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Copper–gold ore processing with ion exchange and SART technology

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ABSTRACT

Anglo Asian Mining has developed a 50,000 oz Au/yr open pit gold mine at Gedabek in Western Azerbaijan. The deposit at Gedabek is a copper–gold porphyry, comprising both oxide and sulphide ore mineralisation, which is being mined at the rate of about 1 million tons of ore per year. Ore processing is by conventional cyanide heap leaching, which produces a pregnant leach solution (PLS) containing 1–2 ppm of gold, together with 1000 ppm or more of copper. The PLS is treated by column ion exchange, using Dow's gold-selective MINIX resin. Loaded resin is stripped with an acidic thiourea solution, from which gold and silver are electrowon on to stainless steel mesh cathodes. Copper concentrations in the leach solutions are controlled by passing part of the PLS flow through a SART process, where the acronym stands for "Sulphidisation, Acidification, Recycling and Thickening". The product from the SART process is a copper/silver sulphide precipitate, which is thickened, filtered and dried and then sold for copper smelting.

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1. Introduction

In May 2009, Anglo Asian Mining, a London-listed, junior gold mining company, started operations at its first mine, which it had developed near a remote town called Gedabek, high in the Lesser Caucasus mountains in western Azerbaijan. Not only was this mine the junior company's first mining operation, it was also the first metal mine to be built in Azerbaijan for over a century. In the nineteenth century, Gedabek had previously been a mining town, when the Siemens company from Germany operated a copper mine there for about 50 years, until the Russian revolution intervened after the end of the First World War, when the Germans closed the mine and returned home. By then, oil had been discovered in Azerbaijan, both on-shore and off-shore in the Caspian Sea, and so the country rapidly became an important source of energy for the growing industrial demands of the USSR. During the Soviet era, mineral exploration continued in the Gedabek region, but no further mining development took place during the rest of the twentieth century, until Anglo Asian began operating its new open pit gold mine with state-of-the-art ion-exchange processing technology to produce 50,000 oz of gold per year.

2. Deposit description

2.1. Regional geology

Azerbaijan straddles the mountain ranges of the Greater and Lesser Caucasus, which are part of the Alpine-Himalayan mountain chain that marks the collision of the African and Indian continental plates with the Eurasian plate. The continental collision is manifested by the Alpine tectono-magmatic cycle, which shows a progressive development from predominantly oceanic magmatism in the Jurassic, through to predominantly continental magmatism in the Tertiary. This magmatic episode was responsible for one of the world's major metallogenic belts, the Tethyan, which can be traced from Pakistan through Iran and Turkey to the Balkans. Notable deposits within this belt include a spectrum of hydrothermal deposit types ranging from Cyprus-type massive sulphide deposits, through porphyry copper and gold deposits, to epithermal gold deposits.

2.2. Local geology

The Gedabek deposit lies in the Lesser Caucasus mountains in western Azerbaijan at an altitude of 1600 m, close to the border with Armenia and about 60 km from Ganja, Azerbaijan's second city. The deposit exhibits many characteristics typical of porphyry copper–gold deposits, but it is peculiar in the development of distinct bodies of massive and semi-massive sulphide, as well as

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the more normal ‘porphyry style’ disseminated and stockwork mineralisation.

The Gedabek deposit is believed by Azeri geologists to be a composite (“telescoped”) deposit of two contrasting types of mineralisation: an older volcanogenic massive sulphide (VMS) deposit and a younger porphyry stockwork. The massive sulphide bodies are composed principally of pyrite and chalcopyrite with minor amounts of sphalerite, galena, tetrahedrite and barite. There are five known large massive sulphide bodies, with plan areas of 8000–26,000 m^2, and several smaller ones. These bodies are distributed within the porphyry over a strike length of about 600 m and over a vertical interval of up to 200 m. Past production from these lenses during the Siemens period is reported to have totaled 1.7 Mt of ore, with 56,000 t of copper and 134 t of Au–Ag–Cu doré recovered.

2.3. Mineralogy and gold deportment

The sulphide mineralogy of the Gedabek deposit is dominated by pyrite, with lesser chalcopyrite and minor amounts of sphalerite, covellite, chalcocite, galena and arsenopyrite. The py/cpy ratio is generally in the 12–15 range. The gangue mineralogy is dominated by quartz (approx. 50%), with lesser feldspars, muscovite, and andalusite. Minor barite and iron hydroxyoxides are also present.

Gold is found in two main forms: (i) gold minerals, including native gold, electrum and petzite [Ag_3AuTe_2]; (ii) submicroscopic gold in sulphides and goethite. The highest concentrations of sub-microscopic gold occur in arsenopyrite (40 ppm Au) and covellite (9 ppm Au), but because of its dominance, pyrite is the principal sulphide carrier of sub-microscopic gold. Silver occurs as native silver, electrum, acanthite [Ag_2S], hessite [Ag_2Te] and petzite, of which hessite is the most common, followed by native silver. Silver is also likely to occur in solid solution in covellite. Five telluride minerals are present, of which Bi-tellurides, hessite and altaite [PbTe] are the most common. The so-called oxide ore is characterized by minerals typical of the hypogene oxidation zone of copper porphyry deposits, including malachite, azurite, goethite and other iron hydroxyoxides.

2.4. JORC resources and reserves

The measured, indicated and inferred mineral resources of both the oxide and sulphide mineralisation based on a cut-off grade of 0.3 g/t of gold is given in Table 1, together with the proved and probable open pit ore reserve estimation, based on the same cut-off grade. The table shows that the current JORC gold resource at Gedabek is just over 1.2 M oz Au in all categories, while the mineable ore reserve is 744 K oz Au.

3. Mining

The Gedabek mine is a conventional open pit, truck and shovel operation, with a current mining rate of about one million tons of ore per year, resulting in an annual gold production of approximately 50,000 oz. Rock breakage is accomplished by blasting, which is carried out once per day. Blast holes are drilled on a 2.5 m × 2.5 m pattern in ore and 3 m × 3 m in waste rock, to a depth of 3 m. The blast holes are each charged with 10 kg ANFO/Geonit mix and detonated electrically. Grade control drilling is used ahead of blast hole drilling to delineate ore blocks and classify them as either, high grade oxide (>1 gAu/T), low grade oxide (<1 > 0.3 gAu/T), sulphide ore, or waste rock. A typical analysis of the oxide ore feed for heap leaching is given in Table 2.

4. Processing

4.1. Overall flowsheet

The Gedabek process plant, which began operation in May 2009, uses conventional cyanide heap leaching, combined with gold extraction by resin ion exchange and SART technology for copper control. A schematic flow diagram of the overall process is shown in Fig. 1.

4.2. Ore preparation

ROM ore is prepared for heap leaching by three stages of crushing – primary jaw crusher, followed by secondary and tertiary cone crushers, to give a product 100% minus 25 mm. The output from the primary crusher is passed over a 25 mm screen and the −25 mm material passes into an agglomeration drum (2.2 m diam. × 10 m length), together with lime (3 kg/t ore) and cement (5 kg/t ore). The over-size rock from the primary screen is fed to the cone crushers and, after secondary and tertiary crushing to −25 mm, it is conveyed to the heaps, together with the agglomerated fines.

4.3. Heap leaching

The crushed and agglomerated ore is stacked on the leach pads in 12 m lifts by a radial arm stacker. A maximum of two and half lifts per heap are used (max. 30 m high). The heaps are constructed on pre-prepared pads, which are double lined with HDPE sheet with geo-membrane between the layers for leak detection.

Barren leach solution (BLS) is pumped from the BLS pond and the solution is sprayed on to the surface of the heaps through sprinklers positioned at 2 m intervals. The rate of leach solution application is 10 l/m^2/h. Ore on the heaps is typically leached for a period of about 6–9 months, dependent on the time of year and weather conditions. The maximum gold extraction that can be

Table 1
JORC resources and reserves.

Classificati	Tonnage	Grades			Products		
	(t)	Au (g/t)	Cu (%)	Ag (g/t)	Au (oz)	Cu (t)	Ag (oz)
Resources							
Measured	22,349,562	1.028	0.255	8.249	738,958	57,069	5,927,487
Indicated	14,762,015	0.665	0.167	5.649	315,424	24,696	2,681,064
Measured & indicated	37,111,577	0.884	0.220	7.215	1,054,382	81,765	8,608,551
Inferred	11,027,402	0.626	0.119	4.787	222,040	13,125	1,697,102
Reserves							
Proved	15,586,952	1.172	0.285	9.203	587,099	44,389	4,611,806
Probable	4,725,928	1.033	0.319	10.292	156,939	15,091	1,563,725
Proved & probable	20,312,879	1.139	0.293	9.456	744,038	59,479	6,175,531

Table 2
Analysis of typical oxide ore feed to heap leaching.

Element	Composition (%)	Element	Composition (g/t)	Element	Composition (g/t)
Al	2.7	Pb	598	Sn	21
Si	15.5	Ni	7	Sb	27
P	0.2	Ga	19	Te	5
S	0.8	Ge	8	La	91
Cl	<0.002	As	270	Ce	<17
K	0.8	Se	4	Hf	<32
Ca	0.8	Br	5	Ta	<39
Ti	<0.008	Rb	18	W	11
V	<0.002	Sr	551	Hg	<3
Cr	<0.002	Y	11	Tl	6
Mn	0.1	Zr	85	Bi	8
Fe	7.0	Nb	<4	Th	<2
Cu	0.2	Mo	39	U	<9
Zn	0.1	Co	96	In	8
Ba	2.8	Ag	25	Cd	9

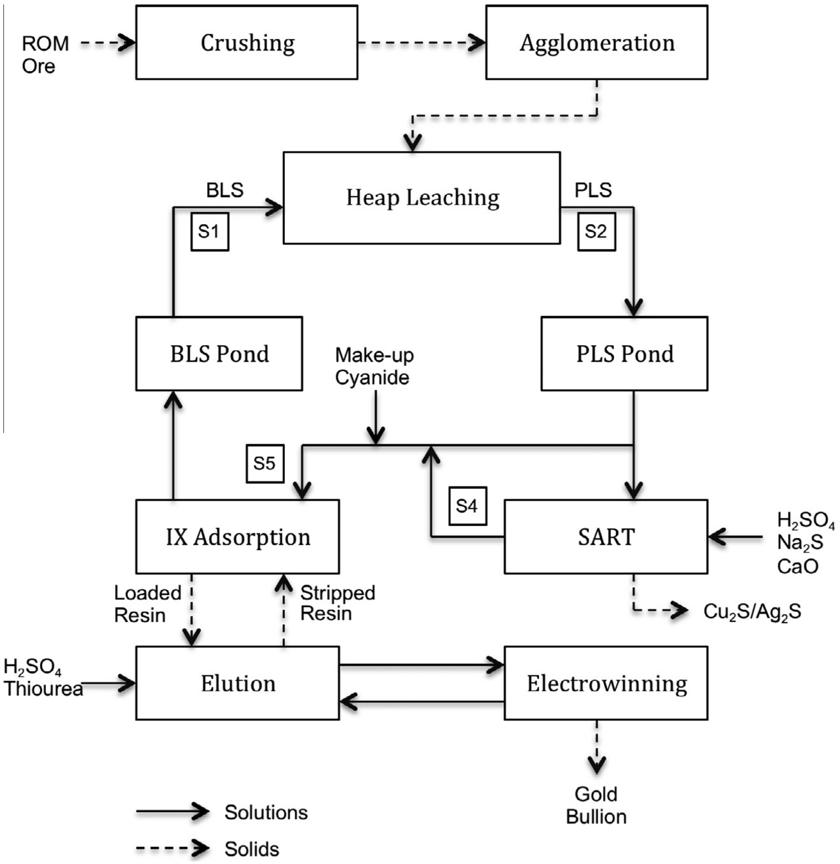

Fig. 1. Flowsheet for gold ore processing at Gedabek. (Solution compositions given in Table 3).

achieved from Gedabek ore by heap leaching is around 70%, after which the ore heap is considered spent and ready for a new lift to be placed on it.

4.4. PLS treatment – CIX

Pregnant leach solution from the heaps is collected in the PLS pond, from where it is pumped to the ADR (Adsorption/ Desorption/Recovery) process plant at a rate of 400 m^3/h. Because of the copper minerals in the Gedabek ore, the PLS contains high concentrations of copper (see Table 3); typically the Cu/Au concentration ratio in the leach solution is ~1000 and, under these conditions, it is not practically feasible to use conventional activated carbon to adsorb the gold. The technology used at Gedabek to extract gold from the PLS is column ion exchange (CIX) using the Dowex Minix gold-selective strong base ion exchange resin (XZ-91419), produced by the Dow Chemical company. This resin, which was originally developed by Mintek in South Africa, is highly selective for gold over copper (Kotze et al., 1993; Green et al., 2002). In order to control the concentration of dissolved copper in the recirculating leach solutions, 25% of the PLS (100 m^3/h) is diverted through the SART plant, where copper and silver are precipitated from solution (*see below*). The SART treated solution rejoins the main PLS flow before it arrives at the ADR plant. Make-up cyanide is also added before the PLS enters the IX adsorption columns to increase the free cyanide concentration to 1000 mg/l. This helps to suppress the adsorption of copper on the resin (Dai et al., 2010) by encouraging the formation of Cu(CN)$_3^{2-}$ and Cu(CN)$_4^{3-}$, which are only

Table 3
Typical process solution compositions.

	Solution	Gold (mg/l)	Silver (mg/l)	Copper (mg/l)	CN (Free) (mg/l)	pH
S1	BLS	0.20	1.6	530	1000	10.5
S2	PLS and SART (in)	0.79	2.3	660	320	10.0
S3	SART (intermediate)	0.78	0.03	50	N/A	5.4
S4	SART (out)	0.77	0.07	65	1300	10.5
S5	ADR (in)	0.79	1.8	510	1000	10.0

weakly extracted by the resin, compared to the more readily extracted dicyano-copper complex, $Cu(CN)_2^-$. The reactions occurring during the absorption cycle can be represented as:

$$]\text{-}^{+}NR_3X^- + Au(CN)_2^- =]\text{-}^{+}NR_3Au(CN)_2^- + X^- \quad (1)$$

$$]\text{-}^{+}NR_3X^- + Ag(CN)_2^- =]\text{-}^{+}NR_3Ag(CN)_2^- + X^- \quad (2)$$

$$]\text{-}^{+}NR_3X^- + Cu(CN)_2^- =]\text{-}^{+}NR_3Cu(CN)_2^- + X^- \quad (3)$$

where]- is the matrix of the resin, NR_3 is an amine radicle and X^- is an anion, which at Gedabek is either sulphate or bisulphate.

The adsorption plant consists of four IX packed columns, each 2.5 m in diameter and 2.1 m high, with internal volumes of 9 m^3. Each column contains 6.5 m^3 of resin. The columns are operated in parallel in down-flow mode, with each column being fed with 130 m^3/h of PLS during its loading cycle. Each column goes through a sequence of operations, comprising charging, loading, washing and discharging. At any given time, three columns are loading, while the fourth is off-line, being washed, discharged and then re-charged with stripped resin from the elution columns. Loading is carried out for 24 h, by which time the resin will contain about 160 mg/l Au, 120 mg/l Ag and 230 mg/l Cu. The average adsorption efficiencies for Au and Ag are 70% and 15%, respectively, while Cu adsorption is negligible. The loaded resin in the column is then washed with fresh water and pumped to an elution column.

Operational experience at Gedabek has shown that resin adsorption efficiencies can be negatively affected by the presence of excess flocculant in the feed solution and by fine solid particles, either precipitated from solution, e.g. gypsum, or fine ore particles carried over from heap leaching. This problem is mainly due to the use of packed bed ion exchangers at Gedabek, which at the same time tend to act as bed filters. The accumulation of flocculant and fine particles affects the adsorption both by disturbing the fluid flow pattern in the IX vessels and by fouling the resin surfaces. Application of remedial measures such as high pressure back washing, or periodic flow direction change from downward to upward flow can improve absorption performance to a certain extent, but does not solve the problem entirely.

4.5. Elution

There are three elution columns, operated in parallel; each is 1.75 m in diameter and 5.9 m high, with an internal volume of 15 m^3. Each elution column can treat up to 7 m^3 of resin. Loaded resin is eluted with a hot, acidified solution of thiourea –0.2 M H_2SO_4 and 1.0 M thiourea at 50 °C. Elution is carried out in series with electrowinning, with the eluate circulating between the two operations at a rate of 7.5 m^3/h. Typically, the resin is eluted for 4 h, by which time the gold concentration on the resin has dropped to <10 mg/l. The resin is then washed and returned to the adsorption columns. The elution reaction between metals on the loaded resin and the acidic thiourea solution can be represented as (Groenenwald, 1977):

$$\begin{aligned} &]\text{-}^{+}NR_3M(CN)_2^- + 2CS(NH_2)_2 + 2H_2SO_4 \\ &\quad =]\text{-}^{+}NR_3HSO_4^- + M(CS(NH_2)_2)_2 \cdot HSO_4 + 2HCN \end{aligned} \quad (4)$$

where $M^+ = Au^+$, Ag^+, or Cu^+.

Typical metal concentrations remaining on the eluted resin are about 7 mg/l Au, 10 mg/l Ag and 70 mg/l Cu, giving stripping efficiencies of 95%, 92% and 70%, for Au, Ag and Cu, respectively.

4.6. Electrowinning

Electrowinning of gold, together with some silver and copper, from the thiourea eluate is carried out using stainless steel mesh cathodes and lead anodes at a cell voltage of 5 V and a current of 500–800 A:

$$M(CS(NH_2)_2)_2 \cdot HSO_4 + H^+ + e^- = M^0 + 2CS(NH_2)_2 + H_2SO_4 \quad (5)$$

where M^0 = Au, Ag, or Cu.

The electrowinning cells contain 6 anodes and 5 cathodes and the anodes are contained in geo-membrane bags to minimise oxidation of thiourea. Periodically the cathodes are removed from the cell and washed with high pressure water jets to recover the electrodeposited metal particles, which are dried, smelted and cast into doré ingots.

4.7. SART process

The purpose of the SART process is to regenerate cyanide and recover copper from the solutions in gold heap leaching operations (MacPhail and et al., 1998; Adams et al., 2008; Ford et al., 2008; Stewart and Kappes, 2012; Estay et al., 2012). The name SART arises from the core unit operations that define the process: sulphidization (S), acidification (A), cyanide recycling (R), and thickening of the copper precipitate (T). The main stages of the process are acidification and sulphidization, precipitate thickening, sulphide precipitate filtration, solution neutralization, gypsum thickening and gypsum filtration.

Fig. 2 is a schematic flow diagram of the Gedabek SART process. The acidification (pH 5–6) and sulphidization stages are carried out in the nucleation reactor by the addition of concentrated sulphuric acid and sodium sulphide. In this reactor, Cu_2S and Ag_2S precipitation occurs and HCN is generated, which remains mainly dissolved in solution, according to Eqs. (6)–(8):

$$2NaCN + H_2SO_4 = 2HCN_{(aq)} + Na_2SO_4 \quad (6)$$

$$2NaAg(CN)_2 + 2H_2SO_4 + Na_2S = Ag_2S_{(s)} + 4HCN_{(aq)} + 2Na_2SO_4 \quad (7)$$

$$2Na_2Cu(CN)_3 + 3H_2SO_4 + Na_2S = Cu_2S_{(s)} + 6HCN_{(aq)} + 3Na_2SO_4 \quad (8)$$

As shown in Eq. (6), dissolved HCN is formed when acid is added; acidification also promotes breakage of weak metal cyanide complexes (WAD cyanide), such as those formed with the metals Cu, Zn, Ni, Ag, and Hg. The addition of Na_2S results in the precipitation of heavy metal ions in the form of metallic sulphides, which are principally Cu_2S and Ag_2S in the case of the Gedabek PLS, as shown in Eqs. (7) and (8), with an equivalent amount of cyanide being released into solution.

The solids formed by precipitation are removed using stages of thickening and filtration, while the treated solution is sent to the

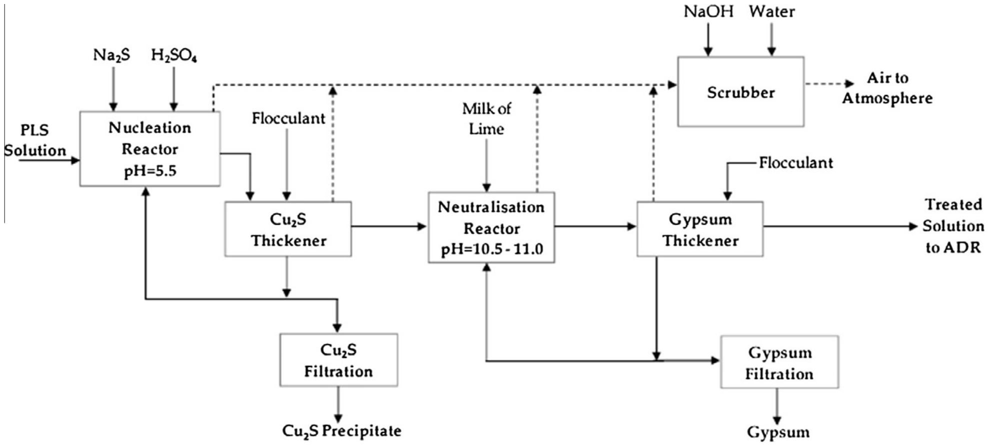

Fig. 2. Block flow diagram of the SART process in the Gedabek plant.

neutralisation stage where milk of lime ($Ca(OH)_2$) is added to raise the pH to 11. The addition of lime converts the dissolved HCN into calcium cyanide ($Ca(CN)_2$) and removes sulphate by the precipitation of gypsum:

$$2HCN_{(aq)} + Ca(OH)_2 = Ca(CN)_{2(aq)} + 2H_2O \tag{9}$$

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O = CaSO_4 \cdot 2H_2O_{(s)} + 2NaOH \tag{10}$$

A SART plant with a capacity of 100 m^3/h to process 25% of the total PLS was commissioned at Gedabek in April 2010. In the SART plant, concentrated H_2SO_4 and Na_2S solution (230 g/l) are added via in-line mixers in the PLS pipeline to reduce the pH of the PLS to 5.5. Approximately 20% excess sodium sulphide over the stoichiometric amount required to precipitate copper and silver according to Eqs. (7) and (8) is used, which results in precipitation efficiencies of 90% for Cu and 97% for Ag. The PLS-reagent mix flows into the nucleation reactor, where Cu_2S and Ag_2S are precipitated and dissolved HCN is generated. The slurry from the nucleation reactor discharges into the Cu_2S thickener (standard design, 8 m diameter) to increase the solids concentration. Part of the thickener underflow is recycled back to the nucleation reactor to serve as seed for the precipitation, while the remaining underflow fraction is sent to the filtration stage. The recycle rate to the nucleation reactor ranges between 3 and 10 vol.% and it is controlled to give a solids concentration in the discharge slurry of 0.5–1.0 wt.%. The filtration of the sulphide precipitate is carried out by two filter presses, producing a precipitate cake having 55% final moisture. The filter cake is then dried in an oil-fired dryer and put into sealed steel drums for storage and shipment.

The Cu_2S thickener overflow passes into the neutralisation reactor, where $Ca(OH)_2$ is added until the pH reaches 10.5–11, which converts dissolved HCN to $Ca(CN)_2$ and induces gypsum precipitation. The gypsum slurry is fed into the gypsum thickener (8 m diameter) to separate the solids from the treated solution. In a similar manner to the precipitate thickener, part of the underflow from the gypsum thickener is recycled back to the neutralisation reactor, while the remaining underflow fraction is sent to filtration. The gypsum filtration is performed by a rotary filter, giving a gypsum filter cake with 80% final moisture, which is discarded. The neutralisation thickener overflow, which is now low in copper and high in cyanide (see Table 3, solution S4), is remixed with the main PLS flow, prior to entering the ion exchange columns in the ADR plant.

The SART process plant also includes a caustic soda scrubber system connected to the main plant equipment in order to capture and treat fugitive emissions of HCN and/or H_2S gases. The reaction tanks and thickeners, which are all sealed units, are kept under vacuum generated by a suction fan. The exhaust air is scrubbed by caustic soda solution (100 g/l) at a scrubbing ratio of liquid to gas 10 l/m^3 before discharge to atmosphere

Table 4
Typical compositions of SART Cu_2S precipitate.

Element	Concentration (wt.%)	Element	Concentration (ppm)
Cu	55–60	Ag	1500–4000
S	16	Hg	50
CaO	1.6	Au	5–10
Na_2O	1.0		
SiO_2	0.4	As, Bi, Cd, Co	<10
Fe	0.3	Ni, Pb,S b, Sn	<10
Al_2O_3	0.3		
Zn	0.25		
K_2O	0.07		
MgO	0.02		

$$HCN_{(g)} + NaOH_{(aq)} = NaCN_{(aq)} + H_2O \tag{11}$$

The HCN concentration in the off gas is continuously monitored by an HCN gas analyzer. Scrubber solution containing dissolved sodium cyanide is returned to the leach circuit.

The current annual production of the Gedabek SART plant is about 500 t of copper and 100,000 oz of silver in a mixed sulphide concentrate that is sold into the market for smelting. Typical compositions of the copper sulphide precipitates from the Gedabek SART plant are given in Table 4. The particle size distributions of these precipitates are typically: D_{50} = 12 μm; D_{80} = 30 μm.

5. Conclusions

The successful operation of Anglo Asian Mining's Gedabek process plant, which uses a unique combination of ion exchange for gold extraction and SART technology for copper control, has demonstrated a new route for the treatment of copper–gold ores, which in the past have proved difficult to handle with conventional gold processing technology.

Ion exchange resins offer many advantages over activated carbon for the treatment of gold-bearing solutions and pulps. Chief amongst these are: simple, low temperature elution; elimination of thermal regeneration requirements; and physical robustness and attrition resistance. In the case of the Minix strong-base resin, there is the additional advantage of excellent selectivity for gold over copper. At Gedabek, where the Cu/Au ratio in the PLS is about 600–700 (see Table 3), the loaded Minix resin has a Cu/Au ratio of between 1 and 2, demonstrating a selectivity ratio for gold over copper of 300–700. After more than four years of operation, there is no significant resin breakage or attrition losses, nor is there any noticeable decrease in the adsorbtion efficiencies of the resin due to ageing.

The SART process at Gedabek, which is one of only about half a dozen industrial applications of this technology in the world, has proved to be a reliable process that gives consistent results and that lends itself to automatic control. It produces a saleable Cu/Ag sulphide by-product that is suitable for smelting and which makes a useful contribution to the overall profitability of the mine.

Appendix A. General process data for the Gedabek plant

Unit process	Value
Heap leaching	
Ore feed size to agglomeration	−25 mm
Addition rate of cement and lime	5 and 3 kg/t ore
Irrigation rate	10 l/m^2/h
pH of BLS to heap irrigation	10.0–11.0
Free cyanide concentration in BLS to heap	1000 mg/l
Ion exchange	
PLS flow rate	400 m^3/h
pH of PLS to IX	10.0
Number of IX adsorption columns	4
PLS flow rate per IX adsorption column	133 m^3/h
IX Adsorption columns (diameter × height)	2.5 × 2.1 m
IX Adsorption column volume / resin inventory	9/6.5 m^3
Number of elution columns	3
Elution columns (diameter × height)	1.75 × 5.9 m
Elution column volume / resin inventory	15/6.5 m^3
Eluant composition	0.2 M H_2SO_4 + 1.0 M thiourea
Eluant temperature	50 °C
Electrowinning	
EW cell dimensions (width × height × length)	0.72 × 0.72 × 1.4 m (4 off)
Number of electrodes (anodes × cathodes)	6 × 5
Anode material	Pb + 1% Sb
Anode bags	Geofelt[a]
Cathode material	SS mesh
Eluant flow rate to EW cells	7.5 m^3/h
EW cell voltage/cell current	5 V/500–800 A
SART	
Solution flowrate	100 m^3/h
Nucleation tank volume	56 m^3
Neutralisation tank volume	56 m^3
Recycle rate to nucleation tank	3–10 vol.%

[a] http://www.geofelt.com/english/index.html.

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