Journal of Mining and Metallurgy, 43 B (2007) 1 - 19

COPPER METALLURGY AT THE CROSSROADS

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(Received 18 June 2007; accepted 14 July 2007)

Abstract

Copper technology changed from the vertical to the horizontal furnace and from the roast reaction to converting towards the end of the last century. However, the horizontal furnace proved to be an inefficient and polluting reactor. As a result many attempts were made to replace it. In the past 50 years new successful melting processes were introduced on an industrial scale that were more energy efficient and less polluting. In addition, smelting and converting were conducted in a single reactor in which the concentrate was fed and the raw copper was produced. The standing problem in many countries, however, is marketing 3 tonnes of sulfuric acid per tonne of copper produced as well as emitting large amounts of excess SO_2 in the atmosphere. Pressure hydrometallurgy offers the possibility of liberating the copper industry from SO_2 problem.

Heap leaching technology has become a gigantic operation. Combined with solvent extraction and electrowinning it contributes today to about 20% of copper production and is expected to grow. Pressure leaching offers the possibility of liberating the copper industry from SO_2 problem. The technology is over hundred years old. It is applied for leaching a variety of ores and concentrates. Hydrothermal oxidation of sulfide concentrates has the enormous advantage of producing elemental sulfur, hence solving the SO_2 and sulfuric acid problems found in smelters.

Precipitation of metals such as nickel and cobalt under hydrothermal conditions has been used for over 50 years. It has the advantage of a compact plant but the disadvantage of producing ammonium sulfate as a co-product. In case of copper, however, precipitation takes place without the need of neutralizing the acid, which is a great advantage and could be an excellent substitute for electrowinning which is energy intensive and occupies extensive space. Recent advances in the engineering aspects of pressure equipment design open the door widely for increased application.

Keywords: copper, metallurgy, pressure leaching

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doi:10.2298/JMMB0701001H

1. Introduction

Copper is an ancient metal; it was produced about 4000 BC. It can be readily obtained from oxide ores by reduction, or from sulfide ores by conversion - a unique reaction whereby molten copper sulfide is directly converted to metal by blowing air [1]:

$$Cu_2S + O_2 = Cu + SO_2$$

At present about 80% of copper is produced by this route. It was not too long ago when copper producers were only interested in copper although the principal raw material is chalcopyrite which contains one third of its weight as sulfur. For each tonne of copper produced, two tonnes of sulfur dioxide were eliminated. For example, in Liddell's *Handbook of Nonferrous Metallurgy* published in 1945 there was no concern of SO_2 produced [2]. With increased environmental regulations, the copper industry was obliged to transform its SO_2 into sulfuric acid. For each tonne copper, 3 tonnes acid are produced. If there is no local need for the acid, e.g., for leaching oxide ores, then the acid has to be marketed. Shipping a corrosive liquid for long distances is not an easy task - it is risky and expensive. However, no attempts are being made to change this situation. A similar situation existed in the recovery of copper from oxide ore by leaching and cementation by scrap iron - an operation that was used for centuries in spite of its handicaps, until finally solvent extraction - electrowinning was introduced in the 1960's. In the present paper, new avenues are explored.

1.1. Pyrometallurgy of copper

Copper was produced over the centuries by the pyrometallurgical route. The technology has undergone many changes (Figure 1) [3]:

1.1.1. The vertical furnace

It is natural that metallurgists will treat rich ores first before they consider

Figure 1. Pyrometallurgy of copper in the past and at present

low-grade material because it is more economical. In the copper industry high-grade massive sulfide ores were broken down into small lumps and charged to a vertical furnace whereby the unwanted rock was removed as a slag and the copper-containing minerals were collected as a matte. Sulfur dioxide was emitted in this process and no attempt was made to capture it. There was only one exception, this being a process that was developed in Norway and which became known as the Orkla Process whereby elemental sulfur was produced (3). In this process, coke was charged together with the ore lumps to the furnace to reduce SO_2 to elemental sulfur which was then condensed and recovered.

1.1.2. The roast-reaction

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 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:

$$2\,CuO + Cu_2S = 4\,Cu + SO_2$$

The Welsh metallurgists were skilled in conducting this process, which became known as the Welsh Process. Matte from as far away as Butte, Montana and Chuquicamata, Chile was shipped to Swansea in Wales for transformation to copper. Sulfur dioxide was also emitted in this step and no attempt was made to capture it.

1.1.3. Conversion

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 few 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 sample principle few years later and as a result, the roast reaction was displaced by the conversion reaction.

$$Cu_2S + O_2 = 2Cu + SO_2$$

1.1.4. The horizontal furnace

When rich massive copper sulfide deposits became scarce, mining engineers turned to low-grade ores. This move 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 was introduced at the lower part of the shaft. As a result, copper metallurgists turned their attention to adapting 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 has dominated the copper industry worldwide during this century. Blister copper obtained was refined electrolytically and the precious metals in the ore were collected in the anodic slimes of the electrolytic bath.

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 disadvantages:

- Inefficient heat transfer since heat is mainly transferred by radiation from the roof, thus more fuel is burned unnecessarily.
- Excessive dust formation since the powdered concentrate is charged at right angles to the gas flow thus necessitating the installation of a large dust recovery system.
- Gases leaving the furnace are at high temperature necessitating the use of a bulky and expensive heat recovery system.

2. MODERN SMELTING ROUTES

Modern smelting routes were directed mainly towards energy economy (4). The most successful are the flash smelting process (Outokumpu Process), the bath smelting process (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 white metal, and conversion of the white metal to blister copper. In bath smelting all these processes take place in one reactor (Noranda).
- Sulfur dioxide is produced in high concentrations and can be economically captured for sulfuric acid manufacture.

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.
- In bath smelting the wear of refractories is more severe than in the flash smelting process when the metal is directly produced due to the high temperatures involved.
- The presence of certain impurities, e.g., antimony and bismuth in the feed material renders the single reactor process (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_2SO_4, the operation of the acid plant is dependent on the SO_2 flow which is by the nature of the processes is intermittent.

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.

2.1. Flash converting

Flash converting has been used by INCO in Canada for many years to treat copper sulfide concentrates, mainly Cu_2S, obtained in powder form during metallurgical separation from nickel sulfide[5]. The Cu_2S concentrates are introduced in a flash smelting furnace whereby metallic copper is obtained. This is a logical route since the feed material is already in powder form. It has been recently proposed to use this technology to solve the problem of intermittent SO_2 flow to the sulfuric acid plant in a copper smelter [6, 7]. In this process the matte from a flash smelting furnace is cooled, crushed, and ground, then fed to another flash smelting furnace to produce blister copper (Figure 2). In other words:

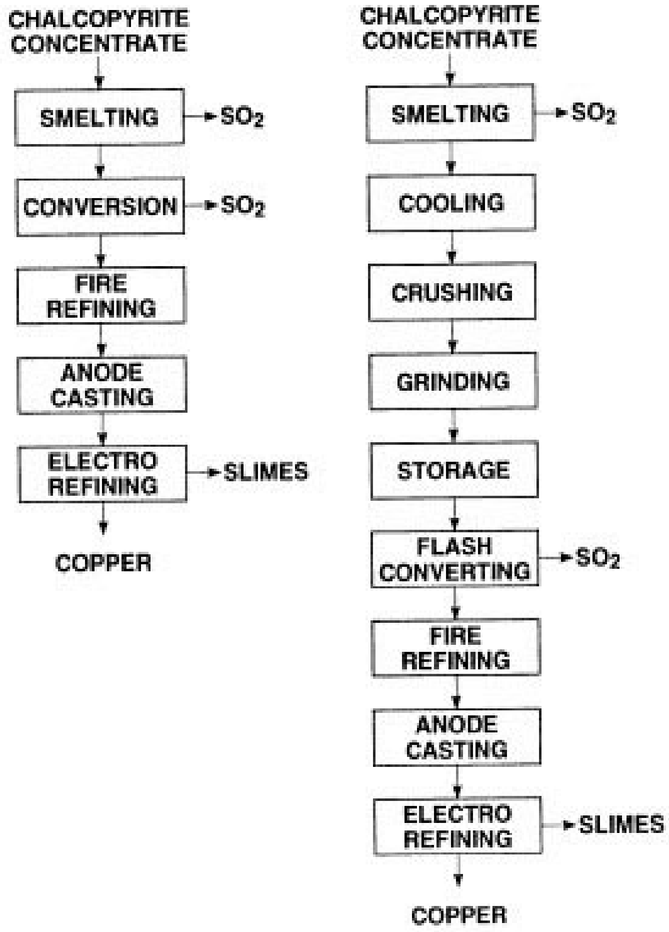

Figure 2 - Flash converting [right] as compared to standard smelting procedure [left]

- The second flash smelting furnace replaced the Pierce-Smith converter.
- The ground matte must be stock-piled in the absence of air and moisture (to prevent formation of sulfates which would otherwise result in impure copper).

Although crushing and grinding are known to be a high capital and operating costs operation and the quenching of molten matte in water is a dangerous operation because of the possibility of explosion due to H_2S formation, the developers of this new technology claim that the overall process is successful and most economical.

3. THE SULFUR PROBLEM

In most countries, the pyrometallurgical route for copper is plagued with the necessity to produce sulfuric acid as a by-product. One tonne of copper is associated with 3 tonnes of acid. With modern smelting technology, the hot SO_2 - 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 tonne of copper will be associated with 1 tonne of sulfur which is easy to store or transport. This technology is, however, is only adopted at Norilsk in Russia.

If the copper producers embark upon producing a finished marketable product from sulfur dioxide they may not only solve their problems but also the problems of phosphatic fertilizer manufacturers. They could produce ammonium sulfate by reacting SO_2 - containing gases with NH_3 to produce ammonium sulfate, thus by-passing constructing an acid plant. In this case 1 tonne of copper will be associated with 4 tonnes of ammonium sulfate. This, however, may not be an acceptable solution because of the huge amounts of ammonium sulfate that would be produced.

4. THE HYDROMETALLURGY OF COPPER

The major advantage of the hydrometallurgical route is that elemental sulfur can be obtained directly during the processing of sulfide concentrates thus liberating the copper industry from the sulfuric acid problem [8]. Figure 3 shows the conditions for its formation below $150^{O}C$. Two points should be considered when evaluating this technology:

- Chalcopyrite is the major copper mineral and all economic projections for the future should be based on this fact [9]. Chalcopyrite is different from other copper sulfide minerals in being the most resistant to leaching unless high temperature and sometimes high pressure are used. Therefore, a process developed for leaching chalcocite will not apply for chalcopyrite since chalcocite can be solubilized under very mild conditions.

- Many copper deposits are associated with arsenic minerals which render their treatment by a hydrometallurgical route more acceptable than a thermal route since residues and effluent can be put under control.

4.1. Dump, heap, and vat leaching

Dump, heap, and vat leaching is being used extensively in the copper, gold, and uranium industries. In the case of copper, this technology has been used for:

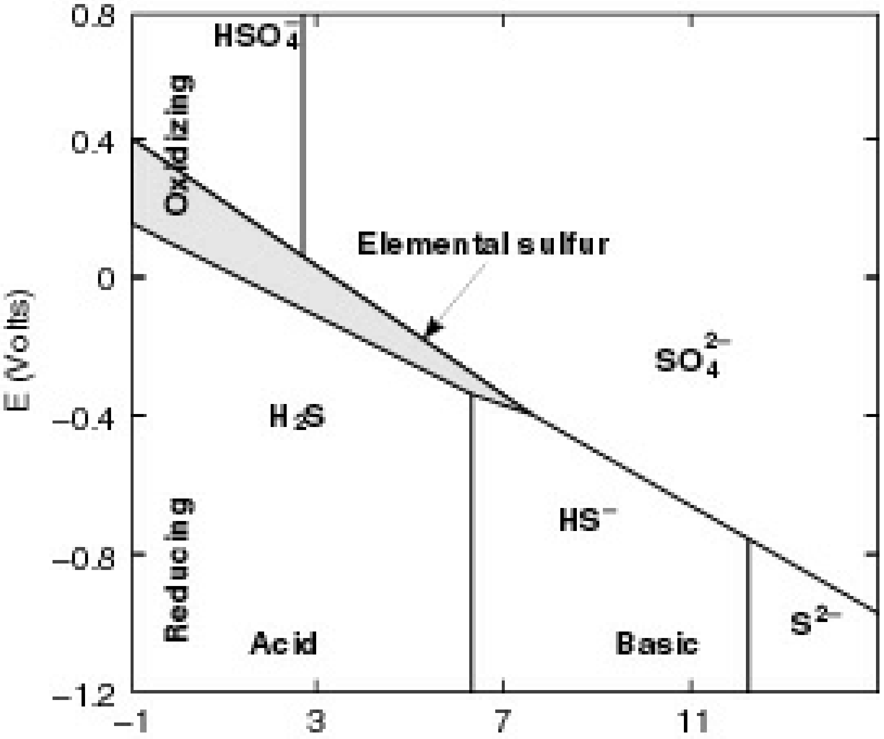

Figure 3 - Conditions for elemental sulfur formation during leaching sulfide concentrates below 150°C

- Copper oxide waste material, and low-grade ores.
- Rich copper oxide ores
- Relatively high-grade copper sulfide ores (1-2% Cu).

The enormous advantage gained in treating sulfides is due to by-passing grinding and flotation steps while treating huge tonnages of crushed material. However, this technology cannot be applied to the following material:

- Chalcopyrite raw material since it is for all practical purposes insoluble under ambient conditions.
- Sulfides containing precious metals since these will be lost in the heaps.

4.2. Pressure leaching

A successful process for treating chalcopyrite concentrates should fulfill the following requirements:

- The process should be exothermic, thus no fuel should be needed and the heat generated could be efficiently recovered.
- The oxidizing agent should be the cheapest available and should not need regeneration.
- The iron and sulfur components of chalcopyrite should be obtained as a residue in a minimum number of steps and sulfur should be in the elemental form.
- The precious metals in the concentrate could be recovered.

These conditions are met during the aqueous oxidation of sulfide concentrates by oxygen in acid medium at high temperature and pressure:

$$CuFeS_2 + 1\tfrac{1}{2}\, O_2 + 2\, H^+ = Cu^{2+} + FeOOH + 2\, S + H_2O$$

The process becomes self-sufficient with respect to the acid used when the copper-containing solution is electrolyzed:

$$Cu^{2+} + H_2O = Cu + 2\, H^+ + \tfrac{1}{2}\, O_2$$

or precipitated by hydrogen under pressure:

$$Cu^{2+} + H_2 = Cu + 2\,H^+$$

The leaching process is usually conducted at about 150°C and at 1500 kPa. By means of a series of flash tanks, maximum heat economy can be achieved. Aqueous oxidation of the copper concentrate can be conducted continuously in a series of pressure reactors. The residue from the leaching operation, after flotation of sulfur, should be agglomerated with Portland cement and stockpiled on an impervious base, in the form of dumps to be treated by cyanidation for precious metals recovery (Figure 4). Selenium and tellurium will be associated with the elemental sulfur while arsenic will be associated with iron oxide.

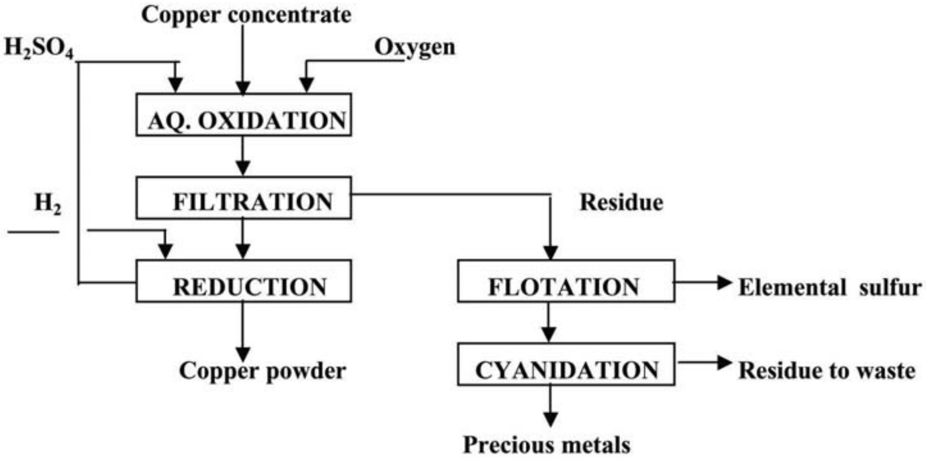

Figure 4. The residue from the leaching of sulfie concentrates, after flotation of sulfur, should be agglomerated with Portland cement and stockpiled on an impervious base, in the form of dumps to be treated by cyanidation for precious metals recovery

A plant started in 2003 to recover copper from chalcopyrite concentrates by

Phelps Dodge at Bagdad mine in Arizona. Leaching takes place at 220^{O}C in autoclaves in presence of oxygen at 700 kPa (total pressure 3 300 kPa) (10). After solid-liquid separation the acidic copper sulfate solution is used to leach copper oxide ore in heaps. The solution is then processed in a solvent extraction electrowinning circuit to recover copper (Figure 5). A new plant is under construction by the same company to operate at medium temperature so that elemental sulfur could be recovered.

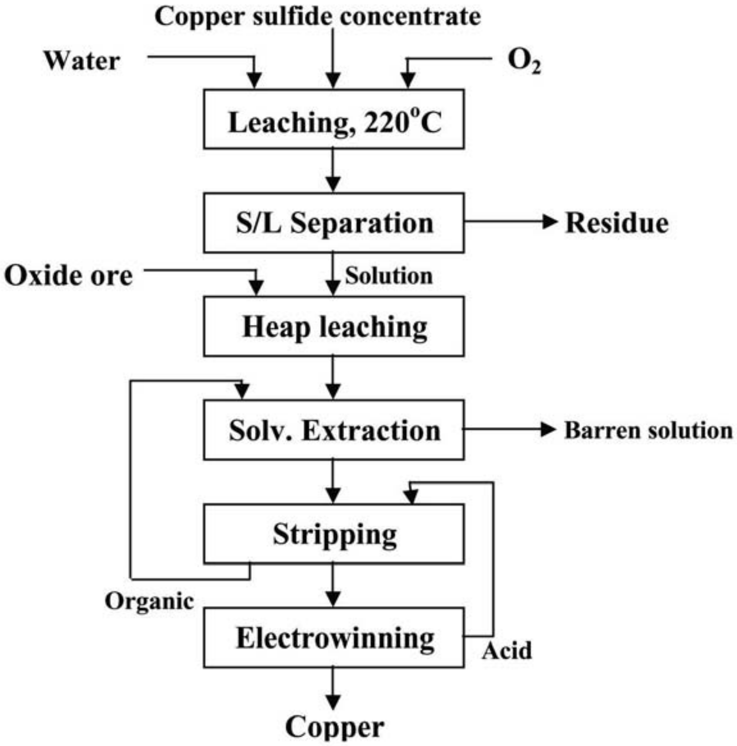

Figure 5. Leaching of chalcopyrite concentrates at Phelps Dodge at Bagdad in Arizona at 220^{o}C in autoclaves in presence of oxygen at 700kPa

5. COPPER IN RELATION TO OTHER METALS

The situation of copper today is like that of zinc before World War I. At that time zinc was produced exclusively by the retort process - - a process that was highly polluting and energy intensive, until the roasting-leaching-electrowinning route was developed. Flash smelting solved the energy problem for copper after World War II, but today a new technology is needed to overcome the sulfur problem that was not solved by flash smelting.

5.1. Aluminum

Copper was second in rank after iron in terms of tonnage up to 1960 when aluminum took over this position and remained there (Figure 6). Since 1940 the price of aluminum has been lower than that of copper (Figure 7), although the aluminum industry is known to be energy intensive and copper production has the advantage over all other metals by being recovered by a simple conversion reaction - an exothermic reaction that yields the metal directly from its sulfide by blowing with air. In addition, copper smelting is nearly always associated with precious metals as valuable by-products. The following points may be part of the reason for the lagging of the copper industry behind that of aluminum:

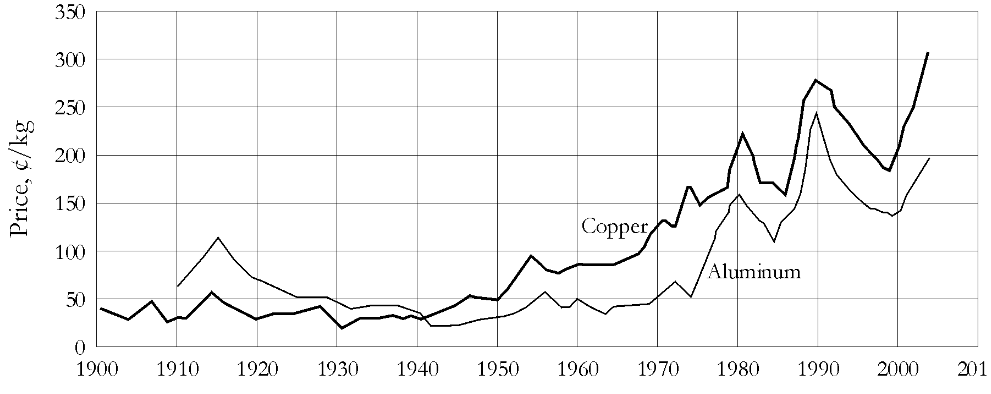

Figure 6. In 1960 aluminum exceeded copper production

- The copper industry is not as fully automated as the aluminum industry. There is extensive molten material handling that is labor intensive.

- The copper industry is bound to sulfuric acid manufacture and to finding a market for this acid otherwise the SO_2 emissions from smelting will cause undesirable environmental problems.

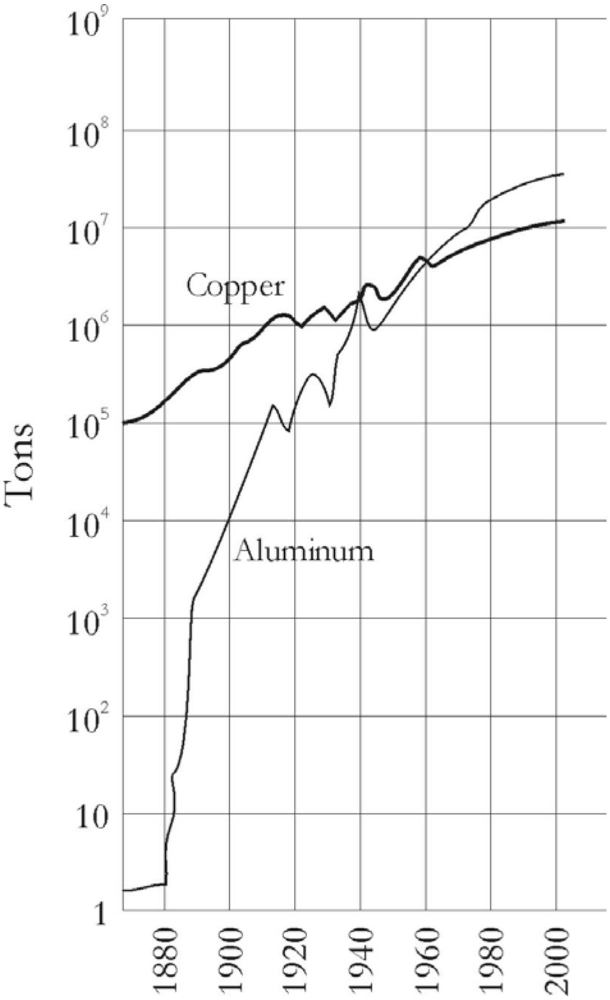

Figure 7. Since 1940 the price of aluminum has been lower than that of copper

5.2. Nickel

Laterites containing 1.3% Ni (and 0.1% Co) are leached in Moa, Cuba in autoclaves at 250^{O} C and 4 000 kPa using concentrated sulfuric acid. The plant includes 4 units and each unit is composed of 4 autoclaves. The plant has been operating since 1942. Since the price of nickel is about three times that of copper, it would be justifiable to leach a copper concentrate containing 3 x 1.3%, i.e., 4% Cu under pressure. Chalcopyrite concentrates usually contain approximately 25% Cu, hence the copper industry should consider acid pressure leaching as a route to solubilize copper and recover elemental sulfur.

5.3. Zinc

The application of pressure leaching of zinc sulfide concentrates in dilute sulfuric acid at 150^{O} C and under oxygen partial pressure of 700 kPa should give an incentive to the copper industry to consider the same technology to solve the sulfur problem. There are now 4 plants operating smoothly using this technology (11). Figure 8 shows one of these plants.

Figure 8. Pressure leaching of zinc sulfide concentrates in dilute sulfuric acid at 150^{O} C and under oxygen pressure

5.4. Gold

Refractory gold ores contain gold particles locked up in a matrix of pyrite and/or arsenopyrite. Such ores are not amenable to cyanidation. To liberate the gold from the sulfide crystal structure and render it accessible to cyanidation, a preliminary pressure aqueous oxidation is necessary. There are at least eight plants using this technology for sulfide concentrates containing as low as 5 ppm gold and some of these plants are located in such remote and undeveloped locations as the tropical jungles of Papua New Guinea (Table I). It should be remembered that pressure technology in this case is not to leach the gold but only to liberate it from the host mineral. Autoclaves the size of a copper reverberatory furnace are now used for this purpose (Figure 9) (12).

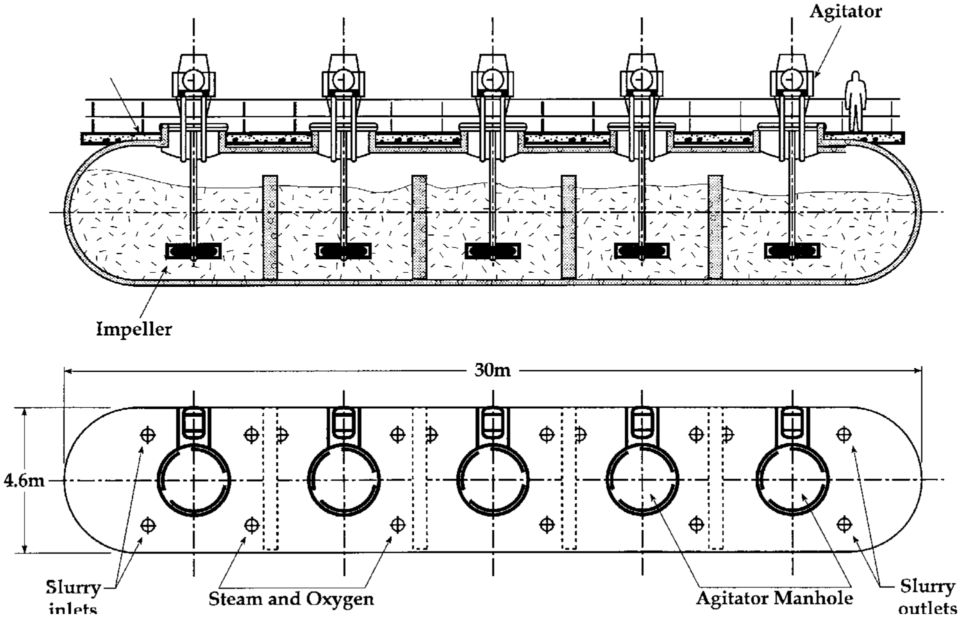

Figure 9. Autoclaves the size of a copper reverberatory furnace are now used for the aqueous oxidation of refractory gold ore

6. Conclusions

In the past few decades intensive effort has been conducted to solve the energy problem in copper production, this effort resulting in the flash and bath smelting technologies. However, no serious work was done to solve the sulfur problem associated with copper. Industry seems to be content with producing large tonnages of H_2SO_4 and still emitting some SO_2 to the atmosphere. Pressure leaching at medium temperature undertaken recently by Phelps Dodge in USA to solubilize copper and get elemental sulfur seems to offer the best solution.

Table 1. Status of Treatment of Refractory Gold Ores by Pressure Hydrometallurgy

Start up	Plant Location	Owner	Feed	Medium	Capacity t/d	Number of autoclaves
1985	McLaughlin USA	Homestake USA	ore	acid	2700	3
1986	San Bento Brazil	Genmin S. Africa	concentrate	acid	240	2
1988	Mercur, Utah USA	American Barrick Canada	ore	alkaline	680	1
1989	Getchell USA	First Miss Gold	ore	acid	2730	3
1990	Goldstrike Nevada, USA	American Barrick Canada	ore	acid	1360	1
1991	Goldstrike Nevada, USA	American Barrick Canada	ore	acid	5450	3
1991	Porgera, Papua New Guinea	Placer Dome Canada	concentrate	acid	1350	3
1991	Campbell Canada	Placer Dome Canada	concentrate	acid	70	1
1992	Con Lihir	Nerco Minerals	concentrate	---	90	1
1993	Goldstrike USA	American Barrick Canada	ore	acid	11580	6
1994	Porgera, Papua New Guinea	Placer Dome Canada	concentrate	acid	2700	6
1977	Lihir, Papua New Guinea	---	---	---	---	

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