GOLD MINING IN WAIHI

Gold is well known as a rare and precious metal which is very valuable and is used to make jewellery. Almost as much gold is used in the electronics industry because it can easily be molded or drawn out into very fine wires, is resistant to corrosion and conducts electricity almost as well as silver.

Gold is obtained by mining gold ore and then extracting the gold from it in a three step process as follows.

Step 1 - Leaching
Gold-containing rock is ground up and mixed with water. Gold is leached from the rest of the rock by reacting it with cyanide and oxygen:

$$4Au(s) + 8CN^-(aq) + 2H_2O(l) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

Step 2 - Concentration
The gold is removed from the solution by adsorbing it onto the surface of activated carbon. Most of the impurities are left behind in the solution.

Step 3 - Gold refining
Gold is stripped off the carbon by mixing it with NaCN and NaOH at 110^{o}C forming a new solution of cyanide and gold. The gold is then converted back to elemental gold in the following electrolysis reactions:

At the anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

At the cathode: $e^- + Au(CN)_2^- \rightarrow Au^0 + 2CN^-$

The pure gold is remelted and poured into moulds to make ingots.

INTRODUCTION

Gold occurs in nature in elemental form, and it is for this reason that it was probably the first metal known and used by man. Through the ages it has been treasured because of its colour, its extraordinary ductility and its resistance to corrosion. In addition, it has been used in medicine and dentistry from the times of the ancient Chinese and Egyptians to the present day. The intense but unsuccessful efforts of alchemists in the Middle Ages to convert base metals into gold built the foundations on which modern chemistry has been built.

Most of the gold produced commercially is mined from sedimentary or igneous rock, as 75 - 90 % of the gold found in these rocks is in the pure metallic state. Base metal sulfides, selenides and tellurides are usually also present along with variable quantities of silver. Some gold (as well as some silver and platinum) is also obtained from the anode slimes from electrolytic copper and nickel refining.

Uses of gold
Gold is the archetypal precious metal and as such it is sometimes stored as a monetary reserve. It was once the case that most currencies in the world were gold-backed (i.e. gold to the value of all the paper and coin money in circulation was stored by the Reserve Bank of that country), but this remains true in very few countries today.

Aside from this the most common current use of gold is in the jewellery industry. In addition, due to its high ductility, corrosion resistance and electrical and thermal conductivity it is widely used in the electronics industry for coating connections to provide good contact and corrosion resistance. Gold-based medicines are also one of the few drugs that are helpful in the treatment of rheumatoid arthritis.

THE GOLD EXTRACTION PROCESS

Gold is found very sparsely distributed throughout the Earth's crust, and even in the areas in which it is concentrated enough to be economically mined the deposits are of the order of 3 g/t. For this reason, the gold extraction process is largely a series of concentration steps. As gold and silver usually occur together and have similar chemistry, these steps do not usually separate the gold and silver.

The ore used by the Waihi Gold Mining company contains, on average, 2.9 g/t gold and 30 g/t silver. These are separated from the surrounding ore firstly by oxidising them in the presence of cyanide. The gold and silver form soluble cyanide complexes that separate them from the surrounding rock and bring them into solution. In the second stage the gold and silver complexes are adsorbed onto activated carbon, leaving most of the impurities behind in solution. Finally they are dissolved off the carbon into a cyanide solution then electrolysed and smelted to give ingots made of a 1:10 mixture of gold and silver. Annually approximately 75 000 ounces (2100 kg) of gold and 650 000 ounces (18 000 kg) of silver are produced in New Zealand in this way.

Step 1 - Leaching

Gold ore from the mine is crushed and then sent to the mill, where the ore is ground down to a fine particle size. As part of the milling process, water is added to the mill with the ore so that a slurry is formed. This slurry is mixed with a sodium cyanide solution and aerated and agitated in tanks. The cyanide causes the normally unreactive elemental gold to be oxidised by the oxygen. This Au^+ then forms a complex with the cyanide. The overall reaction occuring is as follows:

$$4Au(s) + 8CN^- (aq) + 2H_2O (l) + O_2 (g) \rightarrow 4[Au(CN)_2]^- (aq) + 4OH^- (aq)$$

The less alkaline the slurry is, the better the leaching that will occur. The Waihi Gold Mining Company maintains its slurry at a pH of 10.1[1], at which level HCN formation is minimised (thereby ensuring the safety of the employees and reducing cyanide losses) and the best

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[1] $pK_a(HCN) = 9.22$, thus at pH 10.1 $[CN^{-}]$[HCN] >> 1.

$$\frac{[CN^-]}{[HCN]} = \frac{10^{-pKa}}{10^{-pH}} = \frac{10^{-9.22}}{10^{-10.1}} = 7.6$$

meaning that there is 7.6 times as much cyanide and hydrogen cyanide present at this pH.

leaching rate possible is obtained. This leaching process is known as the MacArthur and Forrest gold cyanide process.

Step 2 - Concentration
Once the gold has been leached into solution there remains the problem of how to return it to its elemental form. This is usually done by treating the solution with either activated carbon[2] or zinc powder.

The method used by the Waihi Gold Mining Company involves adsorbing the gold onto activated carbon. The mechanism *via.* which this proceeds is not yet fully understood, but proposed mechanisms include:

- $Au(CN)_2^-$ adsorbing *via.* "anion exchange" with some anionic species on the carbon
- $Au(CN)_2^-$ precipitating onto the carbon as insoluble AuCN
- $Au(CN)_2^-$ reducing onto carbon as metallic gold within the pore structure

Once the gold has adsorbed onto the carbon the carbon is removed from the tanks by screening. By this stage the gold has been concentrated from 2.9 g t^{-1} to about 700 g t^{-1}. This level is below average on a world scale because the ore used by the Waihi Gold Mining Company has unusually high levels of silver, and the two metals are being purified together.

Step 3 - Recovery
The activated carbon on which the gold is adsorbed is mixed with a solution of NaCN and NaOH at 110°C. This strips the gold from the carbon and returns it to solution. The solution contains gold and silver ions and is known as loaded electrolyte. It differs from the earlier cyanide solution in that all the impurities (other than silver) that were present there are no longer present in this new solution.

The elemental gold and silver are then recovered from solution in an electrolytic process known as "electrowinning". The loaded electrolyte is sent to electrolytic cells in which gold and silver are won onto stainless steel electrodes or precipitated out as a fine black mud. The reactions occuring are as follows (although gold is used in this example the silver reactions are the same):

At the anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

At the cathode: $e^- + [Au(CN)_2]^- \rightarrow Au + 2CN^-$

And hence overall: $4OH^- + 4[Au(CN)_2]^- \rightarrow 4Au + 8CN^- + O_2 + 2H_2O$

The 'mud' is smelted and then poured into ingots and sent to Western Australia for refining into pure gold and silver.

An alternative method involves mixing zinc powder into the solution. This is an example of a metal displacement reaction as the gold and zinc change places as follows:

[2] Activated carbon is a highly porous carbonaceous substance containing millions of tiny interlocking pores. It is produced either by charring coconut shells or by extruding peat at between 700 and 800°C in the presence of steam. Activated carbon has an extremely high surface area.

$$2[Au(CN)_2]^-(aq) \; + \; Zn(s) \; \rightarrow \; [Zn(CN)_4]^{2-}(aq) \; + \; 2Au(s)$$

A fine black 'mud' of gold, silver and residual zinc precipitates from the solution. The silver and zinc are leached out with acids while the less reactive gold remains untouched. The gold is melted and formed into ingots.

THE ROLE OF THE LABORATORY

The laboratory is involved throughout the gold mining processes: in determining the composition of ores from new locations to establish whether they are worth mining; in conducting in-process tests for quality control and in testing wastewaters to ensure that they are safe to release into the environment.

Pre-mining

Before any ore is mined in a given area, samples of ore are taken on a grid pattern and tested to determine their gold content. The ore is ground finely, mixed with a cyanide solution and agitated so that the gold oxidises and forms a cyanide complex. The slurry is then centrifuged and the supernatant liquid (which contains all the gold originally present in the rock sample) is aspirated into an AA Spectrophotometer[3] to determine its gold content. The samples that are used in this testing must be large (up to a kilogram) to prevent inaccuracies due to what is known as the "spotty gold" effect. Gold is highly malleable, so the grinding machinery used to mill the ore simply squashes the gold particles present. The gold is thus distributed unevenly within the sample, and this effect is known as the "spotty gold" effect. Because of this large samples must be taken to ensure that they are representative.

In-process testing

Throughout the extraction process, samples of gold-bearing solutions, solids and activated carbon are removed for analysis to determine the efficiency of the process. The compositions of solutions are determined simply by aspirating them into an AA Spectrophotometer. The solids and the carbon samples are fire assayed to determine their gold content and digested with *aqua regia* to determine their silver content.

Gold determination

The solid to be measured is ground in a crucible containing a flux of borax ($Na_2B_4O_7$), soda ash (Na_2CO_3), silica flour, litharge (PbO) and silver nitrate. The flux lowers the melting point of the sample so that the entire sample becomes liquid during firing. The ground solid is then heated in a furnace to 1000^{o}C for an hour. Everything liquifies and the litharge forms into small globules of metallic lead. The globules fall through the surrounding liquid, forming an amalgam with any other metals they come into contact with. After an hour has passed the contents of the crucible are poured into a conical mould to cool down. As the lead amalgam is more dense than the surrounding material it quickly settles to the tip of the conical mould and solidifies along with the glass-like remains of the silicate ore.

When this cone has cooled, the lead tip is separated from the glass and 'cupelled'. Cupellation involves placing the lead 'button' onto a preheated porous surface known as a cupel. The cupel is heated to 1000^{o}C, at which temperature the metals liquify and the lead is

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[3]Atomic Absorption Spectroscopy (AAS) is discussed in the sewage treatment article.

absorbed into the cupel. Gold and silver have a higher surface tension than lead so they are not absorbed and remain as a small 'prill' in the bottom of the cupel. The cupel and prill are then removed from the surface and allowed to cool.

The prill is dissolved in *aqua regia* (a 3:1 mixture of hydrochloric and nitric acids) to oxidise the gold and bring it into solution. The resulting solution is aspirated into an AA Spectrophotometer to determine the gold content.

Silver determination
Silver in the solids and carbons is determined by digesting the sample with *aqua regia*: predetermined amounts of the two acids are added to the sample to dissolve it and it is placed on a heating block to digest. When completed, the resulting solution is diluted and then aspirated into an AA Spectrophotometer.

Waste water testing
Waste water samples taken from the treatment process are monitored thrice daily to ensure that the process is working well and there is no chance of contaminating the Ohinemuri River with cyanide or heavy metals.

ENVIRONMENTAL IMPLICATIONS

Gold mining and extraction presents two main potential environmental problems: cyanide emissions (to the air or water) and heavy metal contamination of waterways. Gaseous emissions of cyanide are limited by keeping cyanide solutions basic. Hydrogen cyanide is not emitted from these solutions because the cyanide is largely present as the cyanide ion CN^- rather than the HCN molecule (see above).

Wastewater is treated in a separate water treatment plant. Two separate streams of water are treated in this plant: mine water and process water. The process water contains heavy metals and cyanide, while the mine water simply contains heavy metals.

Firstly the cyanide is removed from the process water by oxidation to cyanate with hydrogen peroxide using a copper sulfate catalyst:

$$CN^- + H_2O_2 \xrightarrow{CuSO_4} CNO^- + H_2O$$

The cyanate is then hydrolysed by water to harmless carbonate ions:

$$CNO^- + 2H_2O \rightarrow CO_3^{2-} + NH_4^+$$

The process water then joins the mine water (and any storm water collected on site) and is treated to remove heavy metals. This is done by treating the water with lime to increase the pH and precipitate out the metals as their hydroxides:

$$M^{2+}(aq) + SO_4^{2-}(aq) + Ca^{2+}(aq) + 2OH^-(aq) \rightarrow M(OH)_2(s) + CaSO_4(s)$$

Ferric chloride is then added to the water to coagulate the precipitates, the solution is left to settle and the solids removed in clarifiers. The water is then transferred to holding ponds for testing before being released into the Ohinemuri River.

The plant has the capacity to treat 4 500 m^3 day^{-1} process water and 5 000 m^3 day^{-1} mine water.

Article written by David Yuen from information supplied by Diana Ligman and Doreen McLeod (Waihi Gold Mining Company Ltd.) and with reference to:

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