

RECENT TRENDS IN EXTRACTIVE METALLURGY

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Abstract

While pyrometallurgical processes are old technology and were the dominant and logical route used to treat sulfide concentrates they are now challenged by new hydrometallurgical processes. In these new processes there have been attempts in the past few years to avoid using autoclaves in the treatment of concentrates of zinc, copper, and nickel. The situation has been recently reversed and pressure hydrometallurgy is being applied in many operations. An outline of these processes is given and the future trend is discussed.

Keywords: Copper; Zinc; Nickel; Complex sulfides; Pressure leaching; Bacterial leaching; Ausmelt process; Outotec process, Hydrometallurgy; Pyrometallurgy; Electrometallurgy; Warner process.

Introduction

Extracting metals from ores requires a number of operations: some mechanical, physical, and physicochemical known as mineral beneficiation and some chemical known as extractive metallurgy. The

chemical processes can be divided for convenience as pyro-, hydro-, and electro-metallurgy. Pyrometallurgy is the most ancient technology, while hydrometallurgy is about four centuries old. On the other hand electrometallurgy is the most recent and came into existence only after the invention

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of the large-scale electrical generators in the mid nineteenth century. No wonder then that, in some cases, these new technologies are displacing the older ones gradually, either because of improved efficiency and better economics or to comply with environmental regulations. Here are some examples.

Zinc

The retort process and the leaching-electrowinning route

For centuries, metallic zinc was produced by roasting its main mineral sphalerite to get zinc oxide, which was reduced at high temperature to get the metal (Figure 1). The

crude zinc is then refined by distillation at high temperature under vacuum. Horizontal retorts were used for over four centuries. Although many modifications were made to improve this technology it was only during World War I that hydro - and electro-metallurgical concepts were applied to develop a new process that competed with the old technology and finally displaced it in the 1970s (Figure 2).

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

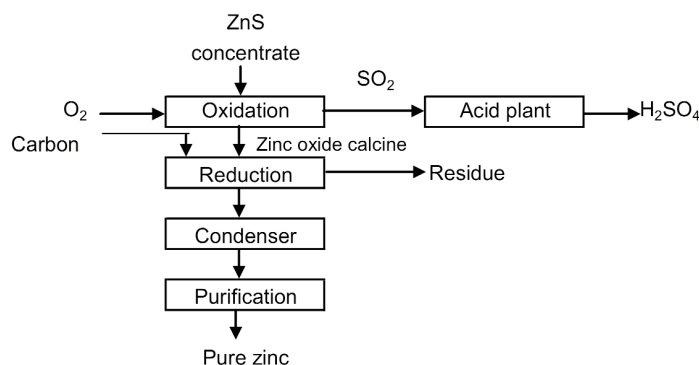


Fig. 1. Zinc from sulfide concentrates, the old pyrometallurgical route

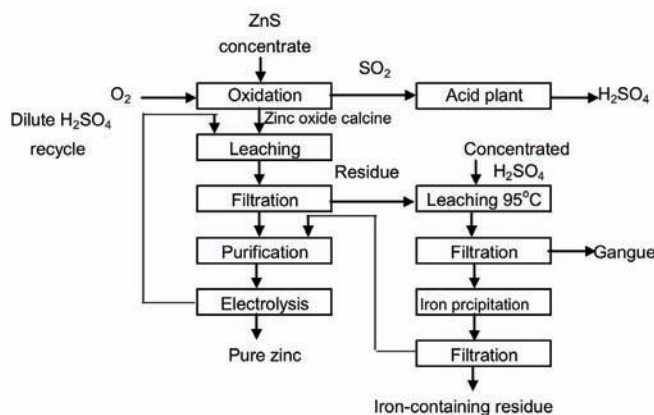


Fig. 2. Zinc from sulfide concentrates, the pyro-, hydro-, electrometallurgical route

residue in form of ferrite, ZnFe_2O_4 , which 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, thus creating a stock piling problem.

Aqueous oxidation

Finally, in the 1980s, a new process was invented in Canada in which the concentrate was leached directly in dilute H_2SO_4 at 150°C and under oxygen pressure of 700 kPa (Figure 3). Autoclaves lined with acid-resisting bricks are used. The reaction is exothermic and yields elemental sulfur i.e., no SO_2 is formed and no sulfuric acid plant is required, no ferrites are formed, and therefore the residue can be disposed of directly and the solution can be purified in

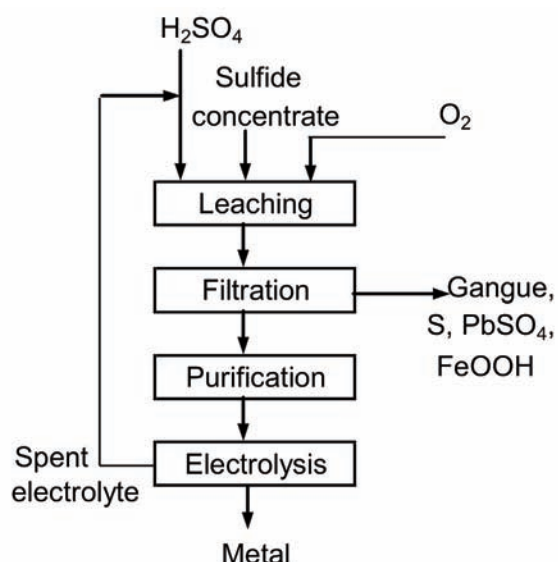


Fig. 3. Production of zinc by pressure leaching technology.

the usual way and electrolyzed to yield pure metallic zinc and acid for recycle to the leaching step.

Atmospheric leaching process

However, in spite of the success of the aqueous oxidation process in three operating plants, there are still attempts to avoid using autoclaves. For example, a plant under construction in San Luis Potosi in Mexico will use a Finnish technology that uses four large reactors operating at 90°C instead of one autoclave (Figure 4). Instead of two

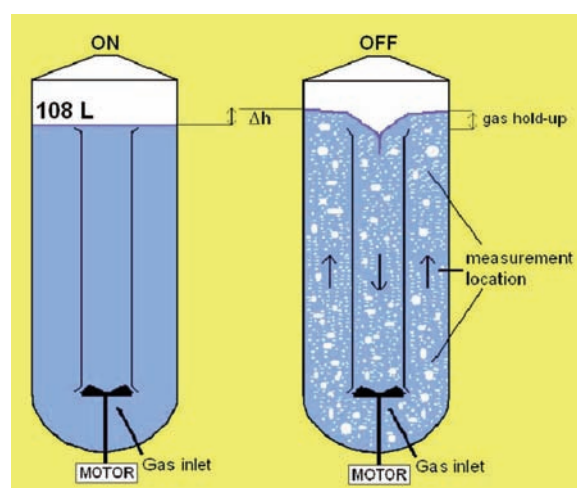


Fig. 4. A reactor designed for leaching zinc sulfide concentrate at 90°C [1].

hours residence time in an autoclave the multiple reactors will be operating for 12 hours under continuous air injection. It is believed that such operation cannot compete with pressure leaching.

Warner process

A process under development in United Kingdom for the recovery of zinc, lead, and

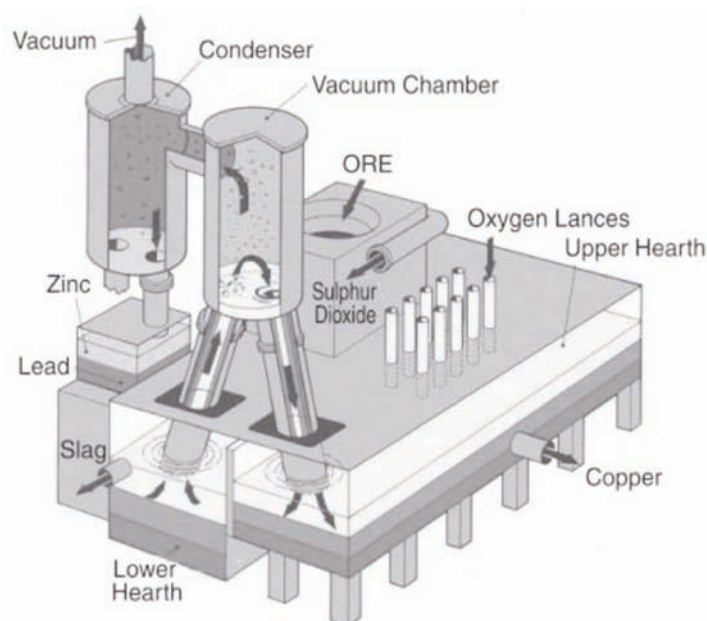


Fig. 5. Warner process for the recovery of zinc, lead, and copper from sulfide concentrates [2].

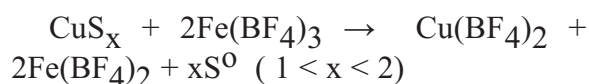
copper from sulfide concentrates operates at high temperature and under vacuum (Figure 5). It involves circulation of molten material on two level hearths and injection of oxygen by lances. Sulfur dioxide must be collected and transformed to acid. It is evident that the process will suffer from extremely difficult operating conditions, inevitable gas emissions, and severe abrasion. When compared with pressure leaching technology shown earlier it will become obvious that it cannot withstand the competition.

Copper

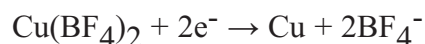
Ausmelt

In a recent paper by Olper et al [3] the authors proposed producing white metal and/or high grade matte in the Ausmelt furnace (Figure 6). The material is then crushed and ground to less than 40 μm then

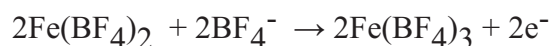
leached at 90°C for 3 hours by a mixture of fluoroboric acid and ferric fluoroborate in a stirred reactor to produce a copper fluoroborate solution:

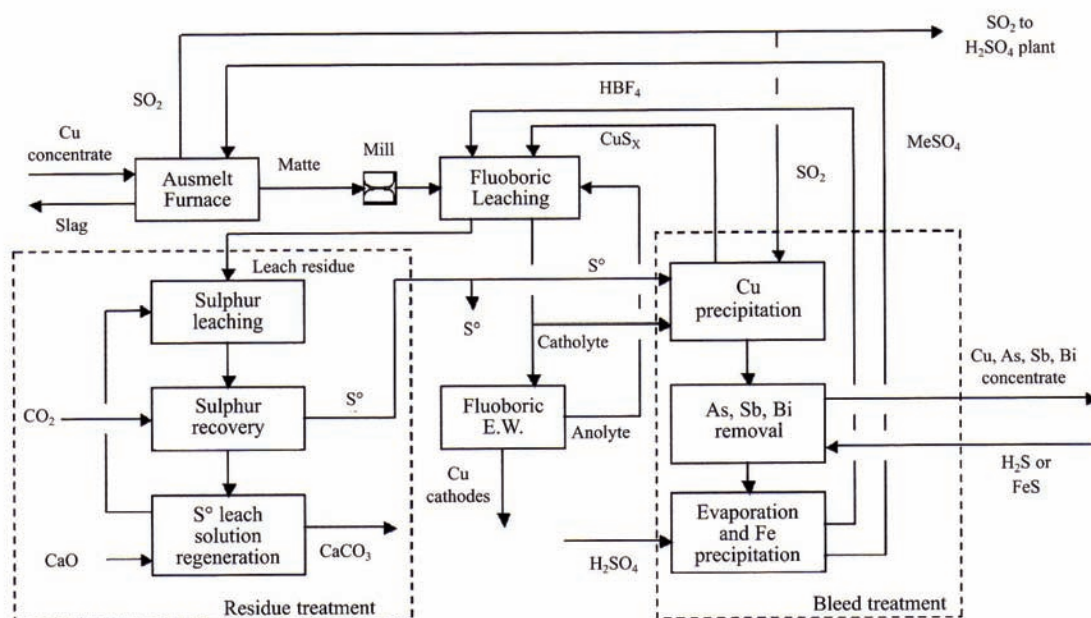
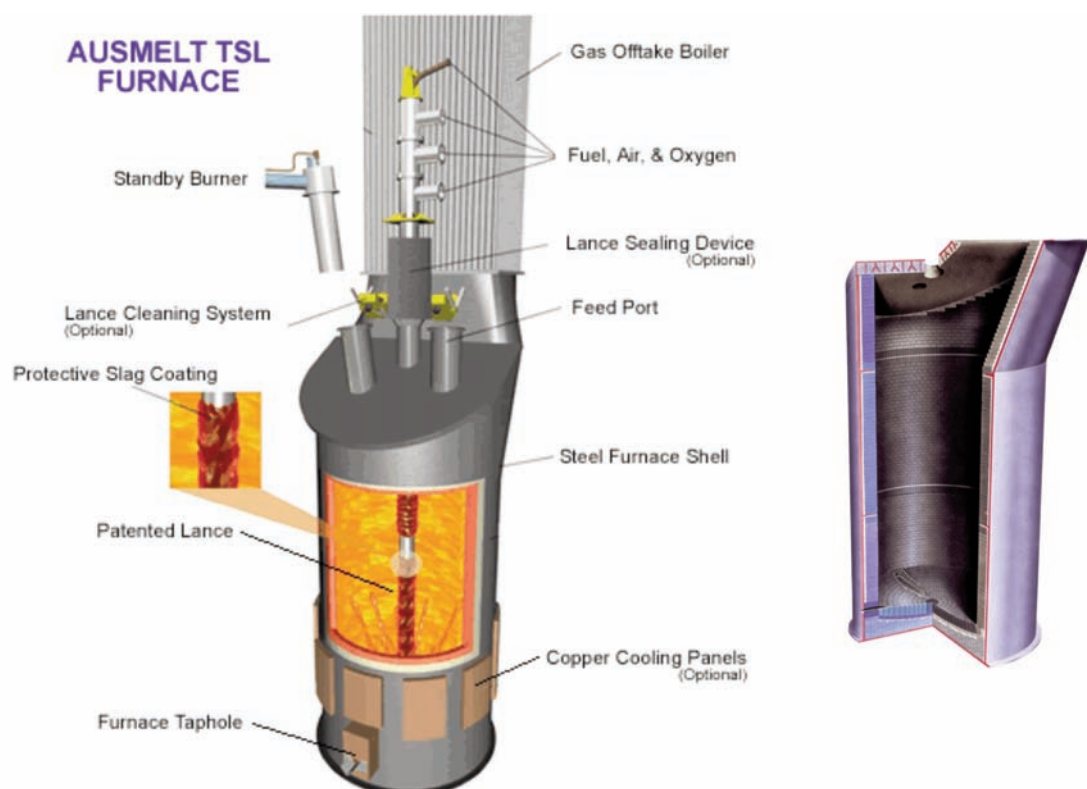


This operation produces a copper fluoroborate solution which is sent for electrolysis and a sulphur residue which contains the precious metals [Figure 7]. The leach solution is then fed to the cathodic compartment of a diaphragm electrolytic cell where copper is deposited on a stainless steel cathode according to:

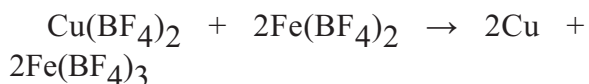


The catholyte passes through the diaphragm to the anodic compartment where ferric fluoroborate is regenerated on a graphite anode:





The overall cell reaction can be expressed as:



The process looks complex using new reagents and diaphragm cells while in traditional copper technology in sulfuric acid medium no such cells are needed.

Bacterial leaching

Bacterial leaching has been successfully applied for heap leaching of copper ores. It was extended to treat auriferous pyrite concentrates to liberate gold and render it amenable to cyanidation. In the past few years there has been interest to apply bacterial leaching to treat chalcopyrite concentrates. For example, a continuous small scale bioleach pilot plant was established to investigate the bioleaching of

chalcopyrite concentrates in 1998 by BacTech at Mt. Lyell in Tasmania. It was found further that the process could be applied successfully on concentrates containing arsenic. The technology was extended and a demonstration scale plant was constructed in 2001 by the joint technology partnership of BacTech and Mintek in conjunction with Peñoles in Monterrey in Mexico (Figure 8).

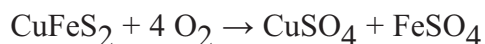
The plant operated for a year with a capacity of 200 tpa copper cathode production and demonstrated well the technical feasibility of a totally integrated process with high levels of copper recovery from arsenic-containing concentrate blend. On completion of the demonstration trial, a feasibility study was conducted for a commercial bioleach plant envisaged as having an initial capacity of 25,000 tonnes of copper. However, due to the low price of copper at that time BacTech did not go



Fig. 8. A view of Peñoles bioleaching plant in Monterrey in Mexico.

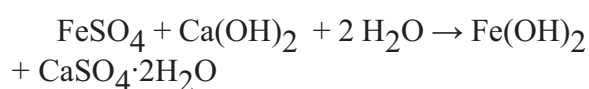
forward with the project to a commercial scale.

It is interesting that in 2002, Alliance Copper, which is a joint venture between BHP Billitob and Codelco in Chile built also a 20,000 tpa demonstration plant near Chuquicamata for US \$ 50 million. The plant was composed of six large reactors, mechanically agitated, and lined with acid-resisting brick. Since a thermophilic bacteria was used in the system it was possible to operate at a temperature of about 90°C and this accelerates the reaction. With the increase in copper prices in 2006 some copper metallurgists believed that the situation was ready to exploit this technology. In spite of this enthusiasm for bioleaching technology, one cannot recommend its use for leaching chalcopyrite concentrates because it cannot be economical for the following reasons. The leaching reaction is as follows:



The leaching reaction is slow - - it is

complete in 4 – 5 days and in addition, some nutrients must be supplied to the reaction mixture. Due to the acid conditions of operation some ferrous will be oxidized to ferric and precipitated generating acid. From this it can be seen that a large amount of oxygen will be consumed, a large amount of lime will be needed to precipitate ferrous sulfate and neutralize the acid, and there will be an excessive disposal and material handling problem of ferrous hydroxide – gypsum mixture:



Eventually the plant was shut down.

Mechanism of bacterial leaching

Microorganisms manufacture enzymes and with their aid they catalyze the oxidation of sulfides:

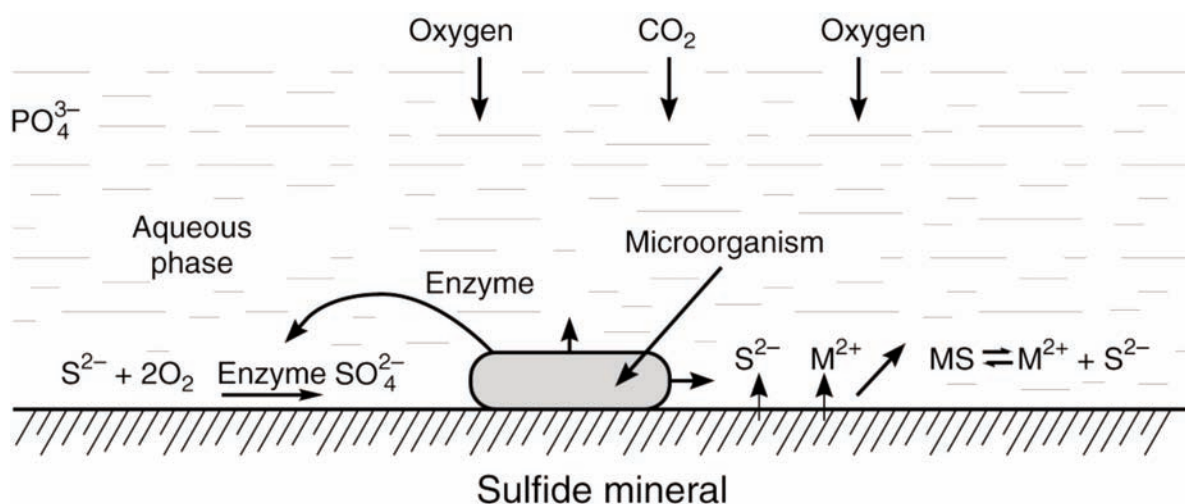
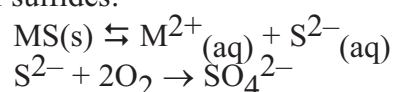


Fig. 9. Schematic representation of the action of microorganisms adhering on the surface of a sulfide mineral.

The adherence of the microorganisms on the sulfide surface makes possible the rapid oxidation of S^{2-} ions liberated by the mineral and catalyzed by the enzymes (Figure 9).

Outokumpu process

Chemists at Outokumpu Research Oy in Pori, Finland have developed Hydro Copper process for the treatment of copper sulfide concentrates based on leaching the concentrates in a strong NaCl solution containing Cu^{2+} ion at pH 1.5 – 2.5 in agitated reactor at 85-95°C in presence of oxygen. Copper goes into solution as Cu^+ while iron is precipitated as hydroxide. After filtration and solution purification NaOH is added to precipitate Cu_2O , which is then slurried in water and reduced in autoclaves by hydrogen under pressure (Figure 10).

Leaching of sulfides in chloride media has been tried before in Clear Process developed

by Duval Corporation in Arizona in the 1970s. The process, however, was not industrialized because the electrowinning of copper from chloride medium produced dendritic powder contaminated by silver that was difficult to process further. It seems that this was the reason for Outokumpu chemists to avoid the electrowinning route and consider the production of Cu_2O and its reduction. The precipitation of copper by hydrogen under pressure from aqueous chloride system is not effective. Another option is the thermal reduction of solid $CuCl$ in a fluidized bed. Outokumpu researchers also found out that Cu_2O disproportionate in dilute H_2SO_4 :



$CuSO_4$ formed can be reduced by hydrogen in an autoclave by known methods. In the Outokumpu process NaOH is used instead of $Ca(OH)_2$ so that NaCl produced can be electrolyzed to recover

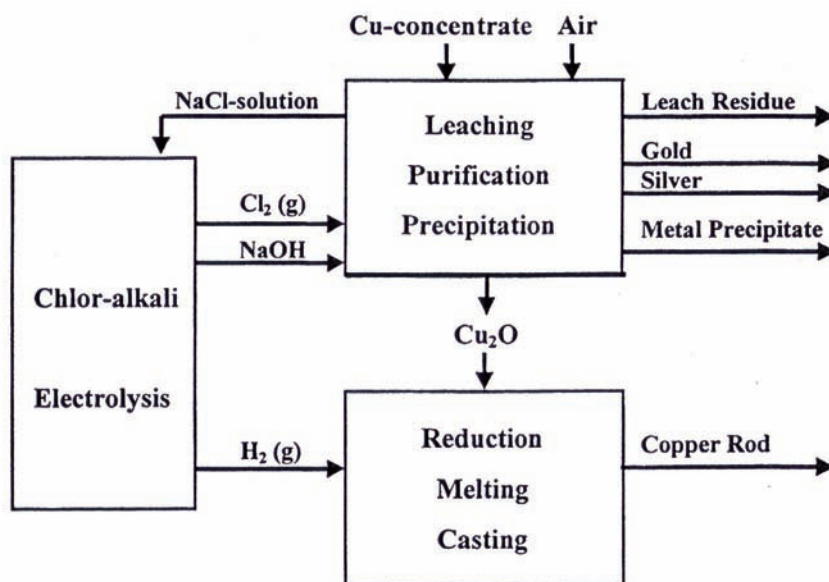


Fig.10. Outokumpu process

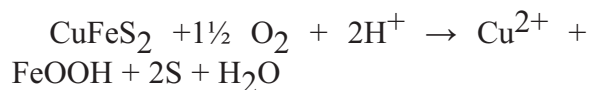
hydrogen for reduction, NaOH for precipitation, and chlorine transformed into HCl. In other words, an important section of the process is the regeneration of the reagents. A major part of the process is devoted to recovery and recycle of reagents which may render the process uncompetitive with pressure leaching process.

Galvanox process

Researchers at the University of British Columbia in Canada developed a ferric sulfate atmospheric leaching process of copper concentrates at 80°C for about 12 hours in presence of pyrite which facilitates leaching due to galvanic action. The leach residue is then treated by flotation to recover un-reacted copper sulfides and pyrite for recycle [3]. The problem with this technology is the increased size of reactors to accommodate the added pyrite, the recycle load of pyrite, and the need to precipitate excess iron oxide because at the temperature of reaction most of the iron will remain in solution.

Sherritt-Gordon process

Pressure leaching technology has been developed in 1960s for sulfide concentrates essentially by Sheritt-Gordon Mines in Canada [now known as Dynatec] operating in a sulfate system (Figure 11):



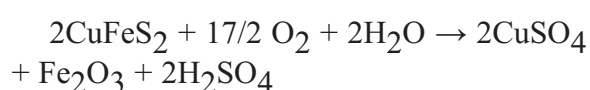
The process is conducted at about 150°C and at 1500 kPa. Coal is added during leaching in the amount of 20 kg / tonne to

prevent elemental sulfur from adhering to the chalcopryrite and retarding the leaching. By means of a series of flash tanks maximum heat economy can be achieved. 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. The process has the following characteristics:

- The oxidizing agent does not need regeneration.
- The iron component of chalcopryrite is obtained as a residue during leaching.
- Selenium and tellurium will be associated with the elemental sulfur while arsenic precipitates as ferric arsenate
- The precious metals in the concentrate could be recovered from the residue.
- The process is self-sufficient with respect to the acid used when the copper-containing solution is electrolyzed.

Recent development

A plant started in 2003 to recover copper from chalcopryrite concentrates by Phelps Dodge [now Freeport-McMoran] at Bagdad mine in Arizona in which leaching takes place at 220°C in autoclaves in presence of oxygen at 700 kPa (total pressure 3 300 kPa) [4]:



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. After successful operation, a new plant designed to operate at 150°C to get elemental sulfur is now under construction at Morenci, Arizona using a flowsheet similar to that shown in Figure 11.

Nickel

Nickel laterites have been successfully

treated in Cuba by hydrometallurgical route since 1940s (Figure 12). The major nickel sulfide mineral is pentlandite, $(\text{Ni,Fe})_9\text{S}_8$ which may occur alone as in Manitoba or associated with chalcopyrite as in Sudbury. In both cases, the nickel is associated with a large amount of pyrrhotite. Many pyrometallurgical processes were developed and applied on commercial scale. They suffered from the formation of large amounts of sulfur dioxide which must be either captured

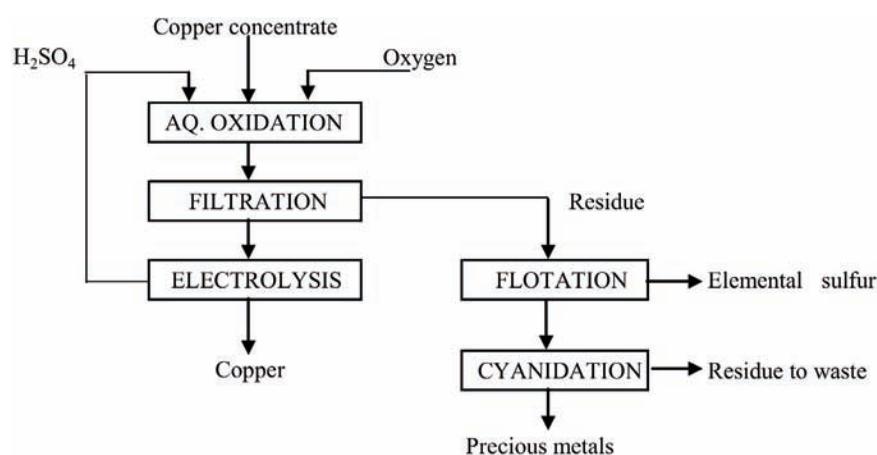


Fig. 11. Pressure leaching of copper sulfide concentrates



Fig. 12. High pressure acid leaching plant at Moa



Fig. 13. Location map of the nickel deposits in the Canadian North at Voisey Bay and the hydrometallurgical plant Argentina in Newfoundland

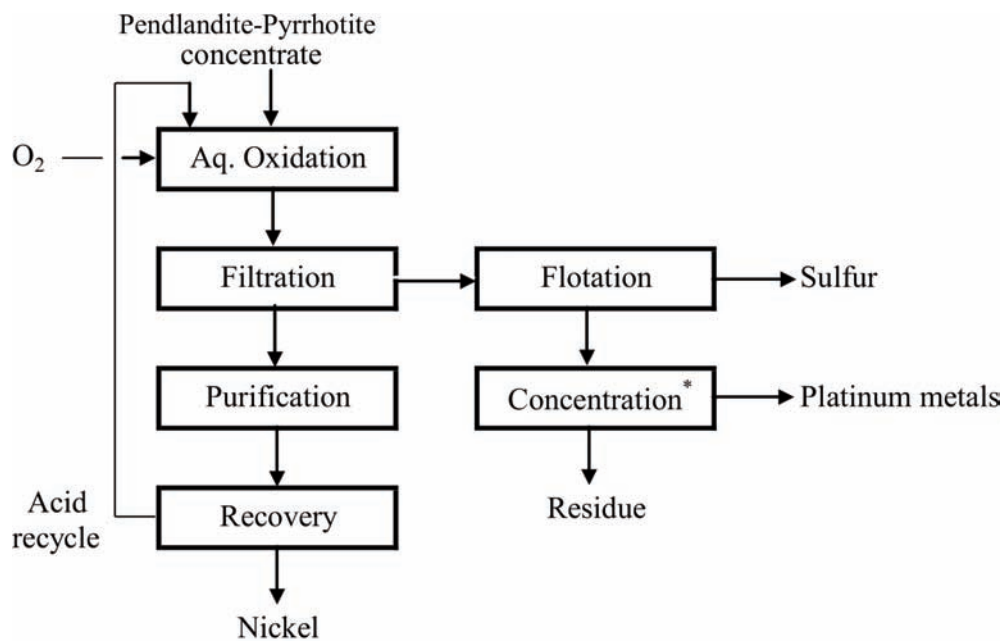


Fig. 14. Pressure leaching of nickel sulfide concentrates

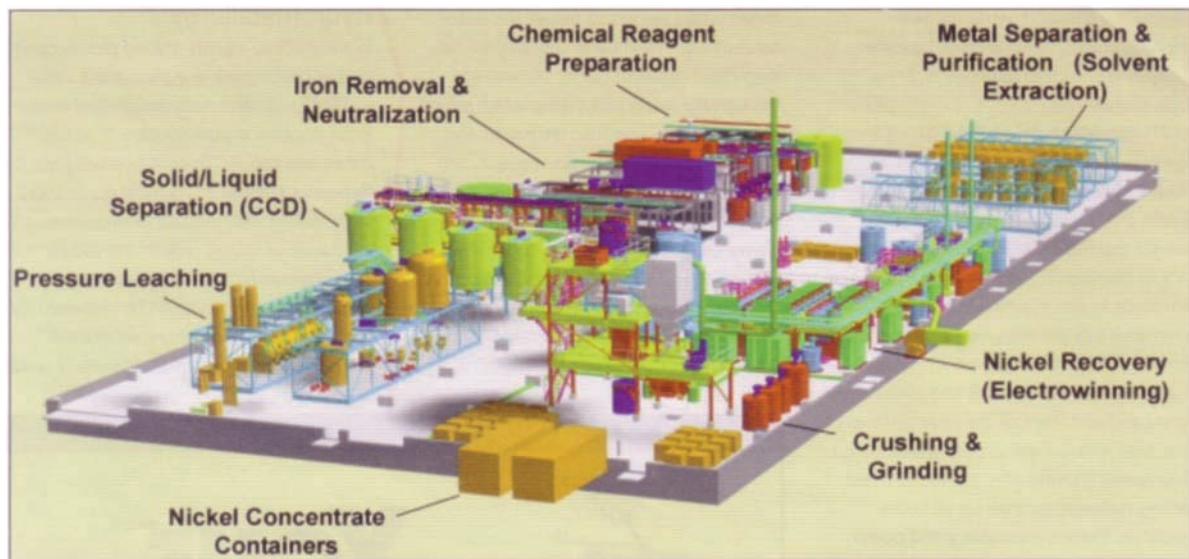


Fig. 15. Nickel sulfide pressure leaching plant under construction at Argentina in Newfoundland

or emitted to the atmosphere and large amounts of slag for disposal. With the recent discovery of the Voisey Bay sulfide deposits in the Canadian North it was decided in 2005 to use a pressure leaching process similar to that used for zinc and copper sulfides shown in Figures 13 to 15 to produce elemental sulfur instead of SO_2 .

Pressure leaching

A pressure leaching plant is shown schematically in Figure 16. The major equipment are an autoclave, a high pressure piston pump, a flash tank, and a slurry pre-heater. Heat economy in maximum since steam is recovered from the hot slurry to preheat the charge. In this process no dust, no slag, and no SO_2 are produced.

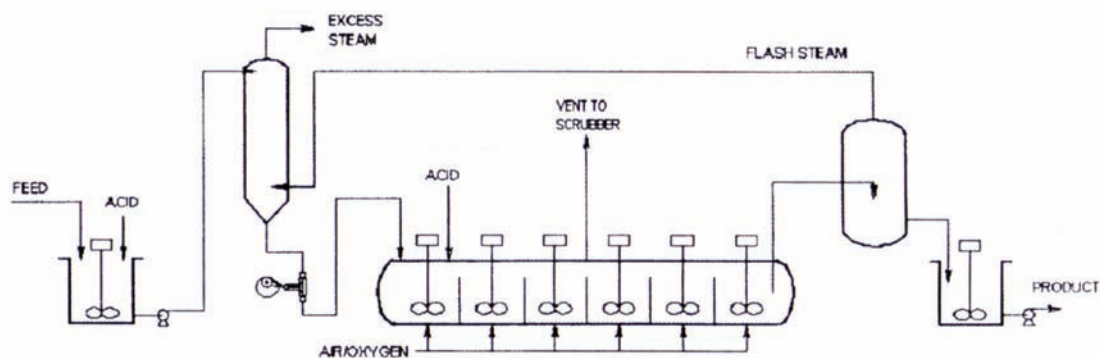


Fig. 16. Pressure leaching plant showing the autoclave in the center, the high pressure piston pump needed to inject the slurry in the autoclave, the slurry pre-heater to the left, and the flash tank to the right. Steam generated in the flash tank is used to pre-heat the slurry in the pre-heater

Conclusions

The recovery of zinc, copper, and nickel from their ores has undergone many technological changes when finally pressure leaching in acid medium followed by electrolysis in conventional sulfuric acid medium has been accepted. This simple technology solves the sulfur problem and is environmentally acceptable. It has been applied for zinc sulfide concentrates in 1980s and recently adopted to nickel sulfides at INCO's Voisey Bay plant in Canada and for copper sulfide concentrates in USA. It is the technology of the future.

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