APPLICATIONS FOR BIOGENIC SULPHIDE REAGENT FOR COPPER RECOVERY IN COPPER AND GOLD HYDROMETALLURGICAL OPERATIONS

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ABSTRACT

Sulphide is an effective reagent in the precipitation of base metals for both metal winning and environmental control. BioteQ Environmental Technologies Inc. has successfully demonstrated in industrial plants that biogenic sulphide reagent can be generated cost effectively and used to win metals such as copper, zinc and nickel from low-grade leach solutions and wastewater. Commercial plants in which sulphide reagent is used to produce high quality treated effluents for discharge directly to the environment are also in operation. Operations utilizing biogenic sulphide reagent for copper recovery from acid drainage and low grade leach solutions are discussed, including those at Bisbee, Arizona, commissioned in 2004 and at the Dexing mine in China, scheduled for commissioning in 2007. In addition, a new application of BioteQ's technology for the recovery of copper from gold-cyanide solutions, and the regeneration of cyanide, utilizing biogenic sulphide in place of chemical sulphide reagents in the SART process is described.

INTRODUCTION

Efficient and environmentally acceptable technologies for water treatment in the mining industry have become more important to improve environmental and process performance and to reduce costs, particularly those related to long term liabilities. This is important in the copper mining industry where the impacts of large scale open pit and underground mining and processing activities can result in a number of water treatment requirements to ensure a supply of water suitable for process use and to prevent contamination of rivers and lakes caused by the discharge of contaminated process waters. Historically, metal contamination has been the principal concern but the discharge of sulphate at concentrations well below that possible from conventional lime plants has recently become a requirement in several jurisdictions.

BioteQ originally developed water treatment technology with which metals could be recovered from waste water streams, such as acid mine drainage, using biogenic sulphide generated from the reduction of sulphate contained in the water. The company now generates sulphide reagent by the much more cost-effective process of reducing elemental sulphur. The use of sulphide reagent lies at the heart of BioteQ's technology and know-how used in its commercial plants to treat water not only for producing clean water for environmental discharge but also for selective metal recovery from both low grade and higher grade solutions [1-3]. More recently, the generation of sulphide reagent at lower costs by reducing sulphur has attracted the interest of other sectors within the copper mining industry, notably for the recovery of copper and cyanide in the processing of gold-copper ores and in the separation by flotation of copper and molybdenum. In all cases, biogenic sulphide reagent can be used to replace chemical reagents such as sodium hydrosulphide. Biogenic sulphide, produced on demand at site, results in a superior metal sulphide product and offers significant cost savings and provides the additional benefit of improved safety due to the elimination of the transportation, handling and storage required for chemical sulphide reagents.

SULPHIDE TECHNOLOGY FOR COPPER RECOVERY

Generation of Biogenic Sulphide and Process Flowsheets

Sulphide reagents are widely used in mineral processing, hydrometallurgical operations and water treatment. The precipitation of metals using sulphide is fast, efficient and can produce barren solutions and effluents with very low concentrations of residual metals. The BioSulphide® technology used by BioteQ to generate biogenic sulphide reagent by the reduction of elemental sulphur at a lower cost than the chemical sulphide reagents has been described elsewhere [1]. In some smaller BioteQ plants, currently operating or under construction, NaHS is used for selective metal precipitation and recovery in a process known as ChemSulphide™.

A typical flowsheet utilizing the biogenic generation of sulphide reagent as hydrogen sulphide to precipitate metals selectively contained in the feed water is shown in Figure 1.

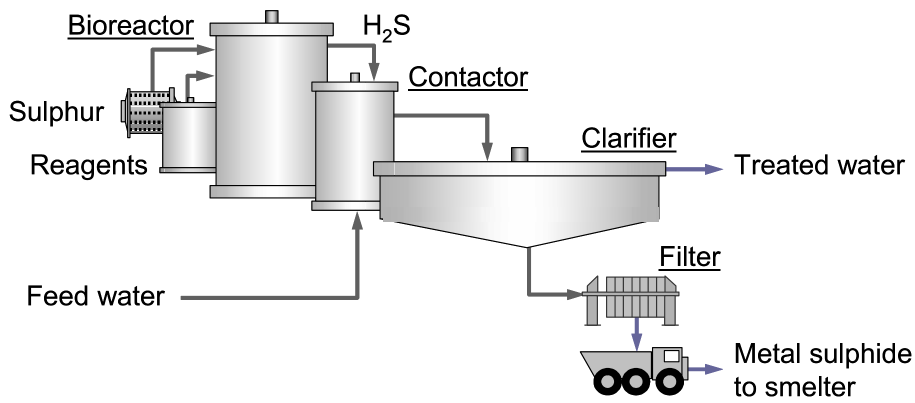

Figure 1 - Simple flowsheet schematic of the BioSulphide® Process

Hydrogen sulphide is generated by the reduction of elemental sulphur in the presence of an electron donor, such as acetic acid, in an anaerobic bioreactor. The gas is passed to an anaerobic agitated contactor where conditions are controlled to precipitate the metal to be recovered selectively as a sulphide. The high-grade metal sulphide precipitate is then recovered by conventional clarification and filtration to produce a filter cake which can be shipped to a refinery. It can be noted that the feed water does not pass through the bioreactor, which can therefore be operated under ideal conditions at all times. The operation of the bioreactor is not subject to process upsets due to changes in water chemistry and flow, unlike other biological processes which have to treat the contaminated water directly.

The main advantages of using the biological H_2S generation include:

- Low cost of sulphide compared to the cost of Na_2S, NaHS, or H_2S;
- Sulphide production on demand with minimal hazards and increased safety mainly due to the low system pressure and low inventory of H_2S. At any point in time the amount of H_2S stored in the bioreactor(s) is a small fraction of the daily H_2S production. This avoids special environmental permitting for sulphide reagent storage;
- Low capital cost mainly due to the ambient temperature and pressure in bioreactors that are designed as conventional stirred tanks compared to pressure vessels with expensive agitator seals; and
- Easy to scale-up and down over a wide range of H_2S production capacities.

If more than one metal is to be recovered, a single or multiple bioreactors can provide sulphide reagent to separate contactor-dewatering circuits. It is possible, for example, to achieve very high separation efficiency to produce high grade sulphide concentrates of Cu, Zn, Ni-Co and Mn.

Since 2002, BioteQ has constructed and operated three commercial operations utilizing sulphide generation and precipitation technology (zinc-copper-cadmium recovery at the Caribou Mine in New Brunswick, copper recovery from stockpile drainage at the Copper Queen Mine in Bisbee, Arizona, and nickel recovery from mine drainage and treatment for environmental discharge at the Raglan Mine, in northern Quebec). Four new plants are under construction in 2007.

BioSulphide® or ChemSulphide™ plants can also be installed upstream of an existing or proposed lime plant as shown in Figure 2. This was the flowsheet configuration of BioteQ's first plant at the Caribou mine.

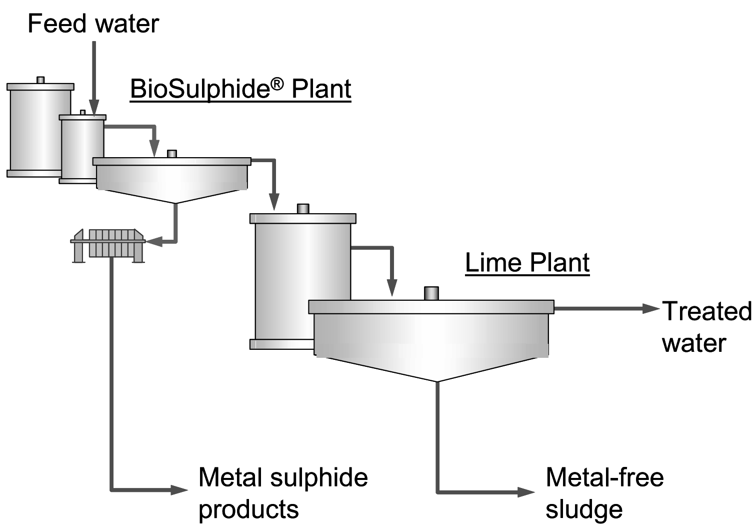

Figure 2. Installation of a BioSulphide® plant for metals removal upstream of a lime plant.

Not only can there be a financial benefit from the revenues of metal sales but lime plant operation can be improved by a reduction in lime consumption and a reduction in the quantity of sludge produced. The sludge would also have a partial or total reduction in the quantity of contained heavy metals, thereby increasing disposal options and reducing the long term liability associated with the storage and maintenance of heavy metal-containing sludge. The sludge, now containing essentially only iron and aluminum hydroxides, possibly together with gypsum, could also have a value as a component in construction materials.

The Bisbee Project

BioteQ's first copper recovery plant was constructed and is operated in joint venture with Phelps Dodge at the Copper Queen Mine, in Bisbee, Arizona. The success of the plant has opened up numerous opportunities to use biogenic sulphide generation for the recovery of metals including copper, nickel, zinc and cobalt at a number of sites around the world. The recovery of copper at Bisbee has demonstrated that the technology has a niche for profitable operation for the treatment of solutions too low in grade or flow for economic application of SX-EW and with a significant lower capital investment, while providing a long term environmental solution for the site.

The Bisbee plant was commissioned in 2004 and was designed to recover up to 3 million pounds per year of copper from the drainage of a large low-grade stockpile with flows of up to 10,900 m^3/day. Figure 2 shows a simplified flowsheet of the operation.

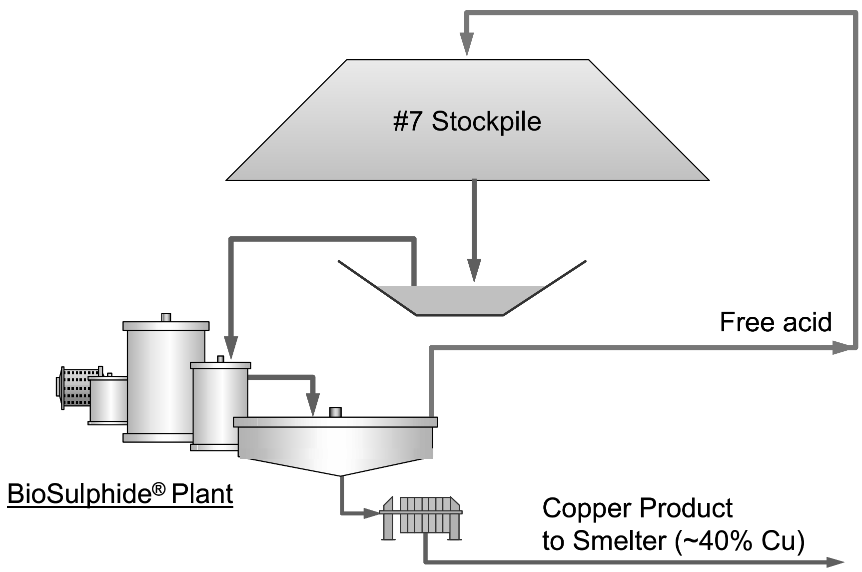

Figure 3. Simplified flowsheet showing the use of biogenic sulphide for copper recovery at the Copper Queen Mine, Bisbee, Arizona

Precipitation of copper from the drainage is rapid and highly efficient, with copper recoveries consistently greater than 99.8% from the feed solution containing copper in the range 220 to 360 mg/L at a flow currently in the range of 8,000 to 9,000 m^3/day. The copper sulphide product is thickened and dewatered using conventional equipment, with the plant effluent containing free acidity returned to the stockpile. The filtered concentrate, containing typically 38 to 45% copper, is shipped to the Phelps Dodge-owned smelter in Miami, Arizona for processing to metal.

Some mechanical issues were experienced early in the project and caused some significant downtime. However, the necessary repairs and replacement of some equipment, together with improved operational procedures, have resulted in very high plant availability since July 2006, with monthly copper recoveries of around 150,000 lb per month being achieved at current solution grades and flow rates. Payback on the US$3.2 million plant is less than 3 years.

The Dexing Project

The Dexing copper mine, located near Dexing City in Jiangxi Province, China, currently produces 120,000 tonnes of copper concentrate per year from flotation concentrate and also operates a heap leach using SX-EW to produce copper cathode from low grade stockpiles. Mine drainage from waste dumps and low grade stockpiles is acidic and contains significant copper values. BioteQ and Jiangxi Copper Corporation, the owners of the Dexing mine, have entered into a joint venture agreement to build a water treatment plant near the existing milling operation at Dexing to treat acid water from several sources at the site. The minimum capacity of the plant will be 1.1 million pounds per year of copper and a maximum capacity of 4.5 million pounds per year if all of the acidic water is treated.

The plant, currently under construction upstream of an existing high density sludge (HDS) lime plant, will initially be a ChemSulphide™ process, although the joint venture plans to increase the plant capacity in stages, which will likely lead to the installation of a bioreactor to produce lower cost sulphide reagent at the higher plant capacity. Preliminary estimates completed by BioteQ, using local consumable and labour pricing provided by Jiangxi Copper, shows a total annual operating cost of US$ 1.44 million, for the maximum capacity plant, or US$0.32 per pound of copper in direct operating expenses. The high grade copper product will be refined at the Jiangxi Copper refinery at commercially competitive rates. Smelting and refining charges are not included in the total annual operating cost estimate. The capital cost is expected to be less than US$ 2 million based on the existing site infrastructure and costs of recent construction projects at the Dexing site.

The application of BioteQ's technology at the Dexing copper mine has highly favourable project economics from the production of copper and the plant will provide significant environmental benefits including:

- Reduced sludge production from lime treatment
- Removal of copper from sludge products
- Reduced operating costs of the existing HDS lime plant

BIOGENIC SULPHIDE REAGENT FOR GOLD-COPPER PROCESSING

Many of the known gold deposits in the world contain cyanide-soluble copper minerals such as chalcocite, covellite, bornite, cuprite, malachite and azurite. The fact that the ore is not currently being mined in many of these cases has been due, in no small measure, to the metallurgical challenges and high cost of treating the cyanide-soluble copper minerals in the ore. The presence of leachable copper in a gold ore body results in low gold recovery and/or high cyanide consumption and destruction costs, as well as complications in the gold recovery circuit, whether gold recovery is by adsorption on activated carbon, electrolysis or cementation on zinc dust. One way in which gold plant operators have attempted to deal with the problem in the past has been to limit cyanide addition to the leach liquor to starvation levels, in the hope of selectively leaching gold and leaving copper in the residue. This has the desired effect of reducing the formation of copper cyanide and reducing cyanide consumption, but is invariably achieved at the cost of reduced gold recovery.

In recent years, the SART process (Sulphidization–Acidification–Recycle–Thickening) has been developed, jointly by Teck Corporation and Lakefield Research, in which the cyanide associated with the copper cyanide complex is released allowing it to be recycled back to the leach process as free cyanide [4-5]. Copper is also recovered as a valuable, high-grade Cu_2S by-product which can grade around 70% Cu. The implementation of this technology allows gold/copper ore bodies to be leached aggressively with cyanide (thereby maximizing gold recovery), without undue concern for copper cyanide formation. The SART process also converts zinc cyanide in a leach liquor (which is often the case if the Merrill Crowe process is used for gold and silver recovery) to free cyanide and the ZnS precipitate.

The SART Process, as originally developed, uses chemical sulphide ions, such as sodium hydrosulphide (NaHS), to precipitate copper and zinc (if present) and convert cyanide to HCN gas, under weakly acidic conditions (pH 5). Chemical sulphide can be replaced by lower cost biogenically-produced hydrogen sulphide, which has the added advantage of lowering the acid demand by one third for copper cyanide treatment and half for zinc cyanide. The chemistry of SART using both chemical and biogenic sulphide has been discussed elsewhere [6].

A simplified process flowsheet in which biogenic sulphide replaces chemical sulphide in the SART Process is shown in Figure 4.

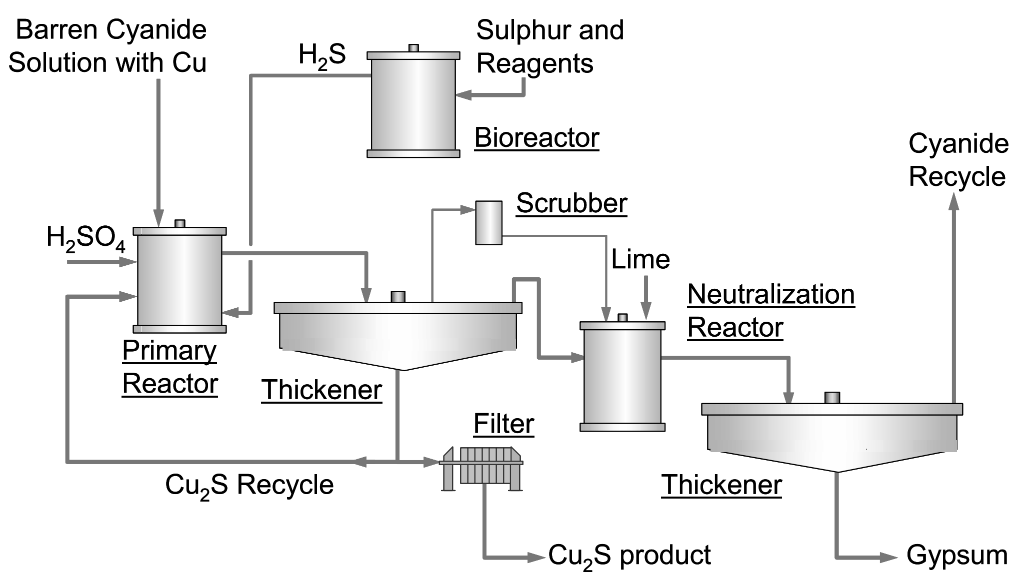

Figure 4 - Flowsheet showing the use of biogenic sulphide to replace chemical sulphide in the SART Process for cyanide recycle and copper recovery in gold-copper ore processing

One of the features of the SART process (compared to other cyanide recovery processes such as AVR and Cyanisorb™), is that cyanide is not pre-concentrated prior to recycling. The cyanide strength of the regenerated cyanide solution is essentially the same or slightly lower than the cyanide strength of the original solution. The process is therefore ideally suited to heap leach operations, where barren solution (after gold recovery) is recycled directly to leach. Nonetheless, the first industrial application for the technology was at the Telfer Mine in Western Australia, where the process was used to regenerate copper cyanide-rich tailings from a CIP plant. For the SART process to be applied in this way to pulps in a milling operation, the tailings must be subjected to solid/liquid separation (filtration or CCD), prior to SART. In order to maximize cyanide recovery, the wash solution used in CCD or filtration must be free of cyanide, and the combined wash plus barren solution must be treated by the SART process. This will produce a large volume of low-grade free cyanide solution, and even if the maximum amount of this water is recycled to the mill and the leach tanks, excess free cyanide-containing water will be produced in the process. Ideally, this water should be directed to a heap leach operation so as not to waste the cyanide, provided there is a heap leach at the same site as the mill.

The strength of the copper price in the current market makes a most compelling economic case for implementation of the SART process. The sale of a high grade copper sulphide by-product will not only cover all operating costs associated with the SART process (allowing cyanide to be regenerated at zero cost) but will add value to the project by generating additional revenues from any copper that is leached by cyanide in the process. As a result of the very robust copper market conditions, the metal has gone from being a project-killer in many gold ore bodies around the world, to an added-value by-product. For example, using NaHS, the operating costs for reagents, power and labour for treatment of a barren leach solution containing 250 mg/L Cu and 310 mg/L WAD cyanide in a SART circuit can be estimated to be \$0.40 per m^3, using H_2SO_4, NaHS and $Ca(OH)_2$ costs of \$100/t, \$1000/t and \$250/t, respectively. Using biogenic sulphide, costs would be reduced. Assuming recoveries of 95% cyanide and 99% copper, unit costs of NaCN and copper of \$0.69/lb and \$2.50/lb, respectively, and a net smelter return of 85% for sale of the copper, revenues of \$1.98 per m^3 can be estimated. Half of this revenue stems from the sale of copper sulphide, illustrating the potential added value of the leachable copper in a gold ore. By comparison, the cost of cyanide detoxification to treat a bleed stream using, for example, the SO_2-air process ranges from \$1.50/kg NaCN to \$3/kg NaCN, depending on the method used and the presence and concentration of other species in the leach liquor. Under the most favourable circumstances, the cost of cyanide detoxification in the above hypothetical example would be about \$0.90/m^3 of heap leach liquor treated. Therefore, the true benefit of the SART process with current reagent costs and commodity pricing is expected to be in excess of \$2 per cubic meter of heap leach liquor treated.

The capital cost of a SART plant will be higher than a cyanide detoxification plant, but this will be more than offset by the revenues generated by copper recovery and the savings realized by cyanide recycle, allowing for a short pay back time on the incremental capital.

BioteQ is currently working with Columbia Metals Corporation Ltd., Canada, to apply its sulphide generating and precipitation technology in a SART circuit at Columbia's La Jojoba and Lluvia de Oro gold projects in northern Mexico. The processing of ores from both mines has challenges due to the presence of cyanide-soluble copper.

BIOGENIC SULPHIDE REAGENT IN COPPER-MOLY SEPARATION

As with the SART Process, biogenic sulphide could replace sodium hydrosulphide in mineral processing for the separation of copper and molybdenum in flotation. BioteQ is currently evaluating a number of opportunities to supply reagent in an arrangement in which they would own and operate the sulphide generating plant at the mine site and supply the reagent to the mine owner/operator on an "over-the-fence" basis.

Sodium hydrosulphide is used to provide reducing conditions to permit efficient separation of copper and molybdenum sulphides in many flotation operations around the world. Although NaHS is very effective for this purpose, it could be replaced by biogenic sulphide reagent as shown in Figure 5. The existing NaHS storage and delivery systems could remain in place and operable so that sulphide system availability can remain high in the event of planned or unplanned maintenance of the biogenic system.

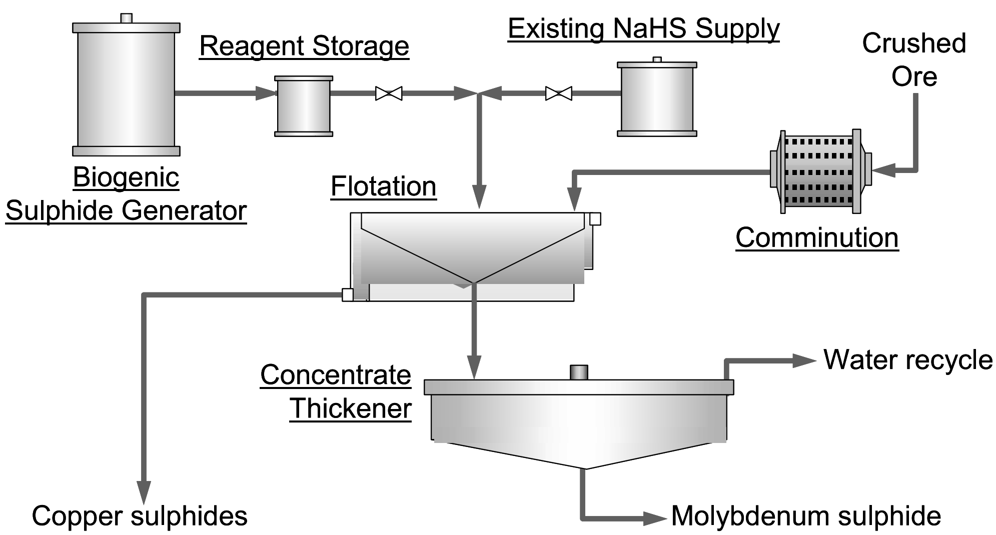

Figure 5. Simplified flowsheet showing the use of biogenic sulphide to replace chemical sulphide in Cu-Mo separation by flotation

Use of biogenic sulphide in copper-molybdenum flotation would have several advantages including:

- Lower cost than NaHS;
- Significantly reduced transportation and storage issues since biogenic reagent is produced on-demand at the mill site;
- No requirement to reduce pH to around 8 for optimum Cu-Mo separation by adding acid or CO_2 due to the highly alkaline NaHS; and
- Adding a biogenic sulphide supply system to an existing NaHS system would allow for very high overall system availability in the event of maintenance or problems with reagent market shortages.

CONCLUSIONS

Sulphide reagents are widely used in the mining, mineral processing and hydrometallurgy in a number of applications including water treatment, metal recovery and flotation. BioteQ utilizes sulphide reagent in its water treatment and metal recovery plants, either generated biologically in the BioSulphide® Process or as chemical sulphide in the ChemSulphide™ Process. Successful commercial operations have shown that high quality effluents can be produced for environmental discharge and that metals can be recovered selectively into saleable high-grade concentrates from acid mine drainage or leach solutions. The generation of lower-cost biogenic sulphide reagent also offers additional applications in hydrometallurgy and mineral processing. The replacement of chemical sulphide reagents by biogenic sulphide in the SART process offers a further cost advantage to a technology which has great potential to permit the economic processing of many previously uneconomic gold-copper ores by recovering and recycling cyanide that has been complexed by cyanide-soluble copper, as well as recovering the copper in a saleable sulphide concentrate. Similarly, biogenic sulphide can be used to replace or provide a low-cost alternative/back up system for chemical sulphide used in the separation of copper and molybdenum in flotation.

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