

PRESSURE HYDROMETALLURGY UPDATE

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ABSTRACT

Pressure hydrometallurgy is over hundred years old. It is applied for leaching of ores or concentrates and for the precipitation of metals or oxides from leach solutions. Hydrothermal oxidation of sulfide concentrates has the enormous advantage of producing elemental sulfur, hence solving the SO₂ and sulfuric acid problems found in smelters. Precipitation of nickel and cobalt under hydrothermal conditions has the advantage of a compact plant but the disadvantage of producing ammonium sulfate as a co-product. In case of copper, precipitation takes place without the need of neutralizing the acid, which is a great advantage. Recent advances in the engineering aspects of pressure equipment design open the door widely for increased application.

INTRODUCTION

Pressure hydrometallurgy has its origin in experiments conducted in 1859 by the Russian chemist Nikolai Nikolayevitch Beketoff (1827-1911) while studying in Paris under Jean Baptiste Dumas (Table 1) [1]. He found that metallic silver can be precipitated from a silver nitrate solution when heated under hydrogen pressure. This work was continued later in Saint Petersburg by Vladimir Nikolayevitch Ipatieff (1867-1952) (Figure 1A) who in 1900 started a series of studies on numerous reactions under pressure. Among these was the precipitation of metals and their compounds from aqueous solutions by hydrogen. He spent the first few years designing a safe and reliable autoclave for these tests. Ipatieff's son joined later in this research. At about that time, also in Saint Petersburg, Karl Josef Bayer (1847-1904) (Figure 1B) studied in 1892 the leaching of bauxite by NaOH at 170°C and pressure in an autoclave to obtain sodium aluminate solution from which pure Al(OH)₃ could be precipitated by seeding.

Pressure hydrometallurgy expanded gradually resulting in introducing new processes and the construction of new and large equipment. It can be divided into two areas: leaching and precipitation (Figure 2).

PRESSURE LEACHING

Pressure leaching has been used industrially [2]:

- *In absence of oxygen.* For solubilizing aluminum from bauxite, tungsten from its ores, and nickel and cobalt from laterites. It has been also used to upgrade titanium oxide in ilmenite, tin oxide in cassiterite, and tungsten oxide in wolframite and scheelite.
- *In presence of oxygen.* For leaching uranium from its ores, zinc from its sulfide concentrates, liberating gold from pyrite and arsenopyrite and treatment of anodic slimes of copper electrolysis.

Recent development

The most recent developments are the following:

- Expansion in the production of synthetic rutile from ilmenite. This technology has numerous advantages over electric furnace reduction to produce pig iron and titanium slag. While titanium slag produced is usually 72-75% TiO₂, synthetic rutile is 92-95% TiO₂ [3]. Chlorine-consuming impurities can be completely eliminated. Hydrochloric acid needed for treatment of ilmenite can be readily regenerated from FeCl₂ by-product by oxyhydrolysis (Figure 3).
- A new 4-autoclave unit was added to the already existing four units in Moa, Cuba for leaching nickel and cobalt from laterites in vertical autoclaves using H₂SO₄.
- A plant in Western Australia for leaching nickel and cobalt from laterites in horizontal autoclaves using H₂SO₄. These autoclaves are the largest so far designed, being 5 meters diameter and 34 meters long (Figure 4) [3]

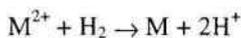
- Numerous plants for decomposing pyrite and arsenopyrite to liberate its gold content prior to cyanidation (Table 2). The largest of these is the one at Elko, Nevada, USA with four autoclaves each is 4.8 meters diameter and 30 meters long (Figure 5) [4]. Recent research has shown further that if the aqueous oxidation of such refractory gold ores is conducted in presence of hydrochloric acid, then gold and silver will be solubilized and recovered from solution by reduction with activated charcoal or any other reducing agent [5]. Thus, cyanidation process can be by-passed (Figure 6).
- The aqueous oxidation of zinc sulfide concentrates solved numerous problems associate with the roasting-leaching-electrowinning process. Since no ferrites are formed there is no need now to have another leaching circuit which generates jarosites and the zinc industry became independent of the necessity to fabricate and market H₂SO₄ (Figure 7).
- The catalytic action of coal during the aqueous oxidation of chalcopyrite [6] was confirmed on large scale by Dynatec (formerly Sherritt Gordon) in Canada [7].

PRECIPITATION UNDER PRESSURE

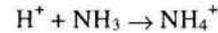
Precipitation of metals (mainly cobalt and nickel) and metal oxides (mainly UO₂) from aqueous solutions at high temperature and pressure can be conducted by hydrogen for cobalt and nickel or sulfur dioxide (for copper).

Precipitation by hydrogen

The early work on the precipitation of metals by hydrogen under pressure carried out in Saint Petersburg at the beginning of twentieth century was confirmed and expanded by Schaufelberger (Figure 8) in 1940's while at the Chemical Construction Corporation in New York and adopted on a commercial scale in Canada by Sherritt-Gordon Mines. Since 1960's all Canadian nickel currency is produced by this technology (Figure 9). For the reaction:

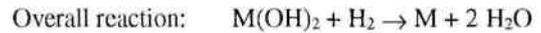
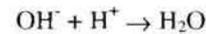
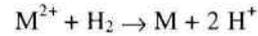
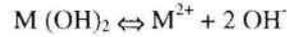


more metal will be deposited if the hydrogen ions are removed as soon as they are formed. For nickel, and cobalt, this is conveniently done by operating in ammoniacal medium:



Although this technology is competitive with electrowinning, it has the disadvantage of producing ammonium salts as a by-product.

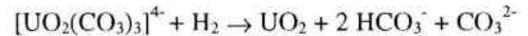
One way to partially overcome this problem is by reducing hydroxide slurries: the acid generated during reduction will be neutralized by the OH⁻ of the hydroxide:



For nickel and cobalt, it was found that this reaction takes place at 270°C which is a much higher temperature than normally used, but the product is of extremely fine particle size. But, to produce the hydroxide, the leach solution must be first neutralized by a suitable reagent.

In the case of copper, however, precipitation can take place in acid medium (Figure 10) [8]. This has been confirmed on numerous occasions by different researchers. This is a great advantage because the acid generated during precipitation can be recycled in the leaching step.

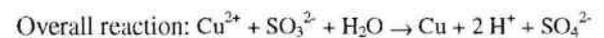
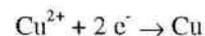
The precipitation of UO₂ from carbonate leach solution takes place according to:



At Kalna in the former Yugoslavia, the reaction was conducted at 150°C and 1,500 kPa in vertical autoclaves containing pellets of partly sintered UO₂ as catalyst. The precipitate builds up on the pellets and each tower is operated continuously until 10 tons of product had accumulated. The reduction end solution which contains only 3 to 5 mg/L uranium is recycled to the pressure leaching stage.

Precipitation by sulfur dioxide

On passing SO₂ into a solution of copper sulfate at room temperature, copper sulfite will precipitate. However, if precipitation is carried out at 150°C and 350 kPa, metallic copper is precipitated according to:



The drawback to this process is the low yield of copper and the corrosion problems due to the acidic environment. This process can be improved by adding an ammoniacal solution of ammonium sulfite instead of SO₂, i.e., neutralizing the acid as soon as formed. The following reaction takes place:



This results in complete precipitation of copper and has the advantage of operating under basic conditions thus eliminating corrosion problems. However, it has the inconvenience of producing ammonium sulfate. Another way of obtaining metallic copper from Cu²⁺-SO₂-H₂O system by hydrothermal methods involves the following steps:

- • Precipitation of the double salt Cu₂SO₃·(NH₄)₂SO₃ by passing SO₂ in ammoniacal CuSO₄ solution at ambient conditions until pH 3 is reached.
- • Slurrying the double salt obtained with water and heating in an autoclave at 150°C to precipitate metallic copper, provided the autoclave is vented to expell the SO₂ generated:



Overall reaction:



The process was tested only on a pilot scale and was abandoned apparently for economic reasons.

THE FUTURE

With the success in pressure leaching processes described above it is expected that future developments will be in the treatment of sulfides concentrates of copper and nickel in acid medium and under oxygen pressure to solubilize the metals and liberate elemental sulfur [9,10]. In this way, there will be no SO₂ emissions and more flexibility in making H₂SO₄. In addition, the copper industry should make use of the experience gained by the nickel industry in precipitating the metal by hydrogen under pressure. As already noted above, copper powder can be precipitated from acidic leaching solutions without the need of neutralizing the acid generated. Hence the acid can be recycled for leaching. The experience of compacting the powder in strips is already available in the nickel

industry. A flowsheet of such futuristic non-polluting process is shown in Figure 11.

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Table 1 - History of pressure hydrometallurgy

Type	Year	Investigator	Location	Reaction
Precipitation	1859	Nikolai N. Beketoff	France	$2 Ag^+ + H_2 \rightarrow 2 Ag + 2H^+$
	1900	Vladimir N. Ipatieff	Russia	$M^{2+} + H_2 \rightarrow M + 2 H^+$
	1903	G.D. Van Arsdale	USA	$Cu^{2+} + SO_2 + 2H_2O \rightarrow Cu + 4H^+ SO_4^{2-}$
	1909	A. Jumau	France	$CuSO_4 + (NH_4)_2SO_3 + 2 NH_3 + H_2O \rightarrow Cu + 2 (NH_4)_2SO_4$
	1955	Sherritt-Gordon	Canada	$[Ni(NH_3)_2]^{2+} + H_2 \rightarrow Ni + 2 NH_4^+$
	1965	Anaconda	USA	$Cu_2SO_3 \cdot (NH_4)_2SO_3 \rightarrow 2Cu + SO_2 + 2 NH_4^+ + SO_4^{2-}$
Leaching	1892	Karl Josef Bayer	Russia	$Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$
	1903	M. Malzac	France	$MS + 2 O_2 + n NH_3 \rightarrow [M(NH_3)_n]^{2+} + SO_4^{2-}$
	1927	F.A. Henglein	Germany	$ZnS + 2 O_2 \rightarrow Zn^{2+} + SO_4^{2-}$
	1940	Mines Branch	Canada	$UO_2 + 3 CO_3^{2-} + \frac{1}{2} O_2 + H_2O \rightarrow [UO_2(CO_3)_3]^{4-} + 2 OH^-$
	1952	H.A. Pray et al.	USA	Solubility of gases in water at high temperature and pressure
	1955	Sherritt-Gordon	Canada	$NiS + 2 O_2 + 2 NH_3 \rightarrow [Ni(NH_3)_2]^{2+} + SO_4^{2-}$
	1959	Freeport Nickel	USA	$NiO \text{ (in laterite)} + H_2SO_4 \rightarrow NiSO_4 + H_2O$
	1975	Gold industry	World- wide	$2 FeS_2 + 7\frac{1}{2} O_2 + 4 H_2O \rightarrow Fe_2O_3 + 4 SO_4^{2-} + 8 H^+$
	1980	Sherritt-Gordon	Canada	$ZnS + 2 H^+ + \frac{1}{2} O_2 \rightarrow Zn^{2+} + S + H_2O$

