

competing) role in the dressing of raw materials for pyrometallurgy. In addition to this, hydrometallurgy is capable of closing the gap between geology, mineralogy, mining engineering, processing methods, metallurgical techniques, materials science and industrial design in such a manner as to use more efficiently hydrometallurgy in primary production and other branches of the industry. Only the complex understanding of the entire problem can ensure in the final analysis economically efficient production of selected nonferrous metals whilst fulfilling all the environmental requirements. However, it should be stressed that some of the metals are produced on a large extent or completely by hydrometallurgy, for example, zinc, gold, uranium or aluminium oxide as the main intermediate product for the production of aluminium.

1.1. Copper hydrometallurgy

‘Hydro’ means water, ‘metallurgy’ is the production of metal, i.e. hydrometallurgy is therefore the science and method of aqueous methods of extracting metals from their ores. In recent years, non-water solutions have also been used for this purpose, Therefore, hydrometallurgy includes extraction methods in which metals, salts of metals or other compounds of metals are obtained by chemical reactions from aqueous or non-aqueous solutions. In the normal conditions, the hydrometallurgical processes are realised in the temperature range 25–250 °C, and the overall pressure may vary from several kilopascals (vacuum) to more than 5000 kPa.

Although many experts treat hydrometallurgy as a new production method, this is not the case. Table 1.2 shows the chronology of copper hydrometallurgy [7]. Already at the beginning of the 20th century, Greenawalt published a monograph concerned with the hydrometallurgy of copper [8].

Sulphide raw materials are the most widely used and the processing of these materials in the form of lean ores requires milling and flotation. These result in the formation of a finely ground concentrate representing the starting material. Of course, these materials cannot be charged into the shaft furnace because the furnace would be immediately clogged up and would prevent the flow of reaction gases and products. This is the reason for the development of horizontal furnaces, heated with fossil fuel. However, the result was the extremely unfavourable situation in the area of contamination of the atmosphere, high consumption of energy and excessive formation of flue ash. This is another reason

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Table 1.2. History of hydrometallurgy of copper

Copper source	Leaching system	Copper obtaining	Place	Year
Mining water	Leaching in mine	Fe cementation	Rio Tinto, Spain	1670
Poor ore	Leaching in mine	Fe cementation	Rio Tinto, Spain	1752
Mine water	Leaching in mine	Fe cementation	Strafford, USA	1820
Mine water	Leaching in mine	Fe cementation	Ducktown, US	1860
Ore	Calcine, heap	Fe cementation	Rio Tinto, Spain	1876
Mine water	Leaching in mine	Fe cementation	Butte, USA	1886
Oxide ore	Tank leaching	Fe cementation	Clifton, USA	1892
Flotation tailings	Pilot plant Roasting/leaching production	Fe cementation	Butte, USA	1912
Oxide ore	Tank leaching	Electrolysis	Ajo, USA	1915
Oxide ore	Tank leaching	Electrolysis	Chuquicamata, Chile	1915
Oxide flotation tailings	Vat leaching NH_3/CO_2	Precipitation of CuO by water steam	Kennecott, USA	1916
Poor ore	Vat leaching NH_3/CO_2	Precipitation of CuO by water steam	Clumet/Hecla, USA	1916
Oxide ore	Vat leaching H_2SO_4	Precipitation by SO_2	Anaconda, USA	1920
Mixed ore	Vat leaching $\text{Fe}_2(\text{SO}_4)_3$	Electrolysis	Inspiration, USA	1930
Oxide ore	Vat leaching H_2SO_4	Electrolysis	Panda, Zaire	1930
Mixed ore	Leaching+flotation	Fe cementation	Miami, USA	1934
Oxide ore	Dump leaching H_2SO_4	Solvent extraction, electrolysis	Ranch Bluebird, USA	1968
Oxide residues	Vat leaching H_2SO_4	Solvent extraction, electrolysis	Nchanga, Zambia	1974
Concentrate	Vat leaching NH_3 (Anaconda)	Solvent extraction, electrolysis	Anaconda, USA	1974
Concentrate	Vat leaching NH_3 (Anaconda)	Solvent extraction, electrolysis	Anaconda, USA	1974
Concentrate	Vat leaching NH_3 (Anaconda)	Precipitation by SO_2 , pilot plant	Tucson, USA	1974
Concentrate	Vat leaching $\text{H}_2\text{SO}_4+\text{HCl}$ (Duval®)	Electrolysis	Sierita, USA	1977
Concentrate	Leaching with $\text{CuCl}_2+\text{NaCl}+\text{NaBr}$ (Intec®)	Electrolysis	Australia	1994
Concentrate	Leaching with $\text{CuCl}_2+\text{NaCl}$ (Hydrocopper®)	Cu_2O precipitation	Pori, Finland	2001

for the examination of the possibilities of using hydrometallurgical methods of processing sulphide concentrates.

In the case of copper, special effort has also been made to find the optimum hydrometallurgical procedure but the results have not as yet been satisfactory. The most important obstacle is the fact that the starting material for the production of copper contains approximately 30% Cu which is only 50% of the zinc content in the starting zinc material produced extensively by hydrometallurgical procedure. The presence of other components in the raw materials for the production of copper (Fe, S, SiO₂ and other minor components) results in considerable problems in the hydrometallurgical production of copper.

At present, there is a competition in the production of copper between hydrometallurgy and pyrometallurgy in the following areas [9]:

Extraction of copper: using conventional melting–refining processes, 98–99% of copper is produced from the initial charge of the concentrate. This indicates that for the hydrometallurgical process of production of copper to be attractive for the industry, the yield must be very high. The copper melting plants are characterised by a higher degree of extraction by dumping of the slag with the iron/copper ratio of approximately 100. The leaching residue from the hydrometallurgical production of copper with this the ratio would be highly suitable. But unfortunately, even at almost 100% yield of copper from the concentrate it is very difficult to obtain such a ratio. The unwashed filter cake, containing 25% moisture and 60 g/l of copper, contains 1.5% of dissolved copper and also part of non-leached copper. This shows that it is imperative to innovate of the methods of production of dissolved copper from moist filter cakes, of course without the formation of other problems with the equilibrium of water in the system.

Problem with iron: the typical copper concentrate releases approximately 1 t of iron per every tonne of produced copper, which is transferred into the slag. If this slag from pyrometallurgical production of copper contains 40% of iron, it is transferred to the dump. However, the leaching residue (with 30% of ferrous jarosite [10–12]) is not acceptable for storage on dumps because the residue is considerably finer than the slag and, in addition to this, it also contains acid solutions leaching the heavy metals and having a detrimental effect on the environment.

Problems with sulphur: hydrometallurgy offers the optimum solution of the problem of sulphur because it prevents the formation

of any sulphur dioxide. At present, there are many hydrometallurgical processes of copper production accompanied by the formation of elemental sulphur. In other processes, it is necessary to consider the formation of sulphates which may be a saleable product, for example, ammonium sulphate, or may be dumped, for example, gypsum or the basic ferrous sulphate salts.

Extraction of noble metals: the copper concentrate usually contains large quantities of silver and gold. In the conventional melting processes, both these metals transfer in the process of refining into the anode sludge with a wide concentration range. In older metallurgical processes, the noble metals remain in diluted residue from which they are difficult to extract.

Toxic waste: toxic metals often found in the process of production of copper include arsenic, antimony, bismuth, lead, zinc, mercury and others. In conventional pyrometallurgy, these elements are transferred into dust and outgoing gases which in older plants contaminated the atmosphere and environment. In more advanced plants, these metals are produced to a certain extent for commercial purposes and partially are eliminated in the slag. However, these elements are still a source of contamination of the environment. In the hydrometallurgical methods, the elements do not penetrate into the atmosphere, but there is still a problem (although perhaps not so acute) with the potential contamination of water. It is therefore necessary to develop cleaning technologies or advanced prevention methods.

At least these and also other problems must be efficiently solved by the proposed hydrometallurgical method of production of copper, if this method is to be capable of competition. However, it is obvious that the changing composition of the raw materials often requires the application of methods which were not economical in the past but it has been shown gradually that these raw materials cannot be processed by any other method. At present, the amount of copper produced by hydrometallurgy increases on the worldwide scale and represents approximately 20% [13]. Figure 1.5 shows the development of production of copper by hydrometallurgy and, for comparison, also gives the development of the total production of copper already presented in Fig. 1.2.

As indicated by the above considerations, the production of copper by any method is a complicated and demanding process. Of course, this also relates to the hydrometallurgical method of production of copper which has its specific features which depend on the processed raw material and also on the type of extraction

Current situation in copper production

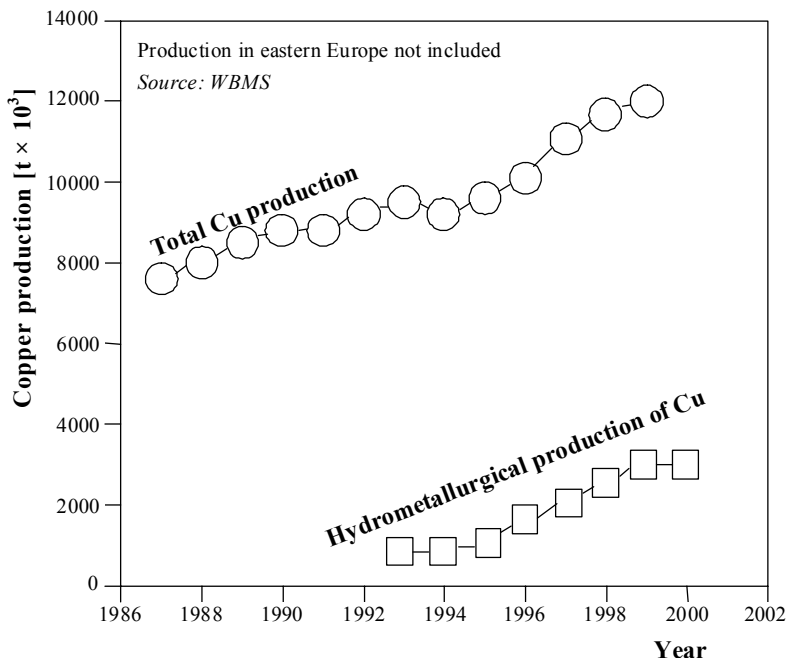


Fig. 1.5. Development of production of copper by hydrometallurgy [14].

agents used. In the individual stages of the hydrometallurgical production of copper, it is likely that the most important stage is the stage of the direct transfer of the metal into the solution, i.e. leaching, because it determines the rate and efficiency of transfer of metals into the solution and, consequently, a large part of the economic parameters of the entire process. The efficiency of the leaching process should be determined by examining the process from the thermodynamic aspect, i.e., to verify whether there are any agents which could interact together. Another important step is the determination of the kinetic conditions of the process, i.e. the duration and the type of conditions in which these reagents react, and also the reaction mechanism is important. On the basis of this information it will be then possible to propose and optimise the process of hydrometallurgical production.

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