Hydrometallurgy

Hydrometallurgy is a method for obtaining metals from their ores. It is a technique within the field of extractive metallurgy involving the use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual materials. Metal chemical processing techniques that complement hydrometallurgy are pyrometallurgy, vapour metallurgy and molten salt electrometallurgy. Hydrometallurgy is typically divided into three general areas:

- Leaching
- Solution concentration and purification
- Metal or metal compound recovery

Leaching

Leaching involves the use of aqueous solutions to extract metal from metal bearing materials which is brought into contact with a material containing a valuable metal. The lixiviant solution conditions vary in terms of pH, oxidation-reduction potential, presence of chelating agents and temperature, to optimize the rate, extent and selectivity of dissolution of the desired metal component into the aqueous phase. Through the use of chelating agents, one can selectively extract certain metals. Such chelating agents are typically amines of schiff bases.

The five basic leaching reactor configurations are in-situ, heap, vat, tank and autoclave.

In-situ leaching:

In-situ leaching is also called "solution mining." This process initially involves drilling of holes into the ore deposit. Explosives or hydraulic fracturing are used to create open pathways within the deposit for solution to penetrate into. Leaching solution is pumped into the deposit where it makes contact with the ore. The solution is then collected and processed. The Beverley uranium deposit is an example of in-situ leaching and also Trojan Mine in Zimbabwe.

Heap leaching:

In heap leaching processes, crushed (and sometimes agglomerated) ore is piled in a heap which is lined with an impervious layer. Leach solution is sprayed over the top of the heap, and allowed to percolate downward through the heap. The heap design usually incorporates collection sumps, which allow the "pregnant" leach solution (i.e. solution with dissolved valuable metals) to be pumped for further processing. An example is gold cyanidation, where pulverized ores are extracted with a solution of sodium cyanide, which, in the presence of air, dissolves the gold, leaving behind the nonprecious residue.

Vat leaching:

Vat leaching involves contacting material, which has usually undergone size reduction and classification, with leach solution in large vats.

Tank leaching:

Stirred tank, also called agitation leaching, involves contacting material, which has usually undergone size reduction and classification, with leach solution in agitated tanks. The agitation can enhance reaction kinetics by enhancing mass transfer. Tanks are often configured as reactors in series.

Autoclave leaching:

Autoclave reactors are used for reactions at higher temperatures, which can enhance the rate of the reaction. Similarly, autoclaved enable the use gaseous reagents in the system.

Solution concentration and purification

After leaching, the leach liquor must normally undergo concentration of the metal ions that are to be recovered. Additionally, undesirable metal ions sometimes require removal.[1]

- Precipitation is the selective removal of a compound of the targeted metal or removal of a major impurity by precipitation of one of its compounds. Copper is precipitated as its sulfide as a means to purify nickel leachates.
- Cementation is the conversion of the metal ion to the metal by a redox reaction. A typical application involves addition of scrap iron to a solution of copper ions. Iron dissolves and copper metal is deposited.
- Solvent Extraction
- Ion Exchange

- Gas reduction. Treating a solution of nickel and ammonia with hydrogen affords nickel metal as its powder.
- Electrowinning is a particularly selective if expensive electrolysis process applied to the isolation of precious metals. Gold can be electroplated from its solutions.

Solvent extraction:

In the solvent extraction is a mixture of an extractant in a diluent is used to extract a metal from one phase to another. In solvent extraction this mixture is often referred to as the "organic" because the main constituent (diluent) is some type of oil.

The PLS (pregnant leach solution) is mixed to emulsification with the stripped organic and allowed to separate. The metal will be exchanged from the PLS to the organic they are modified.] The resulting streams will be a loaded organic and a raffinate. When dealing with electrowinning, the loaded organic is then mixed to emulsification with a lean electrolyte and allowed to separate. The metal will be exchanged from the organic to the electrolyte. The resulting streams will be a stripped organic and a rich electrolyte. The organic stream is recycled through the solvent extraction process while the aqueous streams cycle through leaching and electro-winning] processes respectively.

Ion exchange:

Chelating agents, natural zeolite, activated carbon, resins, and liquid organics impregnated with chelating agents are all used to exchange cations or anions with the solution. Selectivity and recovery are a function of the reagents used and the contaminants present.

Metal recovery

Metal recovery is the final step in a hydrometallurgical process. Metals suitable for sale as raw materials are often directly produced in the metal recovery step. Sometimes, however, further refining is required if ultra-high purity metals are to be produced. The primary types of metal recovery processes are electrolysis, gaseous reduction, and precipitation. For example, a major target of hydrometallurgy is copper, which is conveniently obtained by electrolysis. Cu^{2+} ions reduce at mild potentials, leaving behind other contaminating metals such as Fe^{2+} and Zn^{2+}.

Electrolysis:

Electrowinning and electrorefining respectively involve the recovery and purification of metals using electrodeposition of metals at the cathode, and either metal dissolution or a competing oxidation reaction at the anode.

Precipitation:

Precipitation in hydrometallurgy involves the chemical precipitation of either metals and their compounds or of the contaminants from aqueous solutions. Precipitation will proceed when, through reagent addition, evaporation, pH change or temperature manipulation, any given species exceeds its limit of solubility.

A short history of hydrometallurgy

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A short history of hydrometallurgy

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Dedicated to the memory of Vladimir N. Mackiw (1923–2001), a distinguished Canadian hydrometallurgist

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Abstract

Thousands of years ago people had learned how to build furnaces and use fire to melt rocks and produce metals but the use of aqueous solutions for ore processing came much later, mainly at the time of the alchemists when acids and alkalies became known and used. Modern hydrometallurgy, however, can be traced back to the end of the 19th century when two major operations were discovered: the cyanidation process for gold and silver extraction and the Bayer process for bauxite treatment. Later, in the 1940s, a breakthrough came during the Manhattan Project in USA in connection with uranium extraction. Since then, it has been advancing progressively and even replacing some pyrometallurgical processes. Canadian contribution is significant particularly in the recovery of uranium, nickel, cobalt, and zinc.

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1. Introduction

The roots of hydrometallurgy may be traced back to the period of alchemists when the transmutation of base metals into gold was their prime occupation (Habashi, 1993a). Some of these operations involved wet, i.e., hydrometallurgical methods. For example, when an alchemist dipped a piece of iron into a solution of blue vitriol, i.e., copper sulfate, the iron was immediately covered by a layer of metallic copper. This apparent transmutation of iron into copper is represented in modern terms by the equation: $Cu^{2+}+Fe \rightarrow Cu+Fe^{2+}$, but it was not known at that time that blue vitriol contained 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 dissolved in mercury forming an amalgam but was insoluble in all acids or alkalies known at that time. The discovery of aqua regia by Jabir Ibn Hayyan (720–813 AD) (Fig. 1), the Arab alchemist, may be considered as a milestone marking the beginning of hydrometallurgy. Aqua regia, i.e., royal water, is a mixture of HCl and HNO_3 that dissolves gold; neither of the acids alone has any dissolving action. Aqua regia is still used today for gold refining, and chlorine one of its active ingredients: $3HCl+HNO_3 \rightarrow Cl_2+NOCl+2H_2O$ was utilized extensively for extracting gold from its ores till the 1890s.

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Fig. 1. The Arab alchemist Jabir Ibn Hayyan (720–813 AD), discoverer of *aqua regia* (royal water) for dissolving gold—the king of metals.

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 Río Tinto mines in Spain. In these operations, pyrite containing some copper sulfide 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 sulfate 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", which is apparently derived from the Spanish "cementación" meaning precipitation. This is the same process that was already known to the alchemists and is still in operation today to an appreciable extent.

In the 18th century, one of the most important industries in Quebec was the production of potash for export to France to satisfy the needs of the soap and glass industries. Before the invention of the Leblanc Process for the manufacture of Na_2CO_3 from NaCl, the main source of Na_2CO_3 was from ashes of seashore vegetation, and that of potash was from ashes produced by burning wood in areas where the clearing of forests was in progress on a large scale. The importance of this process to hydrometallurgy lies in the fact that leaching was extensively practiced. During the period 1767–1867, wood ash was collected from domestic stoves and fireplaces, and from lime kilns, then agitated with water, filtered, then evaporated to dryness to yield potash. One ton potash required the burning of 400 tons of hardwood, which is equivalent to the cutting of about 10 acres of forest.

2. The beginnings

The birth of modern hydrometallurgy dates back to 1887 when two important processes were invented. The first, the cyanidation process for treating gold ores, and the second, the Bayer Process for the production of alumina.

2.1. Cyanidation process

The dissolving action of cyanide solution on metallic gold was known as early as 1783 by the Swedish chemist Carl Wilhelm Scheele (Habashi, 1987). L. Elsner in Germany in 1846 studied this reaction and noted that atmospheric oxygen played an important role during dissolution. The application of this knowledge to extract gold from its ores was proposed and patented much later in England by John Stewart MacArthur (1856–1920) (Fig. 2) in 1887 and became known as the cyanidation process. G. Bodländer in 1896 made the important discovery that hydrogen peroxide was formed as an intermediate product during the dissolution of gold.

Fig. 2. John Stewart MacArthur (1856–1920), discoverer of the cyanidation process.

The cyanidation process had already been applied to each mining district in the world and still its chemistry was very obscure. Its impact on hydrometallurgy had been tremendous. Extremely large reactors known as Dorr agitators in which the finely ground ore was agitated with the cyanide leaching agent and equipped with compressed air injection in the pulp had been designed and built by the metallurgical engineer John Dorr. Huge filtration plants designed to obtain clear leach solutions for metal recovery were similarly constructed. The ancient process known as cementation which was applied only for precipitating copper from solution by scrap iron was applied to gold solutions, iron being replaced by zinc. In spite of all these advances in engineering and the wide application of the process, the theory still remained lagging behind. As a result of introducing the cyanidation process worldwide, gold production increased greatly during the period 1900–1910 (Fig. 3).

2.2. Bayer process

The second major hydrometallurgical process of this era was the process invented by Karl Josef Bayer (1847–1904) (Fig. 4) for the preparation of pure Al_2O_3 and known as the *Bayer Process* (Habashi, 1995). This process was concerned with leaching bauxite, discovered in 1821 in France in a small village called Les Baux, near Marseille, with sodium hydroxide solution above its boiling point in a pressure reactor. After separating the insoluble material, the pure solution was then seeded to precipitate pure crystalline aluminum hydroxide which was filtered, washed, dried, and calcined to pure Al_2O_3 suitable for charging to the electrolytic reduction cell invented 2 years earlier. Bayer was an Austrian chemist working in Saint Petersburg, in Russia; his process is used at present in its original version with practically no change. It is interesting to point out the following:

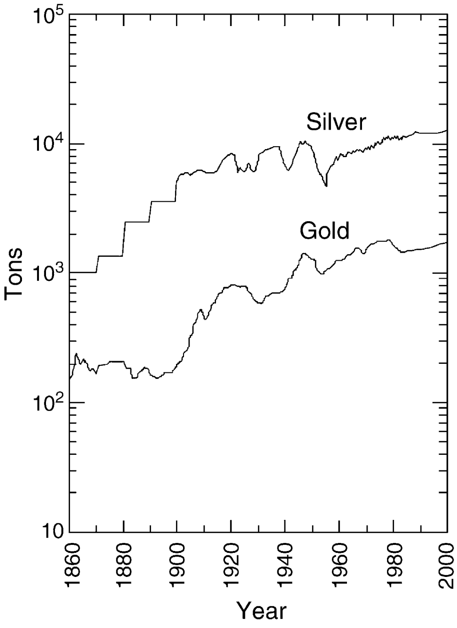

Fig. 3. Increase in world gold and silver production between 1900 and 1910 as a result of introducing the cyanidation process.

Fig. 4. Karl Josef Bayer (1847–1904), inventor of the process for the production of alumina from bauxite.

- The process was originally developed to satisfy the needs of the textile industry since aluminum hydroxide was used as a mordant in dyeing cotton. It was only after the invention of the electrolytic aluminum process in 1886 that the process gained importance in metallurgy.
- Bayer's first contribution was in 1887 when he discovered that $Al(OH)_3$ precipitated from alkaline solution was *crystalline*, easy to filter, and wash free from impurities while that precipitated from acid medium by neutralization was gelatinous and difficult to filter and wash.
- A few years earlier to Bayer's invention, Louis Le Chatelier (1815–1873) in France described a method for making Al_2O_3 by heating bauxite with Na_2CO_3 at 1200 °C, leaching the sodium aluminate formed with water, then precipitating

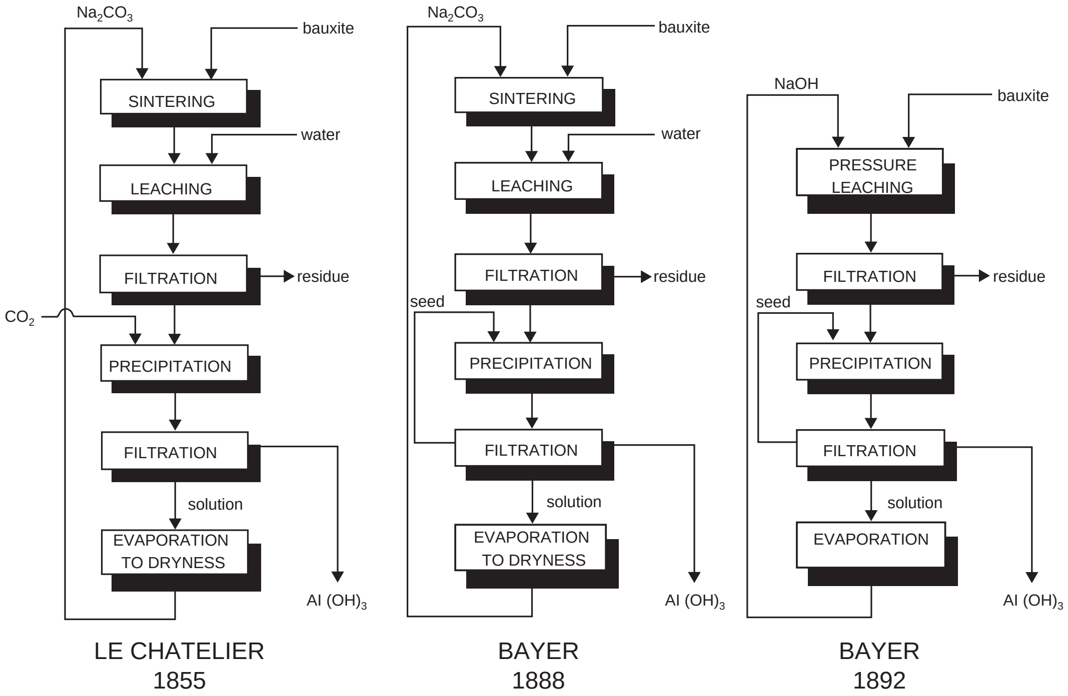

Fig. 5. Bayer process displaced Le Chatelier pyrometallurgical route.

$Al(OH)_3$ by CO_2 which was then filtered, dried, and claimed to pure Al_2O_3. This process was abandoned in favor of the Bayer process (Fig. 5).

3. Further development

At the beginning of the 20th century numerous leaching and recovery processes were proposed, some of them were put into practice, others had to wait for about half a century until they were applied, while others never developed beyond a pilot plant. When examining the patent literature at the beginning of this century it is remarkable to see the large variety of leaching agents proposed. In 1903, M. Malzac in France proposed the use of ammonia solutions for leaching sulfides of copper, nickel, and cobalt. At that time NH_3 was an expensive reagent obtained exclusively as a by-product of the coal industry. It became a cheap commercial reagent only after its synthesis 10 years later by Fritz Haber in Germany. Nitric acid was proposed by Kingsley in 1909 for leaching sulfide ores. Also, at that time HNO_3 was an expensive reagent obtained exclusively from the sodium nitrate deposits in Chile by treatment with concentrated H_2SO_4. It became relatively cheap only after the invention of Haber's process since nitric acid is made now exclusively by the oxidation of ammonia.

Towards the beginning of the 20th century, hydrometallurgy of copper received a particular attention. Oxide ores were leached on large scale by dilute sulfuric acid in Chile. Copper sulfides were also solubilized due to the presence of ferric ion which acted as an oxidizing agent. Instead of precipitating copper from leach solution by scrap iron in the usual way, electrowinning was used in Chile in 1912 (Habashi, 1998). The First World War (1914–1918) created a demand for the zinc for the manufacture of cartridge brass. Zinc for this purpose used to be obtained by the distillation of commercially available metal in Belgium and Germany from ore supplied by Australia. This situation inspired industry in North America to supply additional metal from ores that were not amenable to standard methods. At Trail in British Columbia and Anaconda in Montana, the processes for electrolytic zinc and the leaching of a large tonnage of ZnO by H_2SO_4 was introduced. The process is mainly based on a patent by L. Létrange in France issued in 1881 (Ingallis, 1936). Cadmium gradually emerged as an important by-product of this process.

4. Development during World War II

In the 1940s, the technology of uranium production was introduced in connection with the Manhattan Project—a US project aimed at producing an atomic bomb. Numerous new techniques became suddenly used on large scale. Some of these are, for example, the use of Na_2CO_3 as a leaching agent, ion exchange, solvent extraction, and many processes for precipitation from aqueous solutions. A large number of synthetic resins for use as ion exchangers and, similarly, a large number of organic solvents were specially synthesized for use as extractants for uranium. Separation of the rare earths by ion exchange replaced the tedious fractional crystallization from solution. Later on, solvent extraction replaced ion exchange and an industrial plant went into operation at Mountain Pass in USA producing high purity rare earths using about 1000 mixer-settlers (Habashi, 1993b).

5. Recent advances

In the 1950s, pressure hydrometallurgy was introduced for leaching sulfide concentrates (Sherritt-Gordon process), for laterites (Moa process) (Fig. 6), for tungsten ores, as well as for the direct precipitation of metals from solution. As a result of these developments some Canadian coins were produced for over 40 years using hydrometallurgical technique. Also, during this period, the recovery of uranium as a by-product of phosphate fertilizers was achieved by its extraction from phosphoric acid by organic solvents. Although this process was abandoned a few years later when important uranium deposits were discovered, now it has been revived in view of the expansion in nuclear energy programs.

In the late 1950s INCO built a semi-commercial plant for treating its low-grade pentlandite–pyrrhotite concentrate based on oxidation to eliminate the sulfur content as SO_2, controlled reduction of the oxides to form metallic nickel which was leached by ammonia (Fig. 7). The plant, however, was shut down a few years later, being uneconomical besides the pollution problems associated with the large tonnage of SO_2 emitted in the atmosphere. During the same period the mechanism of dissolution of sulfides was well established and the formation of elemental sulfur during the aqueous oxidation of sulfides became well known (Fig. 8). Work at the Mines Branch in Ottawa (known today as CANMET) demonstrated that pyrrhotite–penthandite concentrate could be treated in autoclaves at 120 °C under oxygen pressure to get nickel in solution while Fe_2O_3 and elemental sulfur remain in the residue (Fig. 9). The process was later applied by the Russians at the Norilsk plant for nickel recovery but unfortunately not by INCO to replace their ammonia process mentioned above.

In the 1960s, the role of bacteria in leaching became known and the widespread use of heap and in situ leaching for extracting copper was practiced.

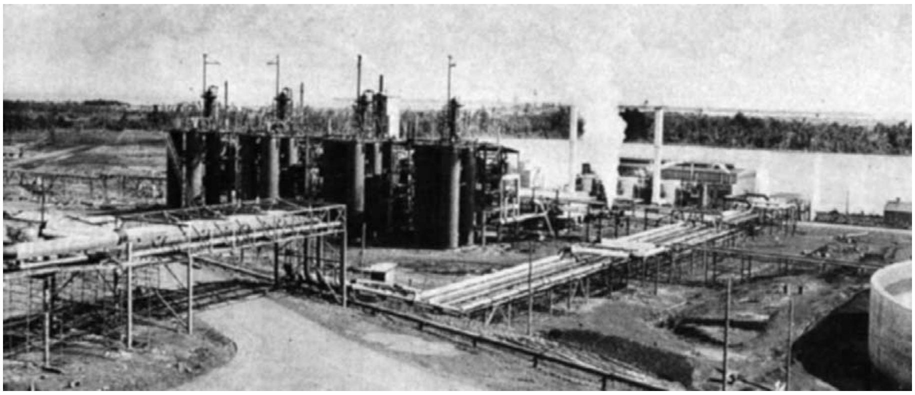

Fig. 6. Laterite pressure leaching plant in Cuba.

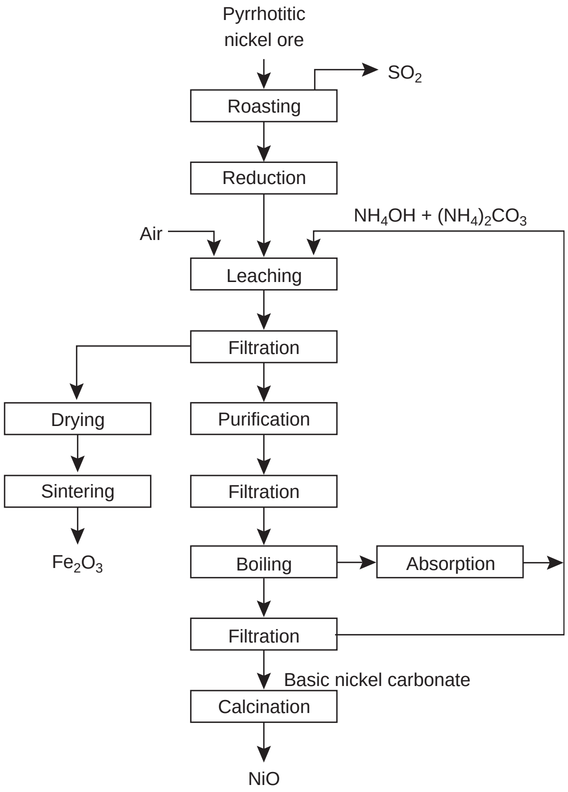

Fig. 7. Flow sheet of INCO ammonia leaching process that was shut down because of economic considerations and SO_2 emissions.

The same technique was later adopted for leaching low-grade uranium and gold ores. In the same period, as a result of de-classifying reports by the US Atomic Energy Commission, the application of organic solvents, mainly oximes, for extracting copper from solution was realized. At present, about 20% of the copper is now produced by hydrometallurgical technique (Habashi, 1999).

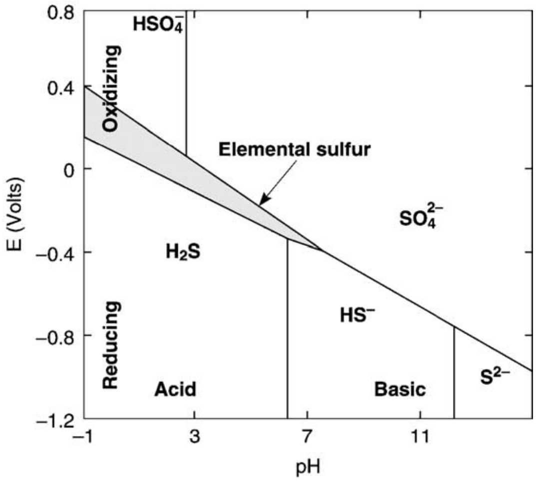

Fig. 8. Regions of stability of elemental sulfur at 100 °C.

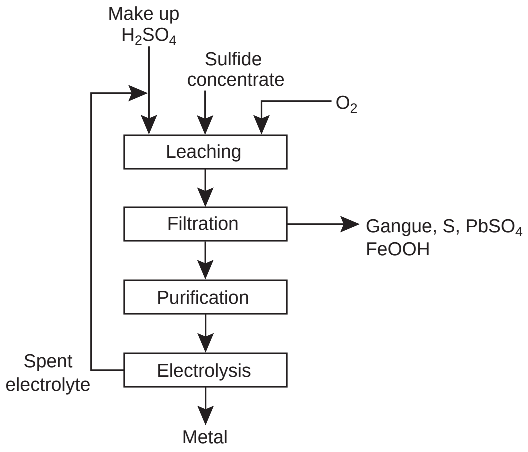

Fig. 9. Flow sheet showing the formation of elemental sulfur during the aqueous oxidation of sulfide concentrates.

In the 1970s the pressure leaching of zinc sulfide concentrates was applied industrially in Canada. The new process, which is essentially the same as that shown in Fig. 9, rendered the production of zinc a fully hydrometallurgical process, thus displacing the horizontal retort process based on roasting ZnS, reduction of ZnO by carbon, and distillation refining of metallic zinc developed in 1740 even after a number of modifications (Fig. 10). The process has also the advantage of liberating the zinc industry from the necessity of producing sulfuric acid. In the 1980s, the hydrometallurgy of gold dominated the scene: widespread application of activated charcoal for gold

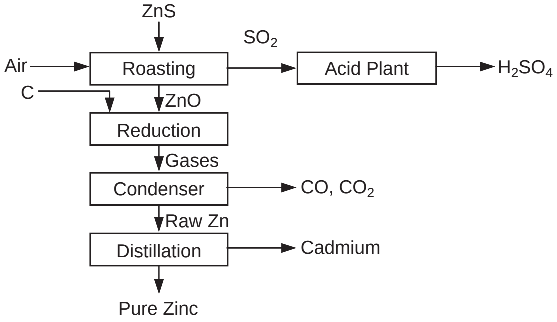

Fig. 10. The pyrometallurgical process for zinc production was replaced by the hydrometallurgical route shown in Fig. 9.

Table 1
Summary of historical development in hydrometallurgy

Early period	
7th century	The apparent transmutation of iron into copper by alchemists ($Cu^{2+}+Fe \rightarrow Cu+Fe^{2+}$)
8th century	The discovery of aqua regia by the Arab alchemist Jabir Ibn Hayyan (720–813 AD). This was the only known solvent for gold. Still used today in gold refining.
16th century	Heap leaching of copper-containing pyrite in the Harz mountains in Germany and in Río Tinto in Spain, and the precipitation of copper from the solutions by iron.
18th century	Production of potash for soap and glass industries by leaching ashes left after burning wood, e.g., in Quebec, where the clearing of forests was in progress on large scale.
Modern era	
1887	The invention of the cyanidation process, i.e., dissolution of gold from ores by a dilute sodium cyanide solution and the precipitation of gold from the solutions by zinc. The invention of Bayer's process: precipitation of crystalline $Al(OH)_3$ from sodium aluminate solution by seeding, followed in 1892 by his invention of pressure leaching of bauxite by NaOH solution.
1912	Recovery of copper from leach solution in Chile by electrolysis.
1916	The use of ammonium hydroxide for leaching native copper ore in Lake Superior District, and for malachite-azurite ore in Alaska. Development of the hydrometallurgical electrowinning zinc process at Trail and Anaconda. The recovery of cadmium as a by-product of the zinc hydrometallurgical process.
1924	Caron process for ammonia leaching of metallic nickel produced by reduction of laterites.
1927	Henglein process for pressure leaching of ZnS at high temperature in the presence of oxygen.
1930	Sullivan process for ambient leaching of copper sulfides by ferric chloride solution.
Development during World War II	
1940s	Development of the uranium technology in connection with the US Manhattan Project aimed at producing an atomic bomb. Introduction of sodium carbonate as a leaching agent for uranium, the widespread use of ion exchange and solvent extraction for uranium recovery, and the separation of the lanthanides by ion exchange.
Recent advances	
1950s	The application of pressure hydrometallurgy for leaching nickel sulfide ores and the precipitation of pure nickel from solution by hydrogen under pressure.
1960s	Discovery of the role played by microorganisms in leaching processes and the widespread use of heap and in situ leaching for extracting copper from low-grade material. The application of pressure leaching to a variety of raw materials, e.g., laterites, tungsten ores, uranium ores. The application of solvent extraction for copper.
1970s	Discovery of galvanic action in leaching sulfide minerals. Recovery of traces of uranium from waste leach solutions after copper precipitation with scrap iron. Pressure leaching of zinc sulfide concentrate in dilute H_2SO_4 at Trail and Timmins in Canada.
1980s	The hydrometallurgy of gold greatly advanced: widespread application of activated carbon technology, and aqueous oxidation of gold refractory ores.

adsorption and the aqueous oxidation of gold refractory ores were industrialized. Large autoclaves are now used for this purpose.

6. Epilogue

Hydrometallurgy is vigorously competing with old pyrometallurgical techniques, and in some cases it has displaced such processes. For example:

- The sodium carbonate sintering process for treating bauxite developed in 1855 was displaced by the pressure leaching process in 1892.
- The pyrometallurgical route for zinc was displaced in 1970s by pressure leaching of ZnS followed by electrowinning of zinc from the purified zinc sulfate solution.
- There is a good opportunity that nickel sulfides could be treated by hydrometallurgical route similar to the ZnS process—elemental sulfur being obtained instead of SO_2.
- The treatment of chalcopyrite concentrate by pressure leaching has been recently piloted by Phelps Dodge in Arizona as a new method competing with smelting.

Table 1 gives a summary of the historical development in hydrometallurgy.

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