Minerals Processing

Feature

Solvent Extraction in Hydrometallurgy

by Kathryn C. Sole*

This review focuses on some recent developments in base-metal hydrometallurgy that rely on solvent extraction technology to achieve high-purity products. As examples of modern flowsheets for the processing of copper, nickel, and zinc ores and concentrates, the Konkola, Bulong, Goro, and Skorpion flowsheets are discussed.

Solvent extraction (SX) is a process by which closely related elements or compounds in solution are separated based on the differences in partitioning of the species between two immiscible phases. In the SX process the species of interest is typically extracted from an aqueous phase into an organic phase. The two phases are mixed to facilitate mass transfer across the interface. The extracted species forms a complex with the aqueous-insoluble extractant and is transferred to the organic phase, leaving all other species in the aqueous phase, known as the raffinate. The immiscible phases are then allowed to separate and the loaded organic phase containing the element or compound of interest is treated for its recovery.

Copper Solvent Extraction

Commercial applications of SX in the copper industry include the production of high-purity copper by the combination of leaching in sulfuric acid, purification of the copper by SX, and recovery of the metal by electrowinning (EW).

Until recently, most applications of copper SX involved the upgrading and purification of the relatively dilute leach liquors that arise from the processing of dumps or heaps of low-grade, readily leached material. Such liquors typically contain between 1g/l-4g/l copper.

Sulfides have traditionally been treated by pyrometallurgical routes. However, increasingly stringent environmental legislation is forcing the consideration of other process routes. Bacterial leaching or pressure leaching can be considered for the hydrometallurgical recovery of copper from sulfide ores. Stirred-tank bacterial leaching of copper sulfide concentrates is approaching commercialisation, with demonstration plants currently under evaluation in Mexico and South America. There is also a growing acceptance of pressure leaching as advances are made in understanding leaching reactions, autoclave design and operation, and materials of construction.

Bacterial leaching of sulfide concentrates produces liquors that contain 20g/l-50g/l copper, while autoclave discharge liquors are as high as 50g/l-90g/l. The processing of leach liquors that contain high concentrations of copper presents, therefore, unique challenges in terms of designing flowsheets that can accommodate the substantial quantities of acid produced by the extraction reaction. A recently piloted flowsheet for the Konkola project in Zambia has made innovative use of SX to solve the problems of acid supply and the treatment of difficult ores.

The Konkola Deep deposit is a sulfide ore that is mined by underground methods. In the immediate vicinity is a large surface oxide deposit known as the Chingola refractory ore (CRO). This latter material, containing economically attractive quantities of copper, also contains substantial amounts of aluminium, magnesium, and calcium oxides and carbonates that consume acid on leaching. In the hydrometallurgical flowsheet proposed for this project, the sulfide material is concentrated by flotation to 40%-45% copper and then pressure leached in sulfuric acid under conditions that minimise the dissolution of iron and convert all the sulfide to sulfate. The autoclave discharge contains 60g/l copper. This is treated through an SX circuit to remove the copper, with the extraction of 50g/l copper generating about 80g/l sulfuric acid in the raffinate stream. This acid is then used to leach the CRO material. Copper is recovered from the atmospheric leach liquor in a second SX circuit. Both SX circuits are integrated with EW to produce a high-grade copper cathode product.

This flowsheet capitalises on the synergy that exists between the leaching of the sulfide copper concentrate (acid producing) and the oxide copper ore (acid consuming). Copper leached in the autoclave provides a convenient way of transferring acid from the sulfide circuit to the oxide circuit. Key to the

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Simplified hydrometallurgical flowsheet for the Konkola Expansion copper project.
concept is the specification of a copper SX circuit operating at a high extraction efficiency of copper, thereby providing a raffinate solution of sufficient acid strength to successfully leach the refractory copper-bearing micaceous CRO minerals. The first SX circuit focuses on maximising the copper extraction using a high extractant concentration and a high flowrate of the organic phase relative to the aqueous phase. The second SX circuit is responsible for generating a raffinate as low in copper as possible.

An integrated pilot plant producing 24kg/h of high purity cathode copper was successfully completed at the Anglo American Research Laboratories (AARL) in late 2000. A comparison of the technical, economic, and social implications of this flowsheet with an alternative pyrometallurgical process is now under evaluation, prior to a decision being made on the process of choice.

Nickel solvent extraction
Nickel occurs naturally in sulfide and laterite ores. Laterites are oxide/silicate ores containing 0.7%-3% nickel and often substantial amounts of magnesium, silica, and iron. Three nickel laterite plants commissioned in Western Australia during 1998/99 could treat low-grade laterite ores. These plants are Murrin-Murrin, Cawse, and Bulong, which all use pressure acid leaching (PAL) in sulfuric acid to solubilise the metals of interest, and all involve SX as one or more of the unit operations.

The Bulong nickel operation, located near Kalgoorlie, WA, was commissioned in 1998 and has a design capacity of 9000t/a nickel and 720t/a cobalt.

Following dissolution of the nickel-cobalt laterite ore at 4500kPa and 250°C, the autoclave discharge is flashed down and thickened. The leach liquor is processed directly for the recovery of the valuable metals. Iron, aluminium, and chromium are removed to levels of less than 1mg/l by precipitation with limestone. In the first of three SX operations, cobalt, copper, zinc, and manganese are separated from nickel by an acid extractant – Cyanex 272.

The raffinate from the cobalt SX circuit is refined by nickel SX to produce a high-grade cathode solution suitable for the production of nickel cathode. This extraction is carried out using versatic acid, a long-chain carboxylic acid, using pH control to limit the coextraction of magnesium and calcium. The nickel-containing strip liquor from this process has a purity greater than 99% with nickel cathode (99.5% purity) produced by EW.

As both the leaching and downstream processes were unproven technology at the time, Bulong’s selection of this flowsheet represented a high-risk venture, and subsequent plant performance has attracted much interest in the industry. Bulong has unfortunately been plagued by engineering and operational problems since start-up. It is believed, however, that the process chemistry is inherently sound, and that this flowsheet has many advantages over other nickel processes that use a series of precipitation and redissolution steps rather than treating the leach liquor directly.

In contrast to Bulong, the Goro process also treats a laterite leach liquor directly but uses a completely different approach to overcoming some limitations of existing nickel SX flowsheets.

The Goro process was developed by INCO for the treatment of a nickel laterite deposit in New Caledonia. The flowsheet involves the coextraction of nickel and cobalt by SX with the extractant Cyanex 301, followed by their separation in a chloride medium by SX using an amine extractant.

The lateritic ore is acid leached under pressure at 270°C. The clarified autoclave discharge liquor is partially neutralised to precipitate aluminium, chromium(III), silica, copper, and iron. Nickel, cobalt, and zinc are then quantitatively and selectively extracted from other metals in solution by Cyanex 301. This extractant has the capability of extracting nickel and cobalt selectively from manganese, while also being very selective over magnesium and calcium. Cyanex 301 cannot be stripped with sulfuric acid, so hydrochloric acid is used.

The downstream separation of nickel and cobalt uses an anion exchanger, such as a
tertiary amine extractant. This technology is well established and has been used in refining applications for many years. Nickel is recovered by pyrohydrolysis as NiO, regenerating HCl for recycle to the Cyanex 301 strip circuit, while cobalt is recovered as a carbonate salt.

An integrated, on-site demonstration plant treating 12t/d of dry ore has been operating since September 1999. INCO recently announced the decision to go ahead with the development of this novel flowsheet, at an estimated cost of US$1.4 billion. This project will be the first commercial application of Cyanex 301. Furthermore, the contacting equipment to be used for the Cyanex 301 SX circuit will be pulsed columns, rather than the traditional mixer-settler equipment currently used in most base-metal plants. The column configuration offers advantages in terms of reduced footprint, reduced organic inventory, control of the atmosphere (in a system where it is important to avoid oxidation), reduced volatile losses, and improved safety. Goro’s construction starts early in 2002, with commissioning expected in 2004. On completion, Goro is predicted to become one of the largest and most cost-effective nickel projects in the world.

Zinc solvent extraction

In primary zinc production, conventional feed materials are amenable to preconcentration, giving a zinc sulfide concentrate that can be treated pyrometallurgically. The Skorpion project in Namibia is an interesting example of the use of leaching and SX/EW to recover zinc from an ore previously considered untreatable from both the processing and economic points of view.

The Skorpion ore is a low-grade silicate, containing 10%-40% zinc and 26% silicon. Following an atmospheric leach in sulfuric acid, iron, aluminum, and silica are rejected from the leach liquor by precipitation. Zinc is then purified by SX with di(2-ethylhexyl) phosphoric acid (D2EHPA), enabling special high-grade zinc to be electrowon. Zinc losses to the leach residue are minimised by reacidifying the thickener underflow and recycling the filtered liquor to the comminution circuit. Impurities are prevented from accumulating in this stream by cementation with zinc dust. To maintain the water balance in the circuit, the wash water (secondary filtrate) is bled from the circuit and the contained zinc reprecipitated as a basic sulfate, \((\text{ZnO})_3\text{ZnSO}_4\). This is recycled to the main circuit and reused for neutralisation.

Sulfuric acid leaching of silicates yields silicic acid \((\text{Si(OH})_4)\) in solution which, if treated incorrectly, may form silica gel that impairs solid-liquid separation. A key component in the success of this process is the control of the leaching and neutralisation conditions (pH, temperature, and residence time) to efficiently reject silica from the circuit.

Zinc EW typically requires an extremely pure electrolyte containing 150g/l zinc. Because of the low zinc content of this feed material, leaching conditions that produce a high-grade liquor cause unacceptably high soluble losses of zinc in the subsequent filtration step. The Skorpion leach liquor also contains significant quantities of fluoride and chloride that are detrimental to zinc EW.

The selection of SX as the purification route serves several purposes. Leaching can be carried out so that a fairly dilute liquor is obtained, thereby minimising soluble losses of the valuable metal and avoiding silica gel formation. In addition to rejecting other base-metal impurities, the halides can be effectively rejected from the circuit by appropriate control of the SX operating conditions. The selectivity of D2EHPA for zinc over calcium eliminates gypsum precipitation in the EW circuit, which is a major contributor to cellhouse downtime in conventional circuits.

Integrated piloting of this flowsheet was successfully carried out at AARL during early 2000, producing 100kg/d of special high-grade zinc. The advanced engineering of the full-scale plant is now under way. Construction started in May 2001, and the first metal is expected in December 2002. Skorpion will be the first plant to use direct SX on the mainstream leach liquor in primary zinc processing and is likely to become one of the lowest cost zinc producers. Almost all base metals can today be recovered or removed as impurities by SX. In modern applications, the need for higher purity products and improved environmental operating conditions have led SX to replace many of the more traditional processing routes. This trend is likely to continue as more complex and lower grade materials are processed.

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