 was the first attempt to solve these problems. But it used mountains of coal to boil water to generate steam which was then condensed by cold water spray to create the vacuum needed to operate the machine.

- James Watt in 1770’s successfully built a machine that economized greatly on the coal needed, by introducing a separate condensing chamber for the steam so that the cylinder could remain hot throughout every stroke. However, it was not until 1784 that the steam

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3 The steam engine, of course, had far-reaching effects in many fields besides iron making.
engine became a reality and started to replace the water wheel. The bellows were no longer needed and air could be blown in the furnace through tuyeres.

- George Stephenson in 1820’s solved the problem of coal transportation by inventing the steam locomotive

COPPER

Copper is also an ancient metal like iron, but it occurs mainly as a sulfide and to a minor extent as an oxide. In ancient civilizations, the oxides were extensively exploited by reduction with carbonaceous material (timber) in small furnaces. When man started to exploit the sulfides, problems arose:

- Emission of large amounts of SO₂ because of the partial oxidation of the sulfides.
- The material melted during heating because of the formation of matte.

The roast-reaction process

Eventually, a process was developed, known as the roast-reaction process, whereby the solidified 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 furnace with fluxes so that the roast-reaction between copper oxide and copper sulfide would take place to produce metallic copper, and at the same time iron was eliminated as a slag:

\[ \text{Cu}_2\text{S} + 2 \text{CuO} \rightarrow 4 \text{Cu} + \text{SO}_2 \]

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

![Figure 6 - Copper production: Past and present.](image-url)
Welsh Process. Matte from as far away as Butte, Montana and Chuquicamata, Chile was shipped to Swansea, Wales for transformation to copper. Sulfur dioxide was also emitted in this step and no attempt was made to capture it (Figure 6).

The converter process

It was also not far from Swansea, where Henry Bessemer invented his revolutionary process to produce steel. The copper industry adapted the same principle few years later, i.e., blowing air through molten matte and as a result, the roast reaction was displaced by the conversion reaction:

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

New pyrometallurgical routes

Modern smelting routes such as the flash smelting process (Outokumpu Process), the bath smelting process (Noranda and INCO) and the continuous Mitsubishi Process make use of oxygen or oxygen-enriched air instead of air and have several advantages [3]. However, there are some disadvantages: large amounts of dust are produced, the slag requires special treatment, and although \( \text{SO}_2 \) can be economically captured and transformed to \( \text{H}_2\text{SO}_4 \), the operation of the acid plant is dependent on the \( \text{SO}_2 \) flow which by the nature of the processes is intermittent. Also a market for the acid must be available (Figure 6).

The hydrometallurgical route

Modern hydrometallurgy is only hundred years old - it started with the Bayer process for alumina production and the cyanidation process for gold. It is particularly suitable for treating sulfide concentrates, because under certain conditions of leaching: acid medium, oxidizing atmosphere, and a temperature around 150°C, elemental sulfur can be produced (Figure 7) [4]. Sulfur can be stock-piled and used when needed to make \( \text{SO}_2 \) or \( \text{H}_2\text{SO}_4 \), or shipped cheaply for long distances. When chalcopyrite, the major copper mineral, is treated by this technology, the following reaction takes place:

\[ 2 \text{CuFeS}_2 + 4 \text{H}^+ + 5/2 \text{O}_2 \rightarrow 2 \text{Cu}^{2+} + \text{Fe}_2\text{O}_3 + 4 \text{S} + 2 \text{H}_2\text{O} \]

When copper is recovered from solution by electrowinning, the acid generated at the anode is equal to that required for leaching, hence the process is self supporting and pollution-free. The copper industry is still hesitant to use this technology in spite of its obvious advantages.

NICKEL

The major part of nickel sulfide ores is smelted and the metal from this source is mainly refined electrolytically. In the late 1950's INCO built a semi-commerical plant for treating its low-grade pentlandite concentrate by the following method which was later abandoned because of unfavorable economics (Figure 8):

- Oxidation to eliminate the sulfur content as \( \text{SO}_2 \) with the formation of nickel and iron oxides.
- Controlled reduction of the oxides to form metallic nickel and transform \( \text{Fe}_2\text{O}_3 \) into \( \text{Fe}_3\text{O}_4 \)
- Cooling of the reduced material in absence of air
Figure 7 - Copper production in the future.

Figure 8 - Nickel production from pentlandite-pyrrhotite: The thermal treatment followed by leaching.

- Leaching metallic nickel selectively with ammonia in presence of air at ambient pressure
- Boiling the solution to precipitate NiO and recover NH₃
- Sintering Fe₂O₄ to form agglomerated Fe₂O₃ suitable for the blast furnace.
Pressure leaching route

Another route adopting aqueous oxidation of pentlandite in acid medium results in the formation of elemental sulfur. The reactions can be written in a simplified way as follows:\(^4\):

\[
\begin{align*}
\text{NiS} & + \frac{1}{2} \text{O}_2 + 2 \text{H}^+ \rightarrow \text{Ni}^{2+} + \text{S} + \text{H}_2\text{O} \\
2 \text{FeS} & + 3/2 \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2 \text{S}
\end{align*}
\]

Overall reaction:

\[
2 (\text{NiS} + \text{FeS}) + 5/2 \text{O}_2 + 4 \text{H}^+ \rightarrow 2 \text{Ni}^{2+} + \text{Fe}_2\text{O}_3 + 4 \text{S} + 2 \text{H}_2\text{O}
\]

When this route is compared with INCO process it is evident that it involves less steps and no SO\(_2\) emission (Figure 9). This is another example showing the superiority of pressure leaching technology. Although this is a Canadian invention it is not used in Canada but in Russia.

ZINC

For four hundred years, zinc was produced by a pyrometallurgical route. In this process zinc sulfide concentrate was roasted to oxide and SO\(_2\). The oxide was then reduced in retorts to metal vapor which was condensed rapidly to yield a low grade zinc. The crude zinc was then refined by vertical retorts of better design but the process still suffered from high fuel costs, low efficiency, environmental problems, and the necessity to capture SO\(_2\) generated in the roasting step.

During World War I the roasting-leaching-electrowinning process was introduced to exploit low-grade zinc concentrates which were not economical to treat by the retort process. The ZnO produced by roasting was leached by recycle acid obtained from the subsequent electrowinning step. The process required extensive solution purification and was generally successful, because it yielded directly high purity zinc but suffered from the following:

- Sulfuric acid must be produced from the SO\(_2\) generated in the roasting step
- A large portion of zinc was in the residue in form of ferrite, ZnFe\(_2\)O\(_4\), because it was insoluble in the recycle acid and had to be treated in a separate circuit. Processes were developed to treat this material but these created other problems, e.g., the final residue was more voluminous than the original, hence a stock piling problem (Figure 10).

Pressure leaching route

A fully hydrometallurgical process was developed in Canada in the 1980's based on the aqueous oxidation of zinc sulfide concentrates in dilute H\(_2\)SO\(_4\) at 150°C and under oxygen pressure of 700 kPa:

\[
\text{ZnS} + \frac{1}{2} \text{O}_2 + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{S} + \text{H}_2\text{O}
\]

In these reactions, pentlandite is represented as NiS + FeS and not (Ni,Fe)\(_2\)S\(_4\) for the sake of balancing the equation in a simplified way. Although this is not exact, yet it represents approximately the behavior of the sulfide.
Figure 9 - Nickel production from pentlandite-pyrrhotite: Aqueous oxidation.

Figure 10 - Zinc production from sulfide concentrates: Thermal treatment followed by leaching.
Autoclaves lined with acid-resistant bricks are used. The reaction is exothermic and yields elemental sulfur. No ferrites are formed, and therefore the residue can be disposed of directly and the solution can be purified in the usual way and electrolyzed to yield pure metallic zinc and acid for recycle to the leaching step (Figure 11). At present four plants are using this technology.

Figure 11 - Zinc production from sulfide concentrates: Aqueous oxidation.

ALUMINUM

The production of aluminum started in 1855 in France by Sainte-Claire Deville (1818-1881) by the reduction of aluminum chloride with sodium:

\[ \text{AlCl}_3 + 3 \text{Na} \rightarrow \text{Al} + 3 \text{NaCl} \]

The metal produced was too expensive. Attempts to reduce the cost by producing sodium cheaply by the new Castner's process were not enough.

The electrolytic process

Charles Martin Hall (1863-1914) in USA and Paul Hérroult (1863-1914) in France independently discovered a new cheaper process by electrolyzing Al₂O₃ dissolved in a cryolite bath and a carbon anode which is the basis of the process used today:

\[ \text{Al}^{3+} + 3 \text{e}^- \rightarrow \text{Al} \]

\[ \text{C} + \text{O}_2 + 2 \text{e}^- \rightarrow \text{CO} + 2 \text{e}^- \]

The production of alumina

During the same period, the pyrometallurgical process for producing Al₂O₃ from bauxite developed by Henri Le Chatelier gave way to the hydrometallurgical process developed by Karl Josef Bayer (Figure 12). This is another example showing a hydrometallurgical process replacing a pyrometallurgical process.
GOLD

Gold was the first metal used by man. It occurs mainly in the native state in alluvial deposits or in quartz veins. But, in recent years large deposits of refractory ore became available in which the minute gold particles are embedded in a pyrite-arsenopyrite matrix from which gold cannot be leached by standard methods. To treat this type of ore, it was necessary to destroy the sulfide structure so that the gold is liberated and can be leached. Thermal oxidation, i.e., roasting was used for many years. Due to its unacceptable environmental problems it is now being gradually replaced by aqueous oxidation, i.e., a hydrometallurgical route. Large horizontal autoclaves about 5 meters diameter and 30 meters long have been constructed to treat a concentrate containing as low as 15 ppm gold [5].

CONCLUSIONS

Hydrometallurgy proved to be a superior route not only for the treatment of bauxite, but also for treating sulfide concentrates. The major advantage is that elemental sulfur can be obtained directly during processing thus liberating the metal industry from the SO₂ and sulfuric acid problem.

REFERENCES


