CHAPTER 12.8

Copper Hydrometallurgy

Martin C. Kuhn and Russell D. Alley

ORIGINS OF HYDROMETALLURGY

Habashi (2014) provides an excellent introduction for the origins of hydrometallurgy:

> The roots of hydrometallurgy may be traced back to the period of alchemists when the transmutation of base metals into gold was their most important occupation. Some of these operations involved wet methods. For example, when an alchemist dipped a piece of iron into a solution of copper vitriol, i.e. copper sulphate, the iron was immediately covered by a layer of metallic copper. The major question, however, that remained unanswered was: how can the transmutation of iron or copper into gold be effected? Gold, the most noble of all metals was insoluble in all acids or alkalis known at that time.
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> The discovery of *aqua regia* by Jabir Ibn Hayyan (720–813 AD), the Arab alchemist, may be considered as the first milestone marking the beginning of hydrometallurgy. ... In the Middle Ages, certain soils containing putrefied organic matter were leached to extract saltpeter (salt of stone, potassium nitrate), a necessary ingredient for the manufacture of gunpowder. The process was fully described by Vannoccio Biringuccio (1480–1539) in his *Pirotechnia* published in 1540.
>
> In the 16th Century, the extraction of copper by wet methods received some attention. Heap leaching was practiced in the Harz Mountains area in Germany and in Rio Tinto mines in Spain. In this operation, pyrite containing some copper sulfphide minerals was piled in the open air and left for months to the action of rain and air, whereby oxidation and dissolution of copper took place. A solution containing copper sulphate was drained from the heap and collected in a basin. Metallic copper was then precipitated from this solution by scrap iron, a process that became known as "cementation process." This is the same process that was already known to the alchemists and was in operation to an appreciable extent until recently when it was replaced by solvent extraction-electrowinning.

ELECTROMETALLURGY

The first application of Alessandro Volta's voltaic pile in metallurgy was in 1807 when Humphry Davy at the Royal Institution in London built a large battery and was able to decompose caustic potash and caustic soda to identify potassium and sodium as metals for the first time. This was followed in the next year, using the same technique, by the identification of barium, calcium, magnesium, and strontium.

Michael Faraday who was Davy's assistant, continued this type of research further and in the early 1830s found the relationships between current used and quantity of metal deposited. He was the first to have clear ideas concerning the quantity of metal deposited and intensity of electricity (i.e., the quantities now measured with regard to amperes and volts). Faraday introduced the terms *ion*, *cation*, *anion*, *electrode*, *electrolyte*, and so on, which are commonly used today.

REFINING METALS

In 1876, copper was refined electrolytically in Germany by the Norddeutsche Affinerie in Hamburg. This was followed by gold refining in 1878 using the Wohlwill process, named after German chemist Emil Wohlwill. The first copper refinery built in America was at Newark (New Jersey) in 1883 by the Balbach Smelting and Refining Company. In 1884, German metallurgist Bernhard Möbius (1852–1898) invented a process for silver refining.

HYDROMETALLURGY IN COPPER PRODUCTION

In 1910, Albert C. Burrage, a Boston (Massachusetts, United States) capitalist, obtained options on the entire mining territory at Chuquicamata (Chile) and offered his options to the firm of M. Guggenheim's Sons in New York (United States). In 1912, the Guggenheims organized the Chile Exploration Company in New Jersey to take over the options and incorporated the Chile Copper Company in Maine (United States).

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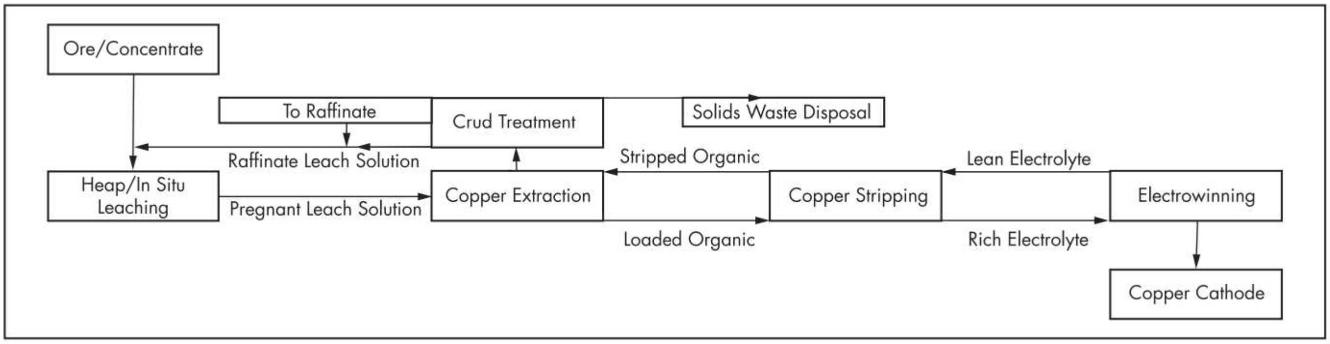


Figure 1 Block flow diagram of the solvent extraction/electrowinning process

The low-grade ore could not be smelted in the ordinary way because of its chlorine content, which meant that an entirely new process had to be devised. This was accomplished by E.A. Cappelen Smith, a consulting metallurgist for the Guggenheims, and a new chapter in the history of copper extraction was recorded. Instead of treating the ore by concentration and smelting, as was the usual procedure, it was subjected to leaching of the copper in huge vats and precipitating copper by electricity. The Chuquicamata ore was the first of the porphyry copper ores to be leached using electricity to precipitate copper metal (Marcosson 1957).

Large-scale leaching of oxide and secondary copper sulfide ores and pioneering electrochemical technology was developed and commercialized in North and South America between 1912 and 1919. General John C. Greenway, general manager of Calumet and Arizona Mining Company (C&A) and New Cornelia Copper Company developed a highly oxidized zone of copper mineralization in the Little Ajo Mountains in Arizona (United States). Utilizing the acid from the C&A copper smelter in Douglas, Arizona, General Greenway and L.D. Ricketts reported to the C&A board that they had developed a process for leaching the New Cornelia Copper Company carbonate ores with sulfuric acid. Construction of a large leaching plant and related facilities was begun in March 1916.

The leaching plant had 11 lead-lined leaching tanks. After the copper had been leached from the ore and the resulting tailings washed and drained, the tails were sent to a tailings dump at the mine site and the solutions (pregnant leach solution, or PLS) were treated in cementation launders to precipitate copper metal as a powder. The cement copper was washed from the launder and reabsorbed into an acid solution and returned to the electrolytic plant. The electrolytic plant consisted of 102 electrolytic tanks, with lead/antimony anodes and copper cathode starting sheets (Rickard 1996).

The next great leap of hydrometallurgical processing in the heap/dump/vat leaching followed by electrolytic copper was developed by General Mills Chemicals laboratories in the late 1950s. The first work was based on the theory and application developed by the U.S. Atomic Energy Commission at Oak Ridge, Tennessee (United States), for the recovery of uranium. General Mills successfully developed and marketed trialkyl tertiary amine for use in the uranium industry. Thus was born from this technology copper solvent extraction (or, as originally called, liquid ion exchange, or LIX).

Using the basic principles of LIX, General Mills began researching the recovery of copper from dilute solutions containing copper. The result of this work was the development of an organic reagent first introduced in 1963 under the trademark name LIX 63. In 1964, LIX 64 was introduced and a new and revolutionary technology was presented to the industry. The major copper producers continued to manufacture copper by conventional means, and the risks inherent with new technology were procured by a small entrepreneurial company, Ranchers Exploration and Development, at its Bluebird mine in Arizona in 1968. Ranchers Exploration and Development successfully installed and operated the new process and led the industry into a huge expansion of hydrometallurgical operations worldwide. Between 1968 and 1994, more than 42 mining operations adopted the solvent extraction and electrowinning (SX/EW) process. From 1968 to 2017, approximately 4.8 Mt (million metric tons) of copper were produced by SX/EW (Kuhn 1993).

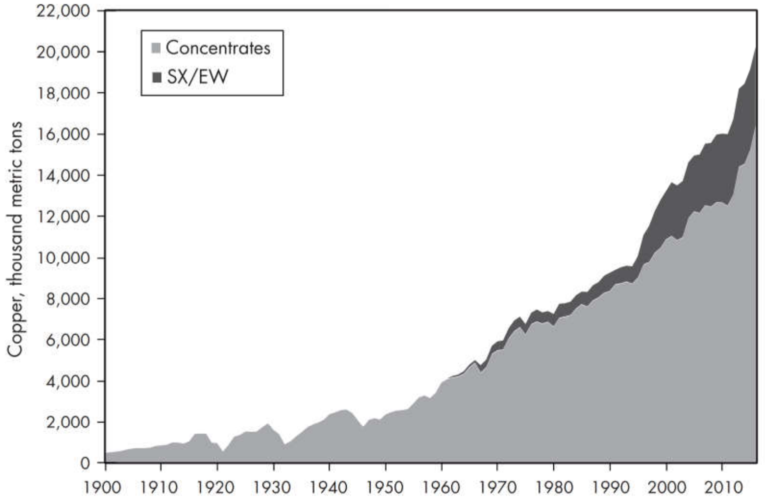
Demonstrated But Not Commercialized Sulfuric Acid–Based Processes

"Solvent extraction and electrowinning (SX/EW) is a two-stage hydrometallurgical process that first extracts and upgrades copper ions from low-grade leach solutions into a solvent containing a chemical that selectively reacts with and binds the copper in the solvent. The copper is extracted from the solvent with strong aqueous acid which then deposits pure copper onto cathodes using an electrolytic procedure (electrowinning)" (Wikipedia 2016).

An example of the SX/EW process for copper is given in Figure 1. In addition to the basic diagram, a unit operation of crud removal and treatment is shown. In general, *crud* comprises ore fines, dissolved silica, and precipitates that mix with an aqueous phase, as well as organic materials that present operating problems and the loss of expensive organic reagents. Crud is removed by vacuuming the mass and centrifuging to separate the liquid and organic from the solids. A portion of the organic can be recovered and regenerated for return to the system.

WORLD COPPER MINE PRODUCTION AND COPPER MINING CAPACITY

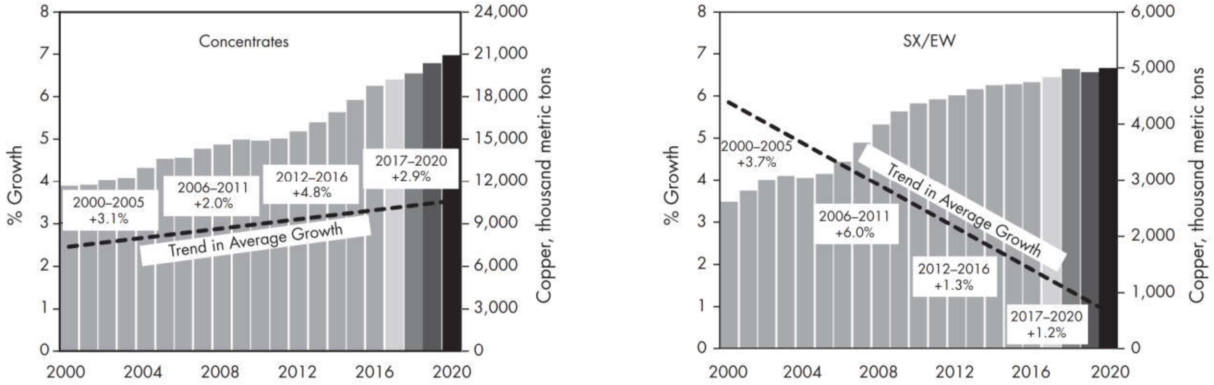
World copper mine production from 1900–2017 is shown in Figure 2, which demonstrates and relative proportion of tonnage produced as either smelted copper from copper concentrates or copper recovered by SX/EW from heap, run-of-mine (ROM) ore, or other sources. Almost all copper is treated electrolytically during its production from ore. It is electrorefined from impure copper anodes or electrowon from leach–solvent extraction solutions. Considerable copper scrap is also electrorefined (ICSG 2017b).



Note: Since 1900, when world production was less than 500,000 t of copper, world copper mine production has grown by 3.2% per year to 20.2 Mt (million metric tons) in 2016. SX/EW production, virtually nonexistent before the 1960s, increased to 3.9 Mt in 2016.

Adapted from ICSG 2017b

Figure 2 World copper mine production, 1900–2016



Note: Copper mining capacity is estimated to reach 25.9 Mt copper in 2020, with 19% being SX/EW production. This will be 10% higher than global capacity of 23.5 Mt copper recorded in 2016. Growth in copper mine capacity is expected to average 2.5%/yr going forward as new capacity is added at existing and some new operations. The ratio between production and capacity is called the capacity utilization rate. The world mine capacity utilization rate was around 86% in 2016.

Capacity data reflects production capabilities, not necessarily production forecasts. Bars represent the tonnages and the dashed lines represent the percentages.

Adapted from ICSG 2017a

Figure 3 Trends in copper mining capacity, 2000–2020

Figure 2 does not demonstrate all copper recovery by hydrometallurgical processes. Prior to 1968, heap and dump leaching operations recovered significant tonnages of copper as cement copper (a hydrometallurgical process); however, cement copper characteristically was shipped to a smelter for conversion into anode copper for electrorefining using copper starter-sheet cathodes or stainless-steel cathodes. Smelted concentrates and cement copper are both converted to copper metal and electrorefined to cathode copper. Electrorefining is a hydrometallurgical process. It could be assumed that all of the copper shown in Figure 2 required some hydrometallurgical processing.

Figure 3 demonstrates a trend of increasing production from concentrates and a decrease in production from SX/EW of copper. This trend suggests decreasing availability or development of oxide and secondary sulfide deposits and increasing production from primary copper sulfide sources.

The copper industry has actively worked since the late 1960s to develop hydrometallurgical processes to compete with smelters and reduce off-gas emissions from smelting operations. The industry response to the U.S. Clean Air Act prompted significant improvements in off-gas handling of smelter emissions, and the improvements resulted in more efficient smelting operations. Numerous hydrometallurgical

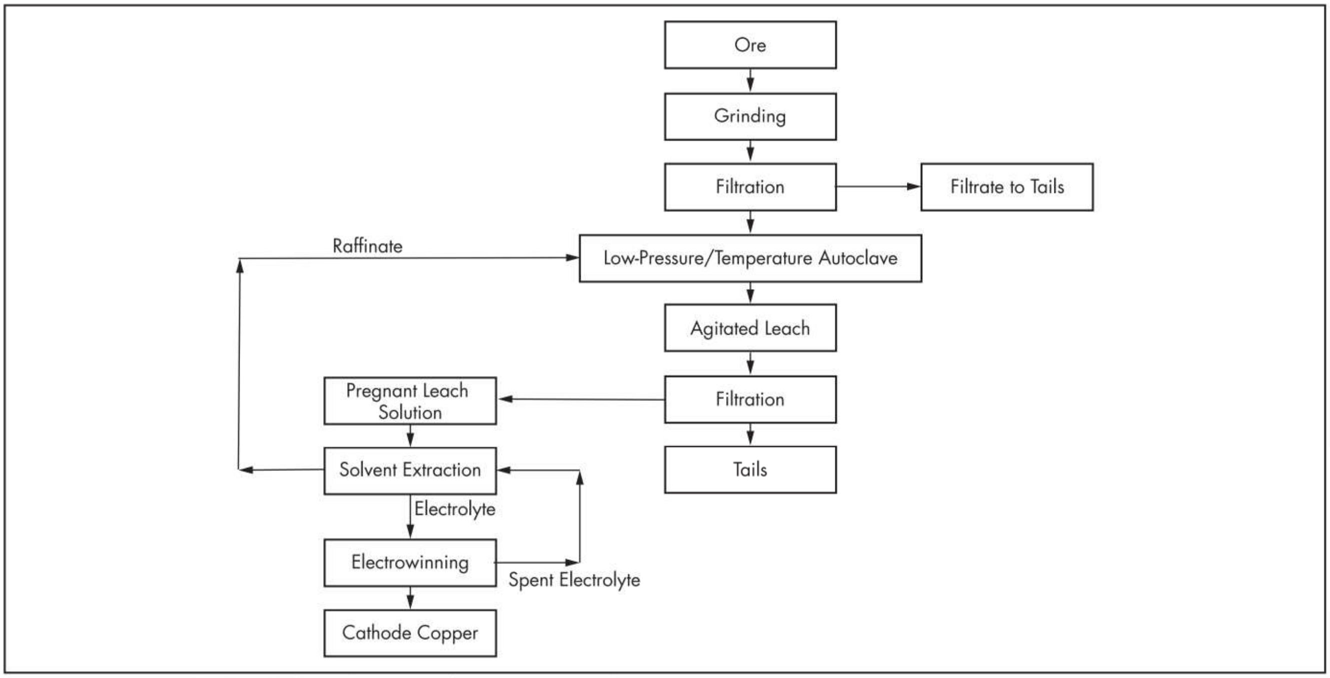


Figure 4 Gunpowder block flow diagram of autoclave leach process

processes to treat copper concentrates have been developed, tested, and in some cases commercialized in the past 60 years. The decision to smelt concentrates or use leach/SX/EW depends upon concentrate mineralogy and the need for sulfuric acid in heap/dump leaching on oxide/secondary sulfide ores. Various hydrometallurgical processes in this discussion are given as examples:

- Commercial hydrometallurgical processes for the recovery of copper
- Other commercialized hydrometallurgical processes for copper production from ores and concentrates
- Tested but not commercialized high-pressure and high-temperature autoclave processes
- Demonstrated but not commercialized sulfuric acid–based processes
- Demonstrated but not commercialized chloride processes

Commercial Hydrometallurgical Processes for the Recovery of Copper

Most hydrometallurgical processes today use similar technologies but are generally developed based on copper mineralogy, copper grade, and concentration processes. Copper from ROM ore can be recovered using sulfuric acid as a leachate on as-mined feed at as-mined material sizes for dump leaching, or crushed/agglomerated ore for heap or on–off pad leaching.

The following six examples of commercial operations using hydrometallurgical processes are discussed in this chapter:

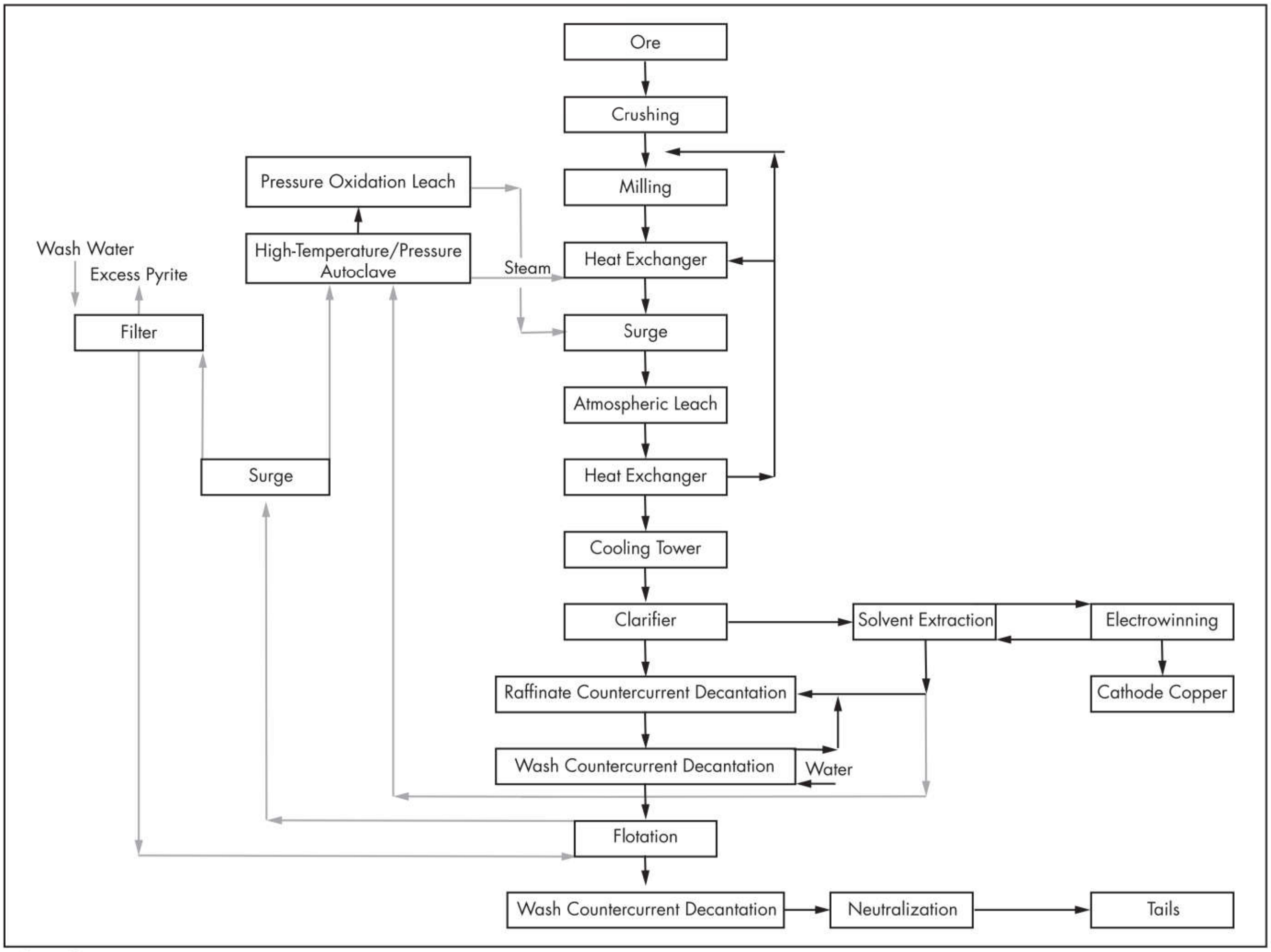
1. **Mount Gordon mine (Australia):** Autoclave leaching of high-grade copper ores
2. **Sepon copper mine (Laos):** High-temperature and high-pressure autoclave, total pressure oxidation (TPO) leaching of copper concentrates
3. **Albion Process:** Low-temperature and atmospheric leaching of ultrafine ground copper concentrates
4. **El Abra mine (Chile):** Typical heap/pad leach of crushed whole ore by sulfuric acid leachate and copper production by SX/EW
5. **Cerro Verde mine (Peru):** Heap leaching of secondary copper mineralization using bacterially assisted oxidation of copper mineralization
6. **Kansanshi mine (Africa):** High-temperature and high-pressure autoclave leaching TPO of primary copper mineralization

Mount Gordon Mine

Operations at the Mount Gordon (formerly Gunpowder) mine in Queensland, Australia, provide an excellent example of whole ore leaching of high-grade secondary copper mineralization using low temperature and low-pressure leach conditions in an acidic environment.

Copper was discovered at the Mammoth ore body in 1927. According to Hespe (2001), "Small operators produced a total of 7,000 tonnes copper in high-grade ore from shallow workings." In 1969–1977, Consolidated Goldfields Ltd. and Mitsubishi Ltd. produced flotation concentrates for smelting ranging from 4,000 to 11,000 t/yr (metric tons per year). Between 1978 and 1982, "Renison Goldfields Consolidated Ltd. experimented with heap leaching and in situ leaching of ... ore to produce copper cement and copper cathode by SX/EW" (Hespe 2001). In 1988, the plant closed and operations were suspended.

Between 1996 and 2000, a low-pressure and low-temperature autoclave technology was developed and successfully implemented for the recovery of copper as cathode copper. Mined high-grade copper ore containing principally carbonate copper and chalcocite (Cu_2S) was ground, filtered, and fed to a low-pressure and low-temperature autoclave followed by agitation leaching to recover copper from chalcocite/carbonate-type mineralization. The leachate was sulfuric acid



Adapted from Dreisinger 2003

Figure 5 Block diagram of the Sepon process

based and the copper liberated as aqueous copper sulfate for recovery in an SX/EW electrolytic plant. The plant "was completed in late 1998," and "in 1999, as the plant was brought on line, 32,133 tonnes of cathode copper were produced at a cash cost of US43.9 cents/lb" (Hespe 2001). Figure 4 displays a simplified flow diagram of the process steps used at the Gunpowder mine. The operation was closed in 2003.

Sepon Copper Mine

The Sepon open pit copper mine is 40 km north of the town of Sepon in the Savannakhet Province of southern Laos (Figure 5). The mine uses high-temperature and high-pressure autoclave TPO leaching of copper concentrates. The mine is operated by Lane Xang Minerals—90% owned by MMG and the remaining 10% by the Lao government. Production began in 2005 (Thomaz 2007; MMG Limited 2017).

Albion Process

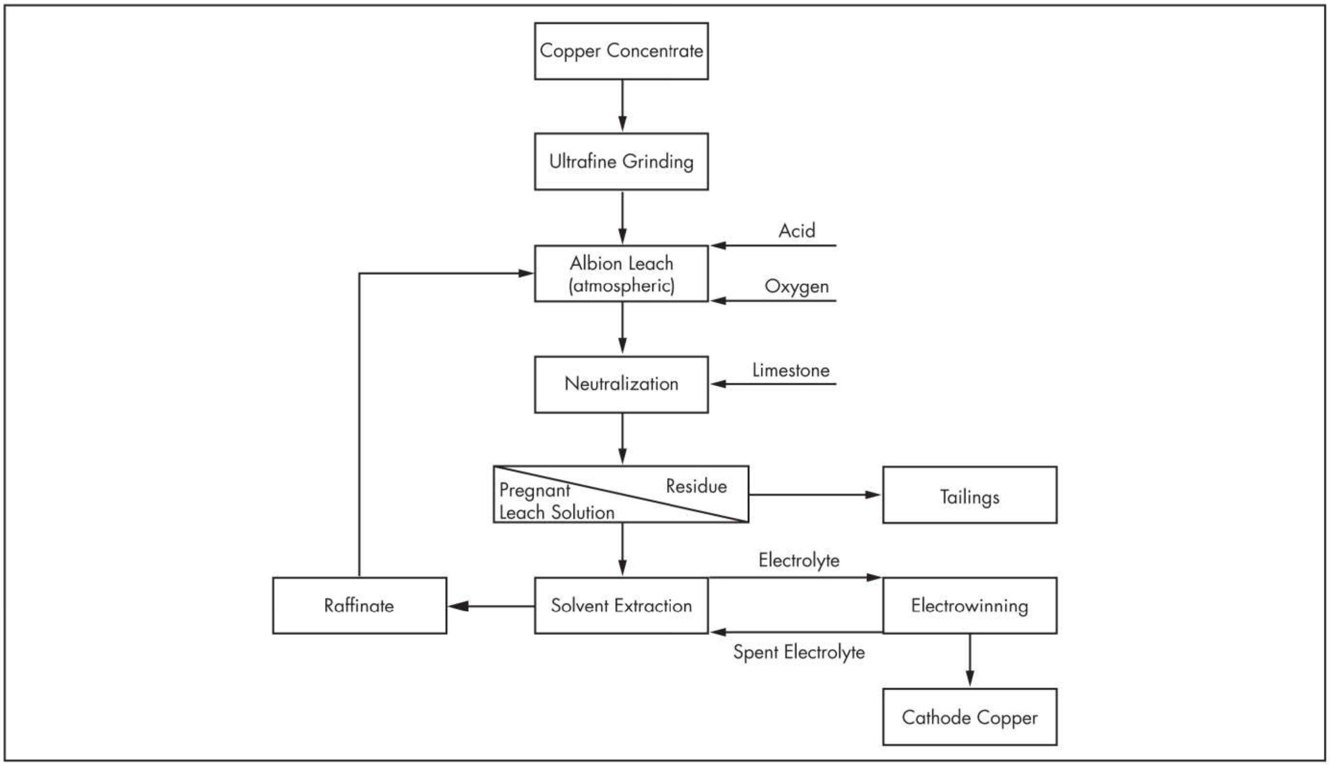
The Albion Process was developed in 1998 by MIM Holdings (Brisbane, Queensland, Australia). The process uses low-temperature and atmospheric leaching of ultrafine ground copper concentrates. The technology was developed in 1994 and is patented worldwide. When applied to the processing of copper minerals, a low-grade rougher or bulk flotation concentrate is finely ground to a particle size in the range 80% passing 8–18 µm using a stirred media mill, such as the IsaMill. The IsaMill is a horizontally inclined stirred mill and is the most advanced ultrafine grinding technology available today, with 36 mills installed worldwide and a total grinding capacity in excess of 60 MW.

The finely ground concentrate is then leached in a sulfuric acid solution to recover copper to the leach solution. The oxidative leaching stage is carried out in agitated tanks operating at atmospheric pressure, with a residence time of 24–30 hours. A copper recovery in excess of 97% would be expected across the leach. The leaching tanks are conventional baffled open reactors operating with centrally mounted impellers, similar in design to a gold leach vessel. Oxygen is introduced to the leach slurry for oxidation and is added as a gas.

The Albion Process is applied in gold, copper, and zinc concentrate processing facilities. A typical flow sheet for a circuit treating copper concentrate is shown in Figure 6.

El Abra Mine

This section describes a typical heap/pad leach of crushed whole ore by sulfuric acid leachate and copper production



Source: MIM Holdings 1998

Figure 6 XStrata Technology's Albion Process for copper concentrates

by SX/EW. The El Abra mine is owned by the Sociedad Contractual Minera El Abra, which is a joint venture between U.S.-based company Freeport-McMoRan (51%) and Chilean state company Codelco (49%). The mine is located in El Loa Province, 55 km north of Calama in northern Chile. The ore body is located at an elevation of ~3,900 m (Freeport-McMoRan, n.d.).

El Abra is a porphyry copper-type deposit that occurs in a narrow (30–50 km wide), north-south-trending mineral belt that also contains the Chuquicamata and Radomiro Tomic porphyry copper deposits. The oxide copper minerals are mainly chrysocolla and pseudomalachite. The sulfide mineralization is predominantly bornite (60%), with chalcopyrite (25%) and chalcocite (15%) (Freeport-McMoRan, n.d.).

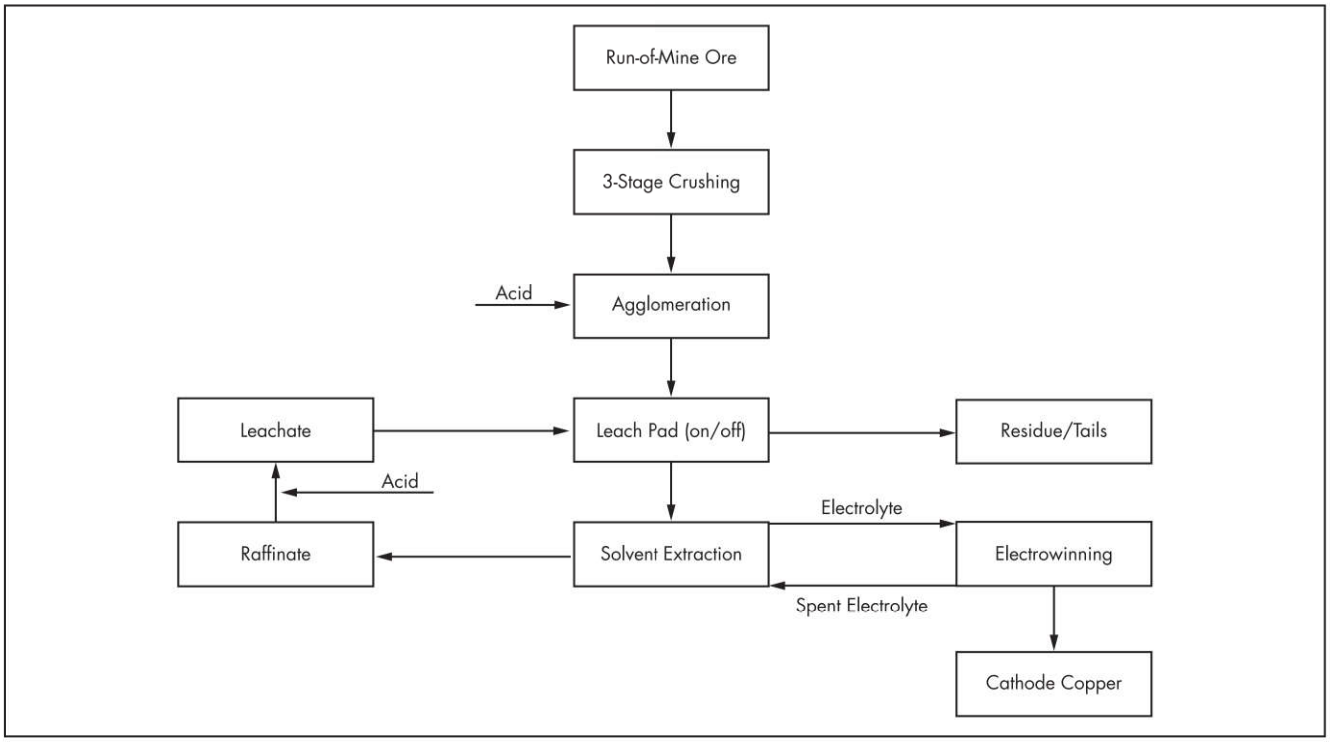
El Abra processed oxide copper ores in its hydrometallurgical plant from 1996 to 2010. The plant has a crushing circuit, agglomeration drums, a dynamic heap (on–off), and SX/EW facilities. The average grade considered is 0.55% of total copper, with a throughput of 92–100 kt/d. A ROM stockpile leaching was integrated to the process in 2001 to treat low-grade oxides. The SX/EW design capacity is 225 kt/yr of copper in cathode form. Production as originally designed was achieved in 2003 (Figure 7) (Freeport-McMoRan, n.d.).

In 2011, as the oxide ore was diminishing, El Abra's Sulfolix project started to treat sulfide ores. The sulfides are currently processed in a permanent heap. The leaching operation is assisted by aeration and bacteria augmentation. Plant throughput increased to 125 kt/d and production decreased to an average of 140 kt/y of copper in cathodes.

Cerro Verde Mine

This section describes heap leaching of secondary copper mineralization using bacterially assisted oxidation of copper mineralization at the Cerro Verde mine in Peru. According to Freeport-McMoRan (2018), in the 1800s, "Spaniards mined high-grade oxide copper ore from Cerro Verde. ... Anaconda Copper owned the property from 1916 until 1970, when the mine was acquired by the Peruvian government. The government mined Cerro Verde's oxide ores and built one of the world's first SX/EW facilities in 1972. Cyprus Amax purchased the operation in 1994" and upgraded it. In late 1999, Cyprus-Amax was acquired by Phelps Dodge, which in turn was acquired by Freeport-McMoRan in 2007. Sociedad Minera Cerro Verde S.A.A., a Peruvian mining company, now operates the open pit copper, molybdenum, and silver mining complex.

Cerro Verde is an open pit copper and molybdenum mining complex located 32 km southwest of Arequipa, Peru, at an elevation of 2,700 m. The ore body is part of the Southern Peru belt of copper porphyry deposits. These porphyry deposits stretch from the Chilean border through the Toquepala and Cuajone deposits to some distance west of Arequipa. Small-scale mining activity is believed to have taken place at Cerro Verde in Inca times and subsequently during Spanish colonization. Between 1868 and 1879, Chilean contractors worked the concessions and reportedly mined thousands of metric tons of oxide ore with grades as high as 15% until the Pacific War of 1879. Thereafter, various small operators worked the site. Between 1880 and 1915, minor activity occurred at the property with <20,000 t of material mined.



Courtesy of Freeport-McMoRan

Figure 7 El Abra mine flow sheet

During 1916 to 1970, Andes Exploration Company (Anaconda) explored Cerro Verde, drilling for mineral and water extending to the adjacent Santa Rosa deposit. In 1970, the concessions reverted to the Peruvian State, allocated to Minero Perú formed to promote development of under-exploited resources. In 1977, industrial operation of the leach/SX/EW plant started, one of the world's first SX/EW facilities. In 1994, Cerro Verde was acquired by Cyprus Amax in a privatization process. During 1999, Phelps Dodge acquired Cyprus Amax and assumed ownership of the mine. In 2007, Freeport-McMoRan Copper and Gold acquired Phelps Dodge, becoming the largest publicly traded copper company in the world. Today, the mine's stockholders are Freeport-McMoRan (53.56%), Sumitomo Metal Mining (21%), Compañía Minera Buenaventura S.A.A. (19.58%), and Peruvian shareholders (5.86%).

The Cerro Verde deposit is comprised of porphyritic quartz monzonite stocks and breccias emplaced in granodiorite. There are three open pits with oxide and secondary sulfide deposits: Cerro Verde, Santa Rosa, and Cerro Negro. Cerro Verde and Santa Rosa are single-mineralized ore body deposits separated by waste at the surface with a common root at depth. The Cerro Negro mine contains oxide copper for leaching process.

Cerro Verde's hydromettalurgical plant is formed by three stages of crushing plant, with a capacity of 39 kt/d, and agglomeration drums. Then the ore is delivered to a high-grade leaching pad, using one overland belt of 4 km and piled in a leach pad using the radial stacker.

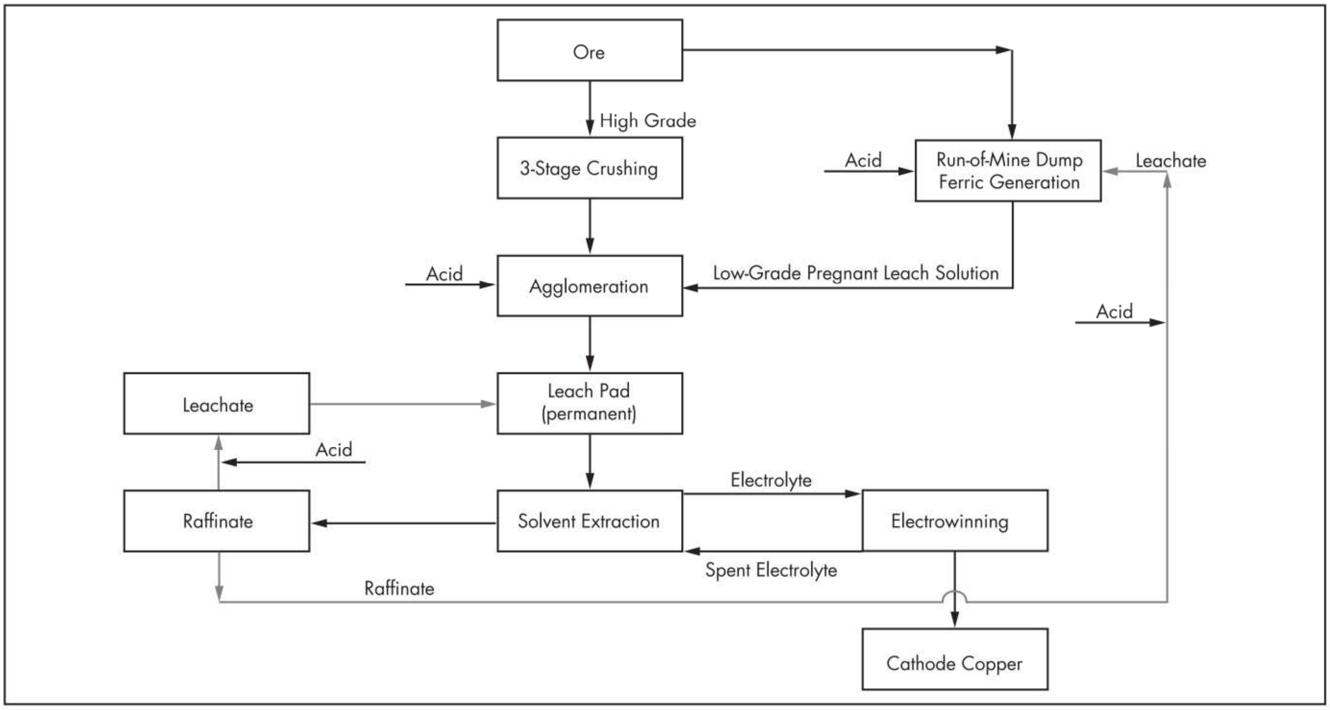
The irrigation leaching is in cascade, the raffinate solution irrigates ROM leach pads, and the intermediate leach solution (ILS) contains ferric iron and copper. This ILS mixes with the raffinate solution and irrigates high-grade leach pads, and those pads produce the PLS to the SX plant. The ferric iron in the ILS allows additional ferric to the leach pads, thereby allowing better and more rapid leaching of sulfide minerals in the heaps. The SX plant has five trains and the EW plant has 230 electrolytic cells. Copper is produced in cathodes of 100% high grade at a rate of ~140 million lb/yr (Figure 8).

In 2014, several lenders provided a 5-year unsecured loan for Cerro Verde to undergo a major expansion. The total projected capital cost was US$4.4 billion. Expansion of the mine and mill was completed in 2015 and increased the concentrator plant capacity from 120,000 t/d of ore to 360,000 t/d, making it the world's largest concentrating facility by the end of 2015. The project was expected to increase annual production to ~272,155 t of copper and 6,804 t of molybdenum. At the end of 2015, Cerro Verde produced 47,673 t of copper in cathodes, 199,309 t of copper in concentrates, and 3,298 t of molybdenum (Business News Americas 2018).

Kansanshi Mine

High-temperature and high-pressure autoclave leaching TPO of primary copper mineralization is used at the largest mine in Africa, the Kansanshi mine. The mine is located ~10 km north of Solwezi and 180 km northwest of Chingola. It is owned and operated by Kansanshi Mining PLC, which is 80% owned by a First Quantum subsidiary (Figure 9).

To produce copper in concentrate, sulfide ore is treated by crushing, milling, and flotation. As oxide ore was depleted and sulfide ore grades were beginning to fall, a decision was made to expand the sulfide milling circuit, which was commissioned at the end of 2008. While the expansion circuit is dedicated to the treatment of sulfide ore, mixed ore is treated through the original sulfide circuit. Oxide ore is treated by crushing, milling, flotation, leaching, and the SX/EW process, which produces a sulfidic and gold-bearing flotation



Courtesy of Freeport-McMoRan

Figure 8 Hydrometallurgical flow process

concentrate as well as electrowon cathode copper. In 2012, the oxide treatment capacity was increased to 14.5 Mt/yr by installing equipment from the Bwana Mkuba copper SX/EW plant. Additional leach, SX, electrowinning, and countercurrent decantation thickeners were commissioned in 2013 and 2014 (First Quantum Minerals 2017).

High-pressure and high-temperature autoclave leaching of flotation concentrates allowed the oxidation and copper leaching from primary copper mineralization. Leached concentrates were advanced to atmospheric leaching and liquid solids separation. PLS liquid fed solvent extraction and copper electrowinning as copper cathodes.

Gold recovery by gravity was expanded with four new gravity concentrators in April 2010. This provided two concentrators per milling train and increased gold recovery from all ore types. Gemini tables were installed to treat the gravity concentrates and produce a high-grade concentrate for direct smelting to gold bullion. The Kansanshi smelter was commissioned in the third quarter of 2014, and first anodes, from melted cathodes, were poured by December of that year. The smelter began commercial production in July of the following year. Primary processing steps include smelting, converting, fire refining, and casting. The smelter has a nominal capacity of 1.2 Mt/yr of concentrate to produce more than 300,000 t/yr of copper metal and more than 1 Mt/yr of sulfuric acid as a by-product. Acid production from the smelter permits the Kansanshi process plant to process mixed cleaner tails through the leaching circuit and produce additional cathode (First Quantum Minerals 2017).

Other Commercialized Hydrometallurgical Processes

In Situ Leaching of Copper Mineralization

The Chinese performed in situ leaching (ISL) of copper by 977 AD, and perhaps as early as 177 BC. Copper is usually leached using sulfuric acid or hydrochloric acid and then recovered from solution by SX-EW or by chemical precipitation (Wikipedia 2018).

According to Hiskey (1994), "The recovery of mineral and metal values by solution mining has been practiced for centuries. What appears at first glance to be a simple, empirical technique, is in actuality a very complicated process involving a large number of critical parameters that encompass several scientific and engineering disciplines. Hydrometallurgy, hydrology, geology and geochemistry, rock mechanics, chemistry, and environmental engineering and management are a few of the specialties utilized by modern operators."

Approximately 25% of the primary copper produced in the United States is derived by leaching. Most of this is a result of huge dump and heap leaching activities from large open pit mines. A small fraction of copper is produced from modest ISL operations treating low-grade rock left from earlier mining activities. Because of its inherent advantages over conventional mining and milling, ISL technology is being considered as a sustainable choice for recovering copper from both oxide and sulfide deposits. Both physical and chemical parameters must be integrated to successfully predict ISL performance (Hiskey et al. 1992).

"Ores most amenable to leaching include the copper carbonates malachite and azurite, the oxide tenorite, and the silicate chrysocolla" says Gorain (2016). "Other copper minerals, such as the oxide cuprite and the sulfide chalcocite may require addition of oxidizing agents such as ferric sulfate and oxygen to the leachate before the minerals are dissolved. The ores with the highest sulfide contents, such as bornite and chalcopyrite will require more oxidants and will dissolve more slowly. Sometimes oxidation is speeded by the bacteria *Thiobacillus ferrooxidans*, which feeds on sulfide compounds."

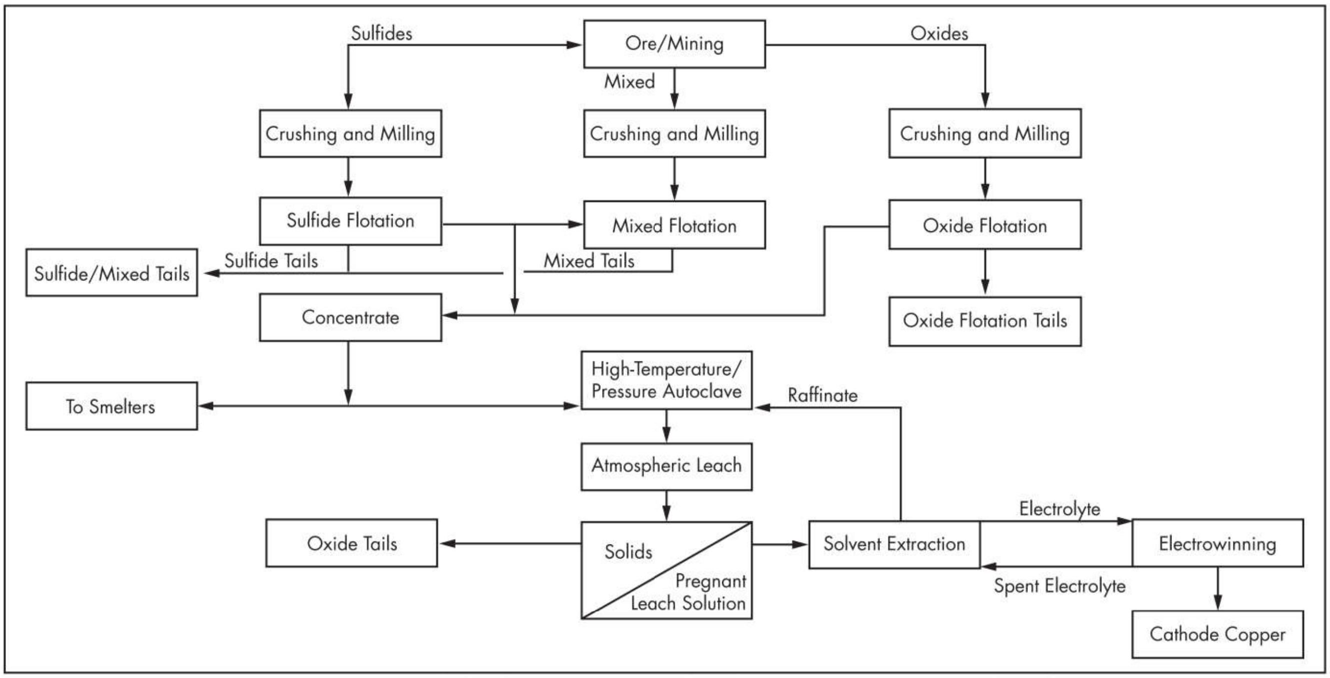


Figure 9 First Quantum Minerals' Kansanshi high-temperature and high-pressure autoclave leaching flow sheet

Copper ISL is often carried out by stope leaching, where broken low-grade ore is leached in a conventional underground mine. The leaching may take place in backfilled stopes or caved areas. In 1994, stope leaching of copper was reported at 16 mines in the United States. At the San Manuel mine (Arizona), ISL was originally used by collecting the resultant solution underground. Then in 1995, it was converted to a well-to-well recovery method and has been proposed for other copper deposits in Arizona (Wikipedia 2018). Two in situ projects for the extraction of copper are currently in the development phase in Arizona.

Commercial Ammoniacal Leaching of Copper Concentrates

According to Arbiter and McNulty (1999):

> The first ammonia leaching plants, applied to copper carbonate and native copper tailings in 1915, were followed more recently by research and development of flowsheets for ammonia leaching of sulfide concentrates. These were applied to two commercial plants. Anaconda's Arbiter Plant started up in 1974 with a design capacity of 36,000 tons/year of cathode copper, to be produced by ammonia leaching with oxygen, followed by solvent extraction and electrowinning. The plant shut down in late 1977 as a result of high maintenance and operating costs, partly due to harsh winters; to complication associated with sulfate disposal; and to changes in mineralogy. BHP's Coloso plant in Chile was designed to produce 80,000 tons/year of cathodes by leaching part of Escondida's concentrate production. Using a similar flowsheet but with air and low temperatures to avoid sulfate production, it started up in late 1994 and shut down in mid-1998, after failing to reach cathode design capacity and experiencing problems with its technology.

Complete ammoniacal leaching of copper from chalcocite and covellite concentrates was demonstrated by Anaconda and BHP. Two areas of processing affected both operations. The recovery and recycling of ammonia and the transfer of ammonia in SX to the electrolyte caused operational problems.

Other Commercial High-Pressure/High-Temperature Autoclave Leach Operations

Freeport (FMI) operated a total pressure oxidation plant in Bagdad, Arizona, and is operating a very large total pressure oxidation plant at its Morenci mining operation in Arizona (Marsden et al. 2003). Both plants successfully produced cathode copper and sulfuric acid for heap leaching. The ability to produce and use sulfuric acid for heap leaching provides a significant financial incentive for the combined hydrometallurgical process. The current Morenci plant utilizes TPO technology. FMI initially built a medium-temperature autoclave plant but recently converted to high temperature.

Commercial Low-Pressure/Low-Temperature Leach Processes

Cobre Las Cruces is owned by First Quantum Minerals, a Canadian company that produces copper, nickel, gold, zinc, and platinum group metals. CLC operates an open pit mine and hydrometallurgical process plant. The project began exploration in 1992 and production started in mid-2009. The site is located within the towns of Gerena, Guillena and Salteras in the province of Seville, in southern Spain, and the pit and plant occupy 946 ha. Anticipated annual production averages 72,000 t Cu, which equates to 25% of Spanish internal demand. A total of 1 Mt Cu is estimated for the 15-year operating period. Spain is the fourth largest consumer of copper in the European Union and ranks 14th in the world (CLC, n.d.).

Table 1 Hydrometallurgical process parameters

	Metallurgical Process							
Unit Operation	**Albion**	**BioCOP**	**CESL**	**HTPOX**	**HydroCopper**	**Galvanox**	**Intec**	**Nikko**
Grinding	Ultrafine	Fine	Fine	Cleaner	Fine	Cleaner	Fine	Fine
Particle size P_{80}, μm	5–20	42	37	53	37	53	40	40
Leachate	H_2SO_4	H_2SO_4	H_2SO_4/Cl^{-1}	H_2SO_4	Cl^{-1}	H_2SO_4	Cl^{-1}	Cl^{-1}/Br^{-1}
Leach temperature, °C	85	65–85	150	220	90	80–220	85	85
Oxidant	O_2	Thermophiles	O_2	O_2	O_2/Cl_2	O_2	Br_2Cl/air	Br_2Cl/air
Iron stabilization	FeOOH	Fe_2O_3	Fe_2O_3	$Fe_2O_3/2FeOHSO_4$	Fe_2O_3/FOOH	Fe_2O_3	Fe_2O_3	Fe_2O_3/FOOH
Precious metals	Cyanide	Cyanide	Cyanide	Cyanide	Cu	Cyanide	Hg/Cu	Carbon
Residence time, hours	48	50	48	48	30	48	20	26
Copper recovery	SX-EW	SX-EW	SX-EW	SX-EW	H_2 to sponge	SX-EW	EW dendrites	SX-EW
Arsenic fixation	$FeAsO_4 \cdot 2H_2O$	$FeAsO_4 \cdot 2H_2O$	$FeAsO_4 \cdot 2H_2O$	$FeAsO_4 \cdot 2H_2O$	$FeAsO_4 \cdot 2H_2O$	$FeAsO_4 \cdot 2H_2O$	$FeAsO_4 \cdot 2H_2O$	$FeAsO_4 \cdot 2H_2O$
S^0 oxidation, %	10	100	5–30	100	2	2	2	2
FeS_2 oxidation, %	40	100	65	100	<5	2	<5	<5

Other Processes

These high-pressure and high-temperature autoclave processes have been tested but not commercialized:

- Cominco Engineering Services Ltd. copper process from Teck Resources Limited
- Galvanox, a galvanically assisted atmospheric leaching technology for copper concentrates (Dixon et al. 2008)

The following sulfuric acid–based processes have been demonstrated but not commercialized:

- Activox process
- Sherritt-Cominco copper process
- Sherritt Gordon low-temperature leach process
- Total pressure oxidation process/placer dome process
- Anaconda super concentrate process
- BacTech biological leach process
- Hecla (Cyprus) roast/leach process
- CQG process

These chloride processes have been demonstrated but not commercialized:

- CLEAR process (40,000 t/yr copper plant operated from 1976 to 1978 and was closed because of materials issues)
- Outotec HydroCopper process
- Canada Centre for Mineral and Energy Technology ferric chloride leach process
- Cuprex metal extraction process
- Cymet process
- Dextec GmbH process
- GCM/HBMS process
- Intec copper process
- Minemet Recherche process for copper
- University of British Columbia–Cominco process
- U.S. Bureau of Mines process for chalcopyrite

Table 1 generally summarizes probable operating conditions for eight potentially viable processes for the recovery of copper from concentrates. The extracted data shown has been summarized by the Minerals Advisory Group from existing published literature (Kuhn 2018).

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