The technology is increasingly being used by the minerals industry to separate, purify and concentrate metals such as nickel, cobalt, copper, zinc, uranium and rare earths. John Chadwick looks at some of the latest developments.

Gustavo Diaz and colleagues at Tecnicas Reunidas point out that “in recent years there has been considerable development of hydrometallurgical processes for copper extraction applying SX combined with electrowinning for the production of high-grade electrolytic copper. As a result, above 20% of world copper production is currently achieved from heap leaching–SX operations of oxide copper ores.

Solvent extraction of zinc has been successfully applied on several industrial plants using the ZINCEX™ technology. Besides, this technology is gaining more popularity with the latest.”

“The low capital and operating costs of SX plants together with the easy operation and the production of top quality electrolytic metals close to the mine site make the economics of the SX processes very attractive, being suitable and feasible in the range of small to medium capacities, where conventional smelting process is not applicable.

“The mining and metallurgical industries are now in the best position to afford projects with mixed or polymetallic copper and zinc bearing materials.

“There are a number of key aspects to be considered in the hydrometallurgical processing of mixed copper and zinc primary and secondary materials:

- Very frequently, those are complex materials and the main metals are distributed as compounds of diverse nature and consequently are very difficult to separate by physical treatment. This characteristic has driven the need to use whole leaching for maximum copper and zinc metals extraction into solution.

- Whole leaching releases valuable copper and zinc to the pregnant solution but also large quantities of other undesirable components like iron, arsenic, cadmium, etc.

- Application of SX techniques for copper and zinc recovery from pregnant leaching solutions containing high levels of impurities will require tailored solutions to get the optimum yields applying the best process conditions and design parameters.

- Other relevant factors like geographical location and available infrastructures, raw materials grade and reserves/availability, acid consumption, power supply and cost, local environmental regulations for disposal, etc, have to be carefully analysed.”

Tecnicas Reunidas designed an integrated flowsheet for the best process performance at minimum cost. The work was done for an ore containing 0.4% Cu, 1.6% Zn, 15% Fe, 21% Ca, 0.5% Mg, 2.5% Al and 50% SiO2.

Nominal production was to be 12,000 t/y electrolytic copper Grade A and 50,000 t/y SHG zinc cathodes.

Comminution achieves a size of 100% minus 20 mm. The ore passes to agglomeration and then is sent to heap leaching. Sulphuric acid is added to keep the pH optimum. The pregnant solution from heap leaching is subjected first to copper SX and EW to recover the copper and second to zinc SX and EW to recover the zinc after removal of some impurities such as iron, silica, etc. The acidic raffinate solution leaving SX is recycled to the leaching operations.

A series of process flowsheet were designed and developed, and a comparative analysis was performed to choose the best process configuration. In the first case, after comminution the Cu/Zn ore is placed on the heap and irrigated with fresh acid and recycled acid raffinate to extract copper and zinc, which are released to the pregnant solution together with some impurities. Then, the impurities (mainly iron) are rejected and the solution goes first to Zn SX/EW and second zinc acid raffinate passes to Cu SX/EW. In the second,
the Cu/Zn ore is leached in the heaps and the copper and zinc are extracted into the pregnant solution. In this case, the Zn SX/EW circuit and the Cu SX/EW circuit are set in parallel. In the third case copper and zinc are extracted into the pregnant solution. Then, the copper is first recovered in the Cu Zn-SX circuit and the raffinate goes to iron removal stage and next to the Zn SX/EW circuit for zinc recovery.

“Aiming to choose the best process option, every alternative was developed at a conceptual level including:

- Design of block diagrams and integration of the main process stages closing the global circuit in a coherent manner
- Gross mass balance to quantify the main streams and the principal components, e.g. copper, zinc, iron, acidity, etc, and also temperature
- Definition and calculation of some unit parameters in order to analyse and compare the three process flowsheet. The selected unit parameters were: consumables, energy, and generation of wastes and effluents.”

In cases 1 and 2, a certain amount of copper may be co-precipitated together with iron leading to some copper losses. Copper extraction in 1 has to be done under acidic conditions, which can affect the selectivity of the organic extractant. Losses in liquid retained in heap leaching may be increased in 2 when dealing with more concentrated solutions.

The authors conclude that Case 3 offers “smoother and simpler operating conditions and higher efficiency, as well as, minimum reagents and utilities consumption.”

Reagent advances
Cytec Industries has developed a simulation software package to assist operators and engineering companies who wish to optimise and design solvent extraction circuits for CYANEX 272. These new modelling capabilities are expected to significantly reduce the amount of laboratory work required by the designer while increasing confidence in the ability to achieve the desired metal separations. This new in-house capability allows evaluation of the expected impact of various changes to the PLS metal composition, reagent concentration, O/A ratios, pH profile, and overall circuit configuration/layout.

Cytec’s modelling and predictive capabilities associated with CYANEX 272 have substantially advanced. The company says “the tool and skills that have been developed will continue to advance as Cytec continues to invest in expanding modelling capabilities.” The program has been used successfully to evaluate operational parameters at existing operations and is being used to assist in multiple design scenarios.

The software can aid in the design of plants by modelling the performance under multiple staging scenarios to find the optimal configuration and potentially minimising the overall staging requirements. It also can be used to optimise existing operations by providing quick guidance to reach the optimal O/A ratio, pH profile, or reagent concentration thus maximising metal transfer while minimising impurity transfer. Cytec believes there is substantial opportunity to improve the economic performance of both existing and future operations. “The modelling capabilities should allow optimisation of CYANEX 272 circuits while allowing easy economic assessment of the benefits of cobalt SX.”

Cytec has developed a new range of formulations with enhanced stability to oxidation. The company says “the ACORGA OR series of extractants provide excellent chemical stability under high oxidation-reduction potential (ORP) while maintaining the desired physical and metallurgical characteristics. Prior to the development of ACORGA OR there has been no copper SX formulations designed to protect against oxidative degradation.”
Extensive test work and pilot plant trials were run under oxidising conditions to evaluate the performance of one of the formulations, ACORGA OR25, to oxidative degradation.

To prevent oxidation of the organic phase due to high ORP values, the Fe2+/Mn ratio in the electrolyte and ORP should be monitored and controlled. During plant upset conditions, steps should be taken to quickly bring the electrolyte ORP back under control.

The use of Cytec’s oxidation resistant formulations can provide an extra level of security to address temporary permanganate issues or other conditions resulting in oxidation (short term or ongoing).

It has developed a new series of reagents (The ACORGA NR Series) for operations with concerns over nitration. These new reagents can be formulated at varying strengths to maximise copper transfer (based on the PLS copper and acid) while maintaining chemical stability under nitrating conditions. Historically plants with high nitrate in their PLS solutions (20 – 40 g/litre) or concerns over nitration risk, have elected to use ketoxime (due to its high hydrolytic stability). The use of ketoxime has the disadvantages of reduced copper transfer, copper: iron selectivity, and low copper recovery when the PLS copper grade is high or the pH is low. Often the ketoxime is too weak of a formulation for efficient SX operation.

Cytec has also identified a number of copper SX operations have been identified which contain significant molybdenum values within the leach liquor. At some of these operations the molybdenum is present due to the continuous leaching of molybdenum oxides within the ore; while at others, the Mo is present from other sources such as scrub liquors from smelting operations. Due to large solution inventories, the molybdenum value within the solutions can be substantial. The actual Mo concentration within the leach solution can vary greatly dependent on the acidity of the leach liquor (i.e. Mo can precipitate out within the heaps/dumps dependant on the acidity used).

So, the company has developed a new modified phosphonic acid reagent formulation (CYANEX® 600) for extracting and purifying molybdenum from these leach liquors. A common problem for recovering molybdenum from these streams in the past has been finding a formulation which would have the right selectivity and kinetic properties to allow the low Mo concentration to be efficiently extracted without altering the standard copper SX/EW process.

The formulation’s unique properties make it possible to selectively remove molybdenum while leaving the majority of the impurity elements behind in the leach liquor. Ideally the recovery process would take place downstream of the standard copper SX plant, removing the molybdenum from the acidified copper raffinate stream prior to further leaching.

Last year Cognis, now part of BASF Mining Chemicals, was granted the US patent for its Split Circuit technology that is particularly applicable to agitation leach-SX of copper ores. The Split Circuit configuration effectively splits the leached solution into high and low grade streams, which in turn are treated separately in the SX process.

The raffinate produced from the high grade solution is returned to the leaching step to precipitate out within the heaps/dumps dependant on the acidity used.

Bateman Settler and BPC installation track record 1998-2010

<table>
<thead>
<tr>
<th>Project</th>
<th>Client</th>
<th>Commodity</th>
<th>Equipment type</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voeise Bay</td>
<td>Vale-Inco</td>
<td>Ni/Co/Cu</td>
<td>Bateman Settler</td>
<td>On-going</td>
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<tr>
<td>Tres Valles</td>
<td>Vale</td>
<td>Cu (20,000t/y)</td>
<td>Bateman Settler</td>
<td>2010</td>
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<td>Nippin N-Chio (demo plant)</td>
<td>NMM</td>
<td>Cu, Ag</td>
<td>Bateman Settler</td>
<td>2009</td>
</tr>
<tr>
<td>Goro</td>
<td>Vale Inco</td>
<td>Ni (55,000t/y), Co (4,500 t/y)</td>
<td>Bateman Settler and 2 BPCs</td>
<td>2009</td>
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<td>Sumitomo</td>
<td></td>
<td>Bateman Settler</td>
<td>2008</td>
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<td>Hoomonoy</td>
<td>UraniumOne</td>
<td>U (450t/y, U3O8 equivalent)</td>
<td>Bateman Settler and 2 BPCs</td>
<td>2008</td>
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<td>Codelco</td>
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<td>Bateman Settler</td>
<td>2008</td>
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<tr>
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<td>UraniumOne</td>
<td>U</td>
<td>Bateman Settler and 2 BPCs</td>
<td>2007</td>
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<tr>
<td>Piedras Verdes</td>
<td>Frontera</td>
<td>Cu (30,000t/y)</td>
<td>Bateman Settler</td>
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<td>Demo plant in Japan</td>
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<td>BPC</td>
<td>2007</td>
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<td>Timna (demo plant)</td>
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<td>Cu</td>
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<td>MDLL</td>
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<td>Weng Fu</td>
<td>Phosphoric Acid</td>
<td>Bateman Settler and 2 BPCs</td>
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<tr>
<td>Olympic Dam</td>
<td>BHPB</td>
<td>Uranium</td>
<td>2 BPCs</td>
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<td>Penoles (Demo plant)</td>
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<td>Mt Gordon</td>
<td>Western Metals</td>
<td>Cu</td>
<td>Bateman Settler</td>
<td>1998</td>
</tr>
</tbody>
</table>
fully re-use the acid that has been generated. Raffinate produced from the low grade leach solution, lower in concentration of both metal species and acid than would conventionally be the case, is used in the washing activity, and a portion is ultimately bled from the circuit as the soluble loss fraction.

In this way, the configuration minimises soluble losses. Other operating improvements are realised with lower neutralisation costs prior to tailings disposal.

Cognis says “the economic benefits of the split circuit are clearly apparent once a detailed mass balance of both the metal species and acid is performed. The relative simplicity of the concept means that incorporation into an existing flowsheet can be done easily and with a minimum of capital outlay.

“The split circuit provides operational flexibility and, in areas of the world where the cost of acid and neutralizing agent are high, the operating cost benefits of the concept can be substantial.”

Bateman Litwin’s Advanced Technologies Division provides state-of-the-art SX know-how and technologies. It says the Bateman Settler™ “with its advanced design and enhanced efficiency provides many advantages compared to conventional settlers used in SX circuits.” These include high process efficiency with low organic losses, compact layout and short construction time, low capital cost and ease of operation and maintenance:

- Metals processed include copper, cobalt, nickel, zinc and uranium
- PLS flow rate of up to 1,750 m³/h per train
- PLS grades from less than 1 g/litre up to 30 g/litre
- Organic strengths up to 30% v/v extractant
- Organic losses as low as 20 ppm
- Fully automated interface control system.

The Bateman Pulsed Column (BPC) is an efficient cost-effective contactor which enhances SX during extraction, stripping and scrubbing or washing processes. It is a continuous and multi-stage extraction process that can handle liquids with suspended solids. The company says these columns can “enhance most industrial SX processes, particularly those with a fast rate of mass transfer.”

**Electrolyte filters**

Outotec is a leading SX/EW technology supplier with an extensive track record in building complete plants. Larox which was recently acquired by Outotec is well known for efficient and reliable filtration process equipment. The combined companies now offer Outotec Larox DM electrolyte filters which are specially designed for excellent removal of entrained organic and suspended solids from electrolyte, using the well proven dual media concept. The Outotec Larox DM electrolyte filter package can be delivered as an integral part of Outotec’s SX/EW technology delivery or as a standalone solution to engineering companies and end users.

Adsorption filtration using the well proven dual media concept reduces entrained organic and particulate concentrations to a level of a few ppm. Production capacities increase, as does the quality of cathode products.

The filters use two separate layers of media for coalescing and for filtration. The upper media layer provides for organic removal while the second layer filters particulates in the electrolyte.

Outotec says “low electrical energy consumption is a cost-saving benefit, as the adsorption filtration technique uses low...”
pumping pressures compared to alternate solutions utilising flotation.

“Automatic (PLC) control of the electrolyte filtration and media cleaning steps at the end of each filtration cycle ensures maximum filtration time in subsequent cycles. Outotec Larox DM electrolyte filters are delivered as an automated operational filtration system which can be fully integrated to any SX/EW solution package.” The package will contain filter vessels, air and liquid internal distributors, filter media, piping and valve skid, blower skid, and automation & instrumentation. A maintenance platform is optional.

“With no moving parts, the media cleaning system ensures maximum media lifetimes. Typically the anthracite media is replaced every 24 months when combined with Outotec’s proven SX process technology.”

Using lean electrolyte for backwashing and returning it to the After Settler after holding in a backwash collection tank (see flow schematic) means these filters do not reduce the capacity of SX production. Filter flow rates as high as 275 m³/h can be consistently handled by a single unit (5.2 m diameter), greatly simplifying the process.

Typically, multiple units are installed in parallel for flexibility and expandability to economically accommodate growing plant capacity requirements.

Research and development

CSIROs’ SX team working within Australia’s Parker Centre for Integrated Hydrometallurgical Solutions has developed and demonstrated novel SX processes for metal separation and tools to enable enhanced diagnosis and remediation of phase separation problems.

Using customised combinations of commercially available organic reagents to improve the metal selectivity of an SX system is an alternative to the expensive option of developing new extractants. The SX team has developed a number of synergistic SX (SSX) techniques.

The CSIRO SX team has developed SSX systems which are currently of great interest to industry. One of these enables the recovery of cobalt from leach solutions whilst rejecting impurities such as manganese, magnesium and calcium without the need for complicated intermediate precipitation and re-leach steps. This patented direct SX (DSX) system uses a combination of LIX63 and Versatic 10. In another SSX system, TBP is added to enhance the stripping and extraction kinetics of nickel so that both nickel and cobalt can be separated from manganese, magnesium and calcium without intermediate precipitation and re-leach steps.

Understanding how operating conditions affect the stability of expensive organic reagents and controlling conditions to minimise reagent degradation is an important aspect of running
successful SX processes. Similarly, phase separation issues in SX circuits can be problematic and originate from many different factors. The team offers significant expertise in the techniques and tools available to solve such issues – from organic stability studies, organic and cruds analysis to the assessment of physical issues such as in-situ droplet size measurement, phase disengagement time, interfacial tension and entrainment analysis.

In addition to desirable metal separation properties, SSX systems also need to exhibit sufficient chemical robustness under expected operating conditions. Full SX circuit continuous studies over several months are routinely performed under proposed operating conditions to optimise operating conditions, assess reagent stability and to gauge the effect of any degradation products on the chemical and physical properties of the resulting organic solution.

Dr Dave Robinson, Research Program Leader: Base Metal Hydrometallurgy told *IM* of a multi-sponsor SX project currently underway (SXT2) that has developed and applied the following tools:

- Velocity probes for determination of fluid velocities within both the aqueous and organic phases in laboratory or operational settlers which has been used to determine flow patterns in real settlers, evaluate alternative fence designs for improved residence time distributions, increased coalescence, reduced pressure drop all leading to implementation of changes that have led to as much as an 85% reduction in entrainment losses in sponsors settlers
- Droplet size probe for use in model and real mixers to evaluate the droplet size distribution generated under differing operating conditions (e.g. phase ratio, flow rates, organic or aqueous composition) with varying impellers and various at differing rpm
- A CSIRO Lewis Cell for independent evaluation of relative kinetics of mass transfer and direct comparison of alternate reagents, alternate operating conditions, effect of modifiers or competing elements
- Tools for on-line entrainment determination of both aqueous in organic and organic in aqueous which are being tested for potential operational use and commercialisation
- Computational and physical modelling capabilities able to evaluate and establish principles of design for improved mixing ad settling in new or modified contactors.

CSIRO believes the Parker Centre pilot plant Murdoch University is a unique facility. It is the largest pilot plant in the Southern Hemisphere and certainly the largest facility located in a public sector research/academic institution. The team is highlighting its availability and the EW scientific expertise and capability within the Parker Centre to assist industry in addressing EW technology issues.

The pilot plant was originally constructed by the BHP Billiton Base Metals Technology Group. The EW cell is based on the cross sectional dimensions of the Escondida mine (Chile) sulphide tankhouse. It is an 800 litre cell that can accommodate five full-scale electrodes at ‘standard’ separation distance. This is what makes this facility unique it can replicate full scale industrial process conditions.

**Safety audit**

CSIRO notes “the ubiquitous problem of acid mist is associated with health, safety, environmental, efficiency and operating cost issues.” It is involved in a project “to establish the important features of acids mist generation, quantify the contribution of critical operational factors and pave the way to safer, more efficient and lower cost operation of EW facilities.”

Graham Hearn, Technical Director of Wolfson Electrostatics says: “After the catastrophic SX fires of a decade ago, static electricity - the insidious by-product of the SX process is now well understood and can
be designed out of new plants and controlled in existing ones.

“As in most industrial fires, the ignition source cannot be identified entirely beyond doubt. However from subsequent detailed investigations of the incidents in SX it is likely that the ignition source was due to electrostatic discharges igniting the organic solvent under normal operating conditions. Consequently, the ignition of solvent below its flashpoint generated huge concerns within the industry particularly with regard to static electricity.

“In the SX process the solvent is used in large quantities and is conveyed between storage tanks, settler tanks and other process vessels by a network of pipes. This creates an electrostatic charge separation between the liquid and the pipe wall. The pipes may vary in material of construction; often being a mixture of metal and plastic within the same plant. Materials such as high-density polyethylene (HDPE) and fibreglass (GRP, FRP) are electrical insulators allowing static charge to accumulate.”

It must be assumed that pipes and tanks in SX plants containing organic solvent and air may produce a flammable atmosphere capable of ignition by electrostatic discharge at normal operating temperatures. Good plant design, however, can greatly reduce this risk by minimising both the production of flammable atmospheres and static charge generation. In summary, SX plants which have a high risk of electrostatic ignition and fire are those which operate under the following conditions:

- Low conductivity organic solvent (below 200 pS/m)
- Relatively low-flashpoint solvent (more volatile solvents are easier to ignite even in mist or froth form)
- High temperatures within pipelines
- Gravity flow (allowing air to be present within the pipe)
- High solvent flow velocity (well in excess of 2 m/s)
- Turbulent flow and splashing due to pipeline constrictions etc.
- Electrically insulating pipework such as HDPE and GRP/FRP
- Ungrounded metal components in or on the plastic pipeline.

Hearn recommends electrostatic safety audits of plants to establish the degree of static hazard present. During the audit the following actions should be performed:

1. Familiarisation with the plant and process and identification of risk areas. The principle risk areas are envisaged as being plastic pipelines carrying organic solvents but the audit should also encompass mixer-settlers, holding/storage tanks and other areas identified as potentially hazardous
2. Measurements on process fluids and pipework; such measurements include quantifying electrostatic potentials, electrical conductivity of organic solvents starting with virgin diluent and then at points throughout the process, electrical properties of pipework, build up of deposits (jarosite), etc
3. Inspection of grounding of metal plant and other conductors
4. Electrostatic hazards from personnel (plant operators, maintenance workers etc)
5. Identification of electrostatic hazards from sources other than those above (as appropriate).

“If a combination of low solvent conductivity and high potentials are observed, it must be concluded that an electrostatic ignition hazard may exist,” he concludes. IM

References

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