



MINATAUR™: the Mintek alternative technology to gold refining

by S.A. Scott* and K. Matchett*

Synopsis

Mintek developed the Minataur™ leach-solvent extraction-precipitation technology as a cost effective, easily operated alternative to conventional gold refining processes. The technology was first commercialized at the Harmony Gold Refinery in 1997 to produce 99.99 per cent gold product and has subsequently led to development of various value-addition steps including the casting of various investment bars, gold wire drawing and gold potassium cyanide powder production. In addition to refining gold to high purity, if an appreciable amount of silver is present in the feed material it is also refined to 99.99 per cent purity. The major advantage that the Minataur™ technology has over other gold refining processes is the relatively low gold lock-up and reduced operating costs. The operating cost¹ as at April 2001 for the expanded Harmony refinery (24-ton per annum gold production) was approximately half that of conventional smelting and toll refining. The extractant employed for solvent extraction is relatively cheap and highly selective for gold, making the technology attractive in situations where significant quantities of platinum group metals or base metals are present.

Introduction

Gold has historically been refined from chloride media using the Wohlwill electrorefining process². The Rand Refinery³ produces a 99.99 per cent gold product by casting impure gold anodes that are electrorefined to the desired purity employing this process. The necessity to cast anodes and the high gold concentration of the electrolyte result in substantial gold lock-up times for the process.

In 1972 Inco Europe Ltd.⁴ installed a solvent extraction (SX) process for the refining of gold using dibutyl carbitol (DBC) as the extractant. Although the selective extraction of gold from chloride media using DBC is favourable, stripping requires direct precipitation of gold from the loaded organic phase, resulting in high organic losses. The high aqueous solubility of DBC also requires distillation of the raffinate to recover the relatively expensive extractant.

The Minataur™ process employs SX using a relatively inexpensive extractant to

selectively extract gold from chloride media. Gold is readily stripped from the loaded organic phase, negating the use of a direct precipitation step. The high selectivity of the extractant for gold over base metals and platinum group metals (PGM) enables the production of very pure loaded strip liquor from which 99.99 per cent pure gold product can be precipitated using sulphur dioxide—also a relatively cheap reductant. The process is amenable to a variety of gold feed materials including jewellery scrap, gold electrowinning cathode sludge, silver electrorefining anode slimes and atomized doré bullion. The precipitated Au product is also suited to further refinement in a range of downstream value-adding processes.

This paper describes the Minataur™ technology and associated silver refining.

Minataur™ Gold Refineries

A list of gold producers currently refining gold by the Minataur™ route, the feed material used and value-added products produced are shown in Table I. Mintek has constructed two more Minataur™ refineries but the availability of feed material has delayed final commissioning of these plants.

Process description

The Minataur™ process comprises three unit operations, namely dissolution of the feed material in an oxidative leach, selective solvent extraction of the gold-chloride species from solution and stripping into an aqueous solution, and reduction to metallic gold from this solution using a suitable reductant. Gold produced during the precipitation step is washed, dried and can be processed further in various value-adding processes. The AgCl

* Mintek, Randburg, South Africa.

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Table 1
Gold refiners using the Minataur™ process

Refiner	Feed material	Downstream value-added products
Harmony Gold Refiners (South Africa)	Au cathode sludge, atomized doré bullion	Drawn wire, various investment bars, gold potassium cyanide powder
Al Ghurair Giga (Dubai)	Atomised jewellery scrap, atomized doré bullion	Investment bars, gold potassium cyanide powder
Agenor (Algeria)	Atomized doré bullion	Kilobars

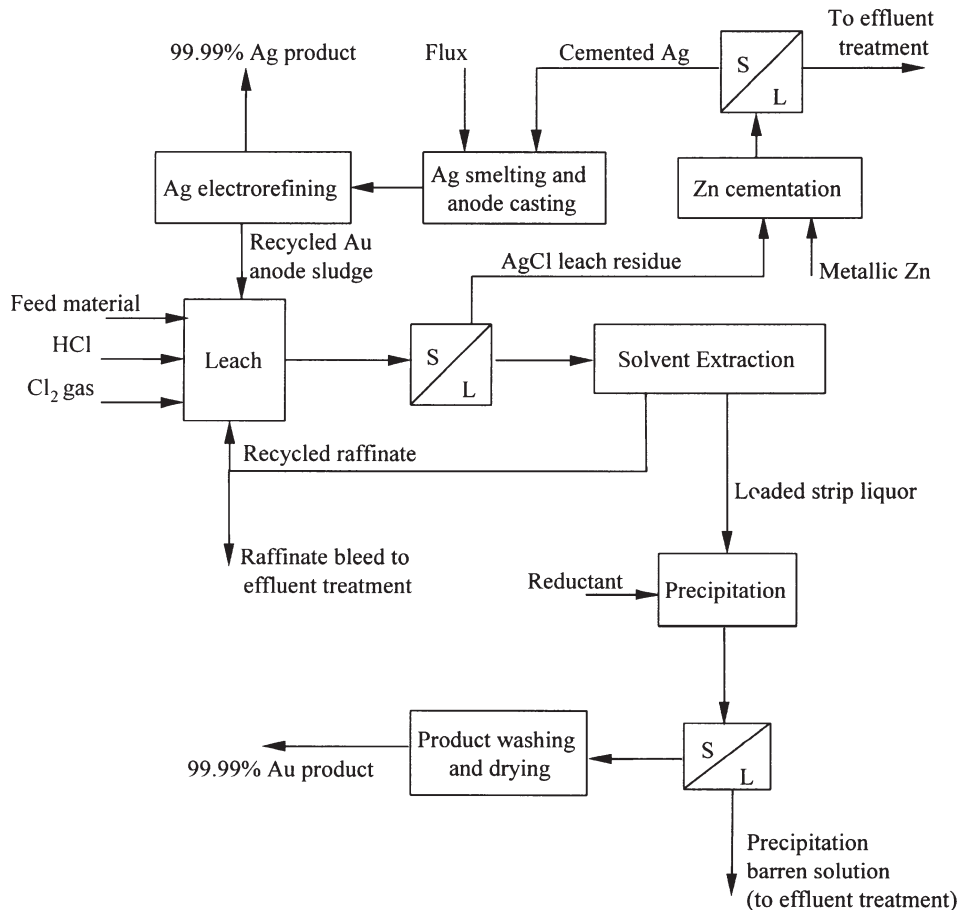


Figure 1—Block diagram of the Minataur™ process

precipitate that forms during gold leaching proceeds to a silver refining circuit for the production of 99.99 per cent silver. A block diagram of the process is shown in Figure 1.

Leaching

Feed material of an appropriate gold content and particle size is oxidatively leached in HCl media under a chlorine gas atmosphere. Leach liquor is made using a portion of raffinate recycled from the SX circuit with the HCl molar concentration adjusted by the addition of concentrated HCl. The mass of feed material used is aimed at producing pregnant leach liquor containing 65 g/L gold after dissolution. Typical feed material contains base metals, silver and other PGM that are leached along with the gold. Due to the slight solubility of silver in chloride media, a AgCl precipitate is formed that is filtered prior to the leach liquor being fed to the SX circuit. Silver is cemented from the AgCl cake from which silver

anodes are cast for electrorefining to produce 99.99 per cent silver granules. Gold anode slimes formed during silver electrorefining are recycled to the Minataur™ leaching step for recovery.

Typical operating conditions and performance of the leaching step as performed at Harmony Gold Refiners¹ is shown in Table II.

SX

After filtration, leach liquor is fed to a 3-stage extraction, 5-stage scrubbing and 4-stage stripping SX circuit. The organic extractant is passed counter current to the aqueous feed, scrub and strip liquors through the plant. The SX cells are conventional box-type mixer-settler units that employ pumping impellers for the transfer of solution from one cell to the next.

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Table II

Operating conditions and performance of the Minataur™ leaching step

Typical leaching time	2.5–5 h
HCl concentration	5.5 M
Average feed gold concentration	75%
Leaching efficiency	>99%
Cl ₂ consumption	0.7 kg per kg of gold

Extraction

Gold is selectively loaded onto the organic extractant and the concentration in the aqueous phase (leach liquor) is reduced from 65–70 g/L down to 100 mg/L (99.85 per cent extraction) that exits the extraction circuit as the raffinate. A portion of the raffinate stream is re-used during leaching to minimise the HCl consumption in this step. Due to the build-up of impurities in the raffinate, approximately 20 per cent of the raffinate is bled from the circuit. The amount of raffinate bled depends on the purity of the feed material used and higher purity feed material allows a greater recycle of raffinate for use during leaching. Effluent treatment steps have been developed for gold recovery from and neutralization of not only the raffinate bleed stream, but all waste streams emanating from the refinery. The extent of effluent treatment can be tailored to suite the requirements of the refinery.

Optimum operation of the extraction circuit depends on the gold and HCl concentrations of the leach liquor feed, organic extractant concentration and phase ratio employed. Although the organic extractant is highly selective for gold, metal species with a similar charge-to-volume ratio as the gold chloride species are also extracted. Extracted metal impurities are subsequently removed from the loaded organic phase by 'selective stripping' in the scrubbing section. The selective extraction of gold over selected metal impurities achieved during extraction is shown in Figure 2.

Scrubbing

The purity of the gold product produced depends upon the amount of impurities present on the organic phase entering the stripping circuit. Hence, before the loaded organic phase is stripped, impurities that would be co-stripped are removed during scrubbing. The extent of impurity scrubbing is dependent on the HCl concentration of the scrub liquor and the phase ratio employed. Impurities are not exclusively scrubbed and the portion of gold that is co-scrubbed is recovered by returning the spent scrub liquor to the extraction circuit. The scrubbed organic (loaded with gold) proceeds to the stripping circuit. At the prescribed operating conditions for scrubbing, the extent of scrubbing of various metal species from the loaded phase is shown in Table III.

Stripping

Gold is stripped from the scrubbed organic phase using de-ionized water to produce an aqueous loaded strip liquor from which gold is recovered during the precipitation step. Stripped organic is recycled to the extraction circuit. Table IV shows the extent of stripping achieved for selected metal species from the organic phase at the specified stripping operating parameters.

Precipitation

The gold content of the loaded strip liquor, typically containing 70 to 80 g/L gold, is reduced by the addition of a

Table III

Extent of impurity scrubbing

Element	Extent of scrubbing (%)
Fe	82
Zn	100
Cu	100

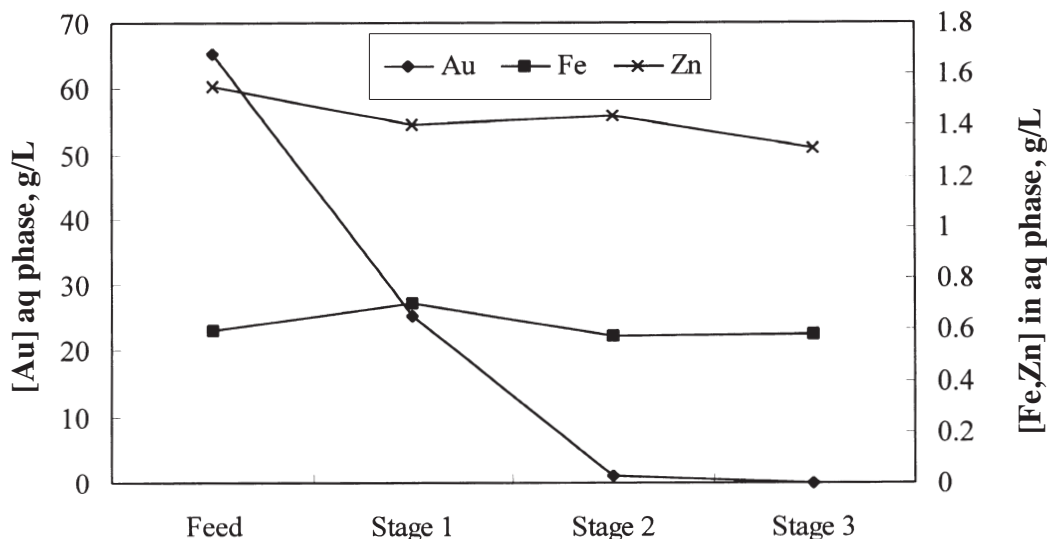


Figure 2—Gold, iron and zinc aqueous phase concentration profiles across the extraction bank

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Table IV
Extent of metal stripping from the organic phase

Element	Extent of stripping (%)
Au	99.8
Fe	100
Zn	100
Cu	100

suitable reductant. The purity of the gold product can be controlled to an extent by the reducing agent used. Oxalic acid has been found to be most successful at producing up to 99.999 per cent pure gold product. This is, however, an expensive reagent requiring heating for the reduction reaction to proceed at an appreciable rate. Sulphur dioxide can be reliably used to consistently produce a 99.99 per cent gold product. The barren solution exiting the precipitation step typically contains 10 mg/L gold, which can be recovered in downstream effluent treatment steps.

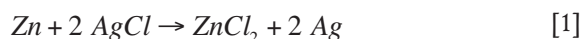
Silver electrorefining

The leach residue from the Minataur™ leach can contain up to 10 per cent gold, which is trapped in precipitated silver chloride formed during the leach. To recover this gold, the silver chloride is converted to metallic silver by the addition of zinc powder and this cementate is smelted to produce a metallic silver-gold alloy and a sodium borosilicate slag. The melt is poured into anode moulds to produce the anodes for silver electrorefining. In electrorefining, the silver is dissolved and then plated at the cathode in a purer form while the gold remains behind as a sludge, which is eventually returned to the Minataur™ leach for ultimate recovery.

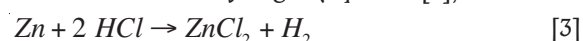
Zinc cementation

The acidic nature of the Minataur™ leach residue necessitates that it be neutralized before entering the pyrometallurgical step of smelting. Entrained hydrochloric acid will be volatilized in the smelting operation and can have serious health and safety implications as well as severely corroding equipment and infrastructure. It is also possible that chlorine could be evolved from the silver chloride during smelting, which would have health and safety implications and cause corrosion problems. The possible release of chlorine from the silver chloride and the aggressive nature of the chloride slag makes the hydrometallurgical reduction of silver chloride to silver metal attractive.

The leach residue is slurried with process water and the pH of the slurry is increased to ~ 5 using lime. Excess zinc powder is added slowly after neutralization to reduce most of the silver chloride to silver metal (Equation [1]). The zinc powder will also precipitate any soluble gold in the leach residue (Equation [2]).



Part of the zinc will dissolve due to the instability of zinc in water and will release hydrogen (Equation [3]).



Once all the zinc has been added, Minataur™ raffinate is added to the slurry to reduce the pH to ~ 2 to dissolve unreacted zinc. The slurry is allowed to settle and the supernatant solution is decanted. The solids are re-slurried with process water and the pH is increased to neutralize any remaining acid. This slurry is allowed to settle again and decanted. The remaining solids are filtered and washed to remove entrained solution. The solids do not filter easily and a compromise between washing efficiency and filtration time or area is necessary. The cake is dried before proceeding to smelting. Potential safety issues are also reduced by not using wet cementate in the induction furnace.

Smelting and anode casting

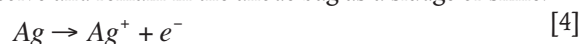
The dried cementate is mixed with sodium borate and silica and melted in an induction furnace. The composition is designed to have a liquidus of ~ 800°C and is superheated to 1200°C. The superheating allows good slag-alloy separation and the melt remains fluid during casting and produces thin anodes. The slag on the silver alloy prevents excessive oxidation of the silver at the metal-atmosphere interface and dissolves oxide impurities such as SiO₂ and ZnO.

The anodes are cast using a set of cascade moulds. Although these can be preheated using gas burners, they maintain their heat fairly well and within approximately two casts, remain hot enough to prevent excessive freezing of the melt.

The slag is brittle and glass-like and is removed by quenching the anodes in water as soon as they have solidified sufficiently to allow handling with leather gloves and tongs. The slag shatters off the anodes and stubborn bits of slag can be removed with a chisel or dremel.

Electrorefining of silver

The silver alloy anodes are electrorefined in conventional Thum cells using a nitrate electrolyte containing silver nitrate, sodium nitrate and nitric acid. Nitric acid and sodium nitrate are added for conductivity, although the nitric acid also prevents silver precipitation. Silver, and metals less noble than silver such as copper, nickel and lead, dissolve at the impure silver anodes to form their respective nitrates (Equations [4] and [5] respectively). Gold and PGM do not dissolve and remain in the anode bag as a sludge or slime.



At the cathode, the silver plates as dendritic crystals by the reverse of Equation [4]. The silver crystals are harvested on a regular basis by scraping them from the cathode at the bottom of the cell, over the lip of the cell and into a collection trolley. The crystals are washed with water and dried before packaging or further processing.

Impurities that have dissolved in the electrolyte from the anode generally do not plate at the cathode in sufficient quantities to compromise the purity of the silver, unless they are present in high concentrations. Once the impurity concentration is such that it will either plate out at the cathode or precipitate from the electrolyte due to saturation of the electrolyte, the cell electrolyte is removed from the cell and replaced with fresh electrolyte. The maximum tolerable

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impurity concentration depends on the grade of silver being produced and the nobility and kinetic characteristics of the impurity. In general, silver crystals of a purity of 99.9 per cent silver are produced and impurities are allowed to build up in the electrolyte until they negatively impact on the product purity. Copper, for example, can generally build up to approximately 80 g/L while lead can generally build up to approximately 5 g/L. However, these values can be affected by other impurities in the electrolyte.

Since the total current at the cathode and anode has to be equal, the concentration of silver in the cell will drop since more silver plates at the cathode than dissolves at the anode as a result of impurity dissolution at the anodes. As the silver concentration decreases, the maximum tolerable impurity concentration decreases and the impurities will plate in order of their nobility and the kinetics governing their deposition. For this reason, it is necessary to maintain the silver concentration in the electrorefining cell by the addition of concentrated silver nitrate solution.

As the anodes dissolve, insoluble gold sludge builds on the impure anodes and eventually prevents electrical contact between the anodes. It is thus necessary to switch off the cells and remove the sludge layer by rabbling the anodes periodically. Rabbling involves either moving the anodes relative to each other to scrape off the layer or brushing the anodes to remove the sludge. The amount of time between rabbling will depend on the purity of the silver anodes in terms of the gold and PGM content. The sludge collects at the bottom of the anode bag and periodically the bag needs to be emptied of this sludge, which is returned to the Minataur™ leach for recovery of the gold.

Provided that good contact is maintained between the anodes and that fresh anodes are continually added, it is possible to reduce the anodes to a fraction of their initial weight. The remaining mass is returned to the smelting step and is recast with the cementate.

Various methods of treating the fouled electrolyte exist for large silver refineries but the scale of the silver refinery of the Minataur™ plant generally does not lend itself to these techniques. It is often easier to merely precipitate the silver from the fouled electrolyte using salt and adding this silver chloride to the rest of the Minataur™ leach residue for cementation and further processing. The remaining fouled electrolyte is treated by the Minataur™ effluent treatment facility. Silver nitrate for the fresh electrolyte is made up from silver crystals produced in the cell and nitric acid. Peroxide is added to reduce the formation of NO_x gases and, once the silver has dissolved, sodium nitrate is added for conductivity.

Once the silver crystals have been recovered and washed, it is possible to cast them into silver bars or to produce further value-added products such as silver nitrate crystals, which are used predominantly in photographic plates, and silver cyanide, which is used in the electroplating industry.

Value addition

Downstream gold fabrication that can be attached to a Minataur™ refinery include investment bar casting, gold wire drawing, manufacture of jewellery items and gold potassium cyanide production. Mintek has also developed related technologies, including feed preparation by atomization, granule and bar casting, and gold chemical manufacturing to complement the basic technology. A new

facility to produce ultra-pure 'five nines' (99.999 per cent) gold, which is used in the electronics industry, has been commissioned. Specific advanced industrial applications of gold, such as alloy manufacturing for the jewellery industry, products for the electronics industry, and powder metallurgy are also being investigated.

Effluent treatment

Effluent streams originating from the Minataur™ process include the raffinate bleed from the SX step, fouled electrolyte from silver electrorefining and gold precipitation barren solution. Residual gold is precipitated from these solutions prior to being neutralized for disposal. Sodium metabisulphite is typically used to reduce the Au content of effluent solutions in a 2-tank cascade arrangement. Base metals can subsequently be precipitated from these solutions to produce clarified solutions that adhere to environmental specifications.

Conclusion

The Minataur™ process has been proven as an alternative to conventional processes for refining gold. The Inco Europe Ltd. process also employs solvent extraction as an alternative to electrorefining but the process suffers high organic losses due to difficult direct-reduction stripping of the loaded organic phase. A similar leach-SX-precipitation process using DBC as the extractant in Brazil proved the conventional electrorefining process more economically viable due to the expense and high aqueous-solubility of the organic extractant employed.

The Minataur™ process employs a relatively cheap extractant that is highly selective for gold and easily stripped with de-ionized water. The purified liquor produced by the SX step can be further purified by selective precipitation with sulphur dioxide to consistently produce 99.99 per cent pure gold or oxalic acid to produce 99.999 per cent pure gold products. The product is amenable to various further value-adding process routes.

Silver refineries have been installed together with Minataur™ gold refineries in five locations throughout the world. Of these refineries, three have been commissioned in Africa although one is not operational due to lack of feed stock. A Minataur™ gold refinery, with the associated silver refinery, has been installed in Italy together with a silver cyanide plant but these have not been commissioned due to lack of feed stock. A Minataur™ gold refinery and associated silver refinery are due to be commissioned in the United Arab Emirates during the first half of 2004.

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