

CYANIDE RECOVERY

CYANIDE RECOVERY TECHNOLOGY COMPARISON

Legislation in most gold mining regions of the world demands that gold plants meet rigorous environmental standards with respect to cyanide. These requirements can be met either by destroying cyanide after a single pass through the gold plant or by recovering cyanide from the tailings and recycling it to leaching.

Although cyanide recovery processes are not yet widely practiced, the technologies are fairly simple, both from chemistry and process engineering perspectives, and they have the potential to yield significant economic and environmental benefits.

AVAILABLE TECHNOLOGIES FOR CYANIDE RECOVERY

There are several processes for recovering cyanide from gold plant tailings that are available to the mining industry.

- Cyanisorb
(AVR: Acidify, volatilize and reneutralize)
- SART
(Sulphidize, acidify, recycle and thicken)
- Hannah
(Strong base resin extraction of free cyanide and metal cyanide species)
- AuGMENT
(Strong base resin extraction of copper and cyanide).

SGS metallurgical group has been involved in the development of all of these processes and can determine the advantages and disadvantages of each.

COST EFFECTIVENESS IS CRITICAL

The cost of cyanide consumption and destruction can be a significant percentage of total operating costs on a gold plant, and unlike other operating costs, yields no economic “return”. The choice of the best strategy for handling cyanide in the tailings can therefore have a major influence on the economic health of a project. The economic impact of cyanide is different in every operation, but it is possible to compare cyanide destruction and cyanide recovery costs for a fairly generic high cyanide-consuming case.

The capital cost of a cyanide recovery plant could pay back in less than 2 years in many cases, particularly when high cyanide consumption is associated with copper mineralisation in the ore. As a broad generalisation, cyanide recovery will produce more favorable economics than cyanide destruction in those cases where potentially recoverable cyanide consumption is greater than 1 kg/t NaCN, or exceeds 1000 tons NaCN per annum.

WHY RECYCLE CYANIDE?

LOWER COSTS

- Recycled cyanide is 2-3 times cheaper than new cyanide.
- Reduced detoxification costs.
- Opportunity to sell by-products such as copper sulphide.

LESS ENVIRONMENTAL RISK

- Reduced loading of potentially harmful salts in the tailings and recycle water (e.g. CNS, CNO, NH₃ and metal cyanides).
- Less new cyanide is needed, so there is less transported, stored and handled, reducing the risk of spills.

BASE CASE ECONOMICS (1kg/t NaCN CONSUMED, 0.4 kg/t Cu LEACHED) (PRICES AS OF 2005)

Cyanide destruction		Cyanide recovery	
New NaCN	\$1.50	operating	\$0.60
Destruction	\$1.00	capital	\$0.30
	\$2.50	Subtotal	\$0.90
		Cu credit	\$0.40
		TOTAL (\$/t)	\$0.50

WHAT CAN AND CANNOT BE RECOVERED?

FREE CYANIDE	CYANATE
Cyanide Complexes of Cu, Zn, Ni, Cd and Co ²⁺	Cyanide Complexes of Fe and Co ³⁺
Thiocyanate*	

*Thiocyanate can be oxidized to regenerate the contained cyanide units, but the cost of oxidation exceeds the value of the recovered cyanide.

COMPARISON OF CYANIDE RECOVERY METHODS

CYANISORB (AVR)

The Cyanisorb process uses the well-known AVR technique (Acidification, Volatilization and RENEUTRALIZATION).

Gold plant tailings are first acidified with sulphuric acid to a pH of 6-7 to convert all the free cyanide to hydrocyanic acid. The tailings are then contacted with air, in a counter-current flow, in a baffled vertical column. The HCN is stripped from the tailings into the gaseous stream, and the air/HCN stream is recycled through a second column containing a strong caustic solution. This solution absorbs the HCN gas from the air by converting it back to free cyanide ions. The air then cycles back to the stripping column. Once the caustic solution in the scrubbing column has converted to a sufficiently high cyanide strength, it is recycled to leach.

The Cyanisorb process is the only commercially-practiced technology for cyanide recovery. Michael Botz of Elbow Creek Engineering developed the technology so that it could be scaled up for commercial operation. About five plants have been built over the years, but only two are currently operating at mines worldwide. Where plants have closed, this has been due to cessation of gold operations for one reason or another, not because of technical problems with the cyanide recovery part of the process. SGS offers this technology via an AVR pilot plant, designed and built by Michael Botz.

Advantages

- Established and proven on a fairly large scale.
- Can be applied to solutions or pulps, although pulps are difficult to treat and suffer high cyanide losses.

Disadvantages

- Only recovers free cyanide. Cyanide associated with Cu, Zn or Ni complexes must be recovered by alternative means.
- Difficult to strip the final 20 to 50 mg/L of cyanide from the tailings.
- Stripping columns are large and costly with respect to both capex and opex. This is particularly true in the case of pulp.
- Stripping columns have scaling problems and require frequent maintenance.
- Large volumes of gas flow through the stripping and scrubbing columns. This HCN/air mixture is potentially hazardous, and the operation must be carefully engineered and controlled to ensure there can never be gas release.

SART (SULPHIDIZATION, ACIDIFICATION, RECYCLING AND THICKENING)

The SART process was developed to treat solutions containing cyanide in the form of weak acid dissociable (WAD) metal complexes (primarily copper cyanide, but also zinc or nickel cyanide). During sulphidization and acidification, the cyanide solution is treated with sulphide ions and sulphuric acid to yield a pH of 4 - 5. Under these conditions,

the base metals precipitate from solution as sulphides (e.g. Cu₂S or ZnS), leaving cyanide in solution as HCN gas. The metal sulphide precipitate is flocculated, thickened and filtered, to produce a saleable concentrate. Recycling of a portion of the thickener underflow back to the primary sulphidization/acidification reactor increase the particle size of the precipitate and improve its thickening/filtration properties. The thickener overflow and the filtrate (containing HCN gas) are treated with lime slurry to raise the pH to about 10. This converts the HCN back to free cyanide, which is recycled to leach.

The SART process is especially suited to the treatment of heap leach liquors that contain elevated concentrations of base metals as WAD cyanide complexes. SART can also be used to treat the tailings from milling operations, such as CIP, CIL or Merrill Crowe barrels. However, because the SART process regenerates free cyanide at essentially the same concentration as in the tailings, the cyanide cannot be recycled without creating a water imbalance in the plant. The excess water will contain cyanide, and must be treated via a cyanide destruction process prior to discharge.

The SART process was developed by SGS' metallurgical group in collaboration with Teckcominco Corporation.

Advantages

- Simple to engineer and operate.
- No HCN volatilization, which means a safer working environment.
- Valuable by-products can be recovered.
- All WAD cyanide is regenerated as free cyanide for recycle.

Disadvantages

- Can only treat solutions. Therefore, the process is not well suited to the treatment of CIP or CIL tailings pulps, unless they are separated into solution and solid streams prior to cyanide recovery. In this case, the wash water introduced during solid/liquid separation must be bled from the process, and the cyanide in the bleed stream is 'lost'.

HANNAH PROCESS

The Hannah process uses a strong base resin to extract and concentrate free cyanide and metal cyanide complexes from gold plant tailings solutions or pulps. The cyanide and base metals are eluted from the resin into a small, concentrated eluate stream, which is processed to remove metals as sulphide complexes, and then recycled directly to leach after neutralization with lime. The eluted resin is regenerated with acid and recycled to adsorption.

The Hannah process is particularly well suited to the treatment of solutions containing copper cyanide, but it can also handle free cyanide, other metal cyanide complexes, and even the thiocyanate anion.

The Hannah Process was developed by SGS' metallurgical group and John A. Thorpe of Thorpe Consulting.

Advantages

- Process treats solutions or pulps with equal efficiency.
- The efficiency of recovery of free cyanide and WAD cyanide complexes in tailings is very high (95 to 99%).
- No HCN volatilization, resulting in a safer working environment.
- Relatively simple to engineer and operate.
- Valuable by-products can be generated.
- No water-balance problems.

Disadvantages

- No known technical disadvantages.
- Not operated yet at commercial scale.

AUGMENT PROCESS

The AuGMENT process uses a strong base resin to extract and concentrate copper cyanide from gold plant tailings solutions or pulps. AuGMENT is particularly well suited to solutions containing copper cyanide at a low CN:Cu ratio of ~3:1, although it can handle higher CN:Cu ratios by advancing resin more rapidly through the adsorption plant.

Copper cyanide is partially eluted from the resin using a strong copper cyanide solution with a relatively high CN:Cu ratio (>4). The eluate is then treated in an electrowinning cell to plate copper metal and regenerate cyanide. The oxidation of cyanide in the electrowinning cell is avoided by pouching the anodes in ion exchange membrane bags. Caustic is pumped into the bags to neutralize the acid generated at the anode. A bleed stream of electrolyte/eluate is acidified to precipitate and remove copper (as CuCN) and regenerate free cyanide for recycle to leaching. The partially eluted resin is regenerated with acid and recycled to adsorption.

The AuGMENT process was developed by SGS' metallurgical group and DuPont Corporation.

Advantages

- Treats solutions or pulps with equal efficiency.
- The efficiency of cyanide recovery from free cyanide and copper cyanide complexes in tailings is very high (95 to 99%).
- No HCN volatilization, resulting in a safer working environment.
- Valuable by-products can be generated.
- No water balance problems.

Disadvantages

- Operation is critically dependent on the rapid analysis and control of the cyanide to copper ratio, in adsorption, elution and electrowinning. As a result, the process will be fairly difficult to monitor, control and operate consistently and efficiently.
- Vulnerable to feed composition changes.
- Not yet operated on a commercial scale.

THEORETICAL CONSIDERATIONS

To remove cyanide and cyanide-bearing complexes from gold plant solutions, the tailings can either be treated directly, as in the Cyanisorb and SART processes, or they can be processed with an ion exchange resin prior to recovery, as in the Hannah and AuGMENT processes. The Hannah and AuGMENT processes upgrade the cyanide strength by the concentrating effect of loading onto the resin, while the Cyanisorb process upgrades the cyanide strength by the AVR process. The SART process recycles cyanide without upgrading.

DIRECT TREATMENT OF CYANIDATION TAILINGS

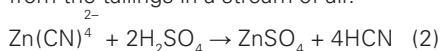
Free Cyanide

If the cyanide is present in the tailings as free or weakly-complexed cyanide (pKa = 9.4), more than 99% of the cyanide is converted to HCN gas by simply lowering the pH of the tailings to about 7. The cyanide is then recovered by air-stripping of the HCN gas from the tailings into an alkaline scrubber.



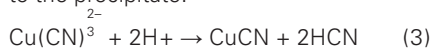
Zinc, Copper, Nickel

If, however, the cyanide is present as a metal cyanocomplex, the pH must be reduced to more acidic values (which vary with the strength of the complex) to break down the complex and produce HCN gas. The weak zinc cyanide complex ($\log \beta_4 = 17.4$), for example, dissociates completely at about pH 5, producing zinc sulphate and 4 moles of HCN. Once again, cyanide is recovered by stripping the HCN gas from the tailings in a stream of air.



The copper cyanide complex does not break down completely even in strong acid solution, unless there is an oxidant present in the solution.

In the absence of oxidant, the tricyano copper species (which is the most stable copper complex under normal cyanidation conditions: $\log \beta_3 = 28$) decomposes to CuCN precipitate plus two moles of HCN, at pH values less than 3. Hence, a third of the potentially recoverable cyanide is lost to the precipitate.



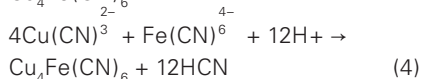
The nickel tetracyanide complex ($\log \beta_4 = 30$) also requires a pH value of less than 3 to dissociate and liberate HCN gas, in a reaction equivalent to equation (2).

Iron and Cobalt

The very strong ferrocyanide ($\log \beta_6 = 35$), ferricyanide ($\log \beta_6 = 44$) and cobaltcyanide complexes ($\log \beta_6 = 64$) do not break down at all, even in strong acid solutions, without destroying the cyanide.

Copper and Ferrocyanide

In situations where both ferrocyanide and cuprous cyanide are present in the same cyanide leach liquor (which frequently occurs with high cyanide-consuming ores), treatment of the solution with acid to pH <4 produces a double metal cyanide precipitate such as $\text{Cu}_2\text{Fe}(\text{CN})_6$ or $\text{Cu}_4\text{Fe}(\text{CN})_6$.



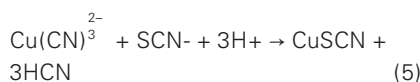
The $\text{Cu}_4\text{Fe}(\text{CN})_6$ species is formed under oxygen-starved conditions in solution, whereas $\text{Cu}_2\text{Fe}(\text{CN})_6$ is formed in a well-aerated solution. From the stoichiometry

of equation (4), it can be seen that the ferrocyanide molecule releases the third molecule of CN from the copper tricyano complex, so the presence of ferrocyanide results in increased recovery of cyanide from the copper cyanide species. The analogous zinc-iron double metal cyanide complex, $\text{Zn}_2\text{Fe}(\text{CN})_6$, is formed under acidic conditions when zinc tetracyanide and ferrocyanide are present in solution.

Copper and Thiocyanate

When both copper cyanide and thiocyanate anions are present in the cyanide leach solution, which frequently occurs during leaching of gold ores that contain reactive copper sulphide minerals, the following reaction takes place in addition to reactions

(1), (3) and (4):



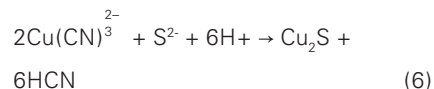
The solubility product of the CuSCN species ($K_{sp} = 1.8 \times 10^{-13}$) is higher than that of the CuCN species ($K_{sp} = 3 \times 10^{-20}$), which means reaction (3) should be favored over reaction (5). However, at low pH values ($\text{pH} \leq 2$) and low HCN concentrations (as in the AVR process), reaction (5) is favored over reaction (3). There are several important advantages of a process utilizing the reaction (5) chemistry over that shown in reactions (3) and (4):

- All three molecules of CN per molecule of copper are released for recovery and recycling, versus two molecules of CN in the CuCN process.
- The precipitate contains no cyanide, and thus is more acceptable as smelter feed.
- There is a bleed for thiocyanate. Otherwise, this reports to the final tailings and could become an environmental issue.

Copper and Sulphide

As an alternative to reactions (4) and (5), for situations where there is insufficient ferrocyanide or thiocyanate in solution ($\text{Cu} > \text{Fe}$, SCN), sulphide ions can be added to the cyanide leach solution to achieve the same objective. In this case,

the formation of cuprous sulphide (or synthetic chalcocite) is favored because of its extremely low solubility ($K_{sp} = 2.3 \times 10^{-48}$). The following reaction takes place:



This reaction is irreversible at low pH ($\text{pH} < 4$) and takes place quantitatively with stoichiometric additions of sulphide ions and acid. Reaction (6) forms the chemical basis of the SART process.

Resin-Based Treatments of Cyanidation Tailings

It is often inconvenient, costly or inefficient to recover cyanide directly from gold plant tailings. This is the case if the tailings pulp is difficult to separate into solid and liquid components (as occurs with high clay, slimy, viscous ores) and also if the tailings solids are high acid-consumers. In these situations, direct acidification of the tailings results in high operating costs (due to high acid consumption) and inefficient cyanide and copper recovery (due to the loss of CuCN precipitate to the tailings). Air stripping of HCN from slurry is also inefficient, requiring a relatively long residence time in the stripping column and high air flowrates.

Anion exchange resins can play a very valuable role in these situations. The resin in pulp process is a well-developed, industrial process, which presents the opportunity to recover cyanide directly from pulp tailings, circumventing solid/liquid separation processes. Moreover, conventional, commercial strong-base resins are well-suited to this application.

The most common cyanide species in gold plant tailings are free cyanide anions (usually 100-500 mg/L) and the cyano complexes of copper, zinc, iron and sometimes nickel. The free cyanide anion has a very low affinity for anion-exchange resins, and can only be extracted efficiently after all the metal cyanide complexes plus most other anions (especially thiocyanate) have been extracted. However, free cyanide can be efficiently extracted if it is pre-complexed with a metal ion such as zinc (or copper)

prior to ion exchange, as discussed below.

The ability of anion exchange resins to efficiently extract copper, zinc and nickel cyanide, as exemplified in the adsorption isotherms shown below, presents an opportunity to recover these complexes when they are present in the tailings of a gold plant.

Nickel cyanide is uncommon in gold plant tailings, while cobalt and iron cyanides form such stable complexes that it is impossible to break them down without simultaneously destroying the cyanide ion. Thus, these complex anions can be efficiently extracted from gold plant tailings by ion exchange, making the tailings amenable for direct discharge to the environment, but they do not yield their cyanide for recycling.

Zinc Cyanide and Free Cyanide Recovery

Zinc cyanide is found in many gold leach circuits, particularly those employing Merrill Crowe for final gold recovery. Although zinc cyanide is a weak complex (log β₄ = 17.4) and yields its cyanide ions to the stronger aurocyanide complex (log β₂ = 38.3) during gold leaching, the build up of zinc must be controlled to minimize the total cyanide concentration in the circuit.

This is usually done by taking a bleed stream to a cyanide destruction plant.

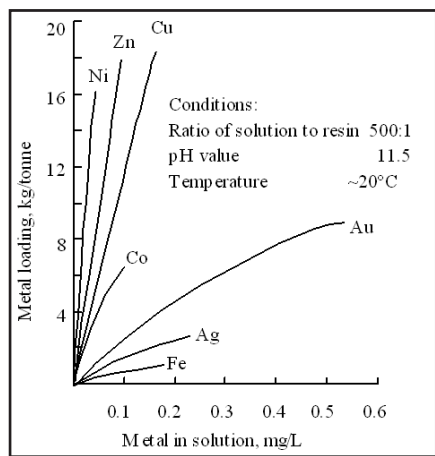
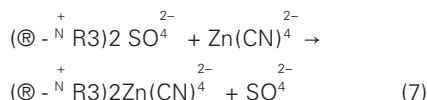


Figure 2: The equilibrium loading of various metal cyanide complexes from a plant leach liquor onto a strong-base resin, A101Du.

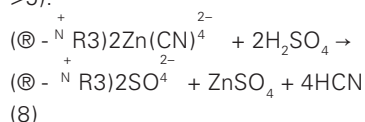
However, cyanide recovery via an ion exchange process will produce superior economics in most cases.

Zinc cyanide loads onto a strong base anion exchange resin via the following stoichiometry:



where the symbol ® represents the resin matrix. The process is very efficient because of the great affinity of strong base resins for the zinc cyanide complex (Figure). Resins are capable of loading to capacity (30-40 g/L zinc, 50-65 g/L cyanide) from quite dilute zinc cyanide solution (<100 mg/L Zn), and are able to produce very low levels of cyanide in the final effluent (<1 mg/L). It should be apparent from the stoichiometry shown in equation (7) that each resin functional group carries two cyanide ions, versus only one CN per functional group if cyanide were loading as the free cyanide ion.

To elute the zinc cyanide, the loaded resin is treated with sulphuric acid, which breaks down the zinc cyanide complex completely, producing zinc sulphate and HCN gas in solution. If the acid solution (100-150 g/L H₂SO₄) and the resin are moved countercurrent to one another, it is possible to produce a strong HCN solution (>5% HCN) containing no excess acid (pH >5).

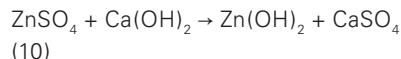


The HCN gas is volatilized from the regenerant solution in a stream of air, which is scrubbed in lime or caustic solution to recover the cyanide as the usable free cyanide ion. Because of the high concentration of HCN in the regenerant solution, the size of the stripping column will be relatively small compared to an AVR plant treating tailings solution directly.

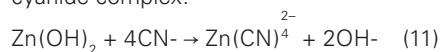


The barren regenerant solution can also be treated with lime or caustic to precipitate zinc hydroxide for sale, discard

or recycling.



This process chemistry is also very readily applied to free cyanide recovery. The zinc hydroxide recovered by neutralization of the barren regenerant (equation 10) can be recycled back to the feed to the ion exchange plant (i.e. the gold plant barrens), where it will readily react with free cyanide ions to produce the zinc cyanide complex:



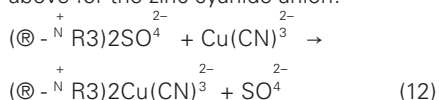
The process chemistry then follows equations 8 to 11, and the economics are the same, as zinc is not consumed in the process.

The only reagents consumed are sulphuric acid (0.5 mole per mole cyanide recovered, or 1 kg H₂SO₄/kg NaCN) and lime (0.5 mole per mole cyanide, or 0.75 kg Ca(OH)₂/kg NaCN).

Copper Cyanide Recovery

Ion exchange resins offer a unique opportunity to not only recycle the cyanide associated with the copper complex, but to also generate revenue via the sale of the copper itself. This revenue will, in many cases, offset the operating costs of the cyanide recovery plant, and the technology has the potential to transform uneconomic ore bodies into exciting opportunities.

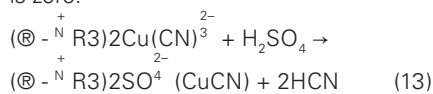
The dominant copper cyanide species in cyanide leach solutions is the tricyano complex, which has a great affinity for strong base resins. The loading mechanism is the same as that shown above for the zinc cyanide anion:



and the capacity of a typical, fully-loaded resin for copper (30-40 g/L) and cyanide (40-50 g/L) is also similar.

However, when an acid-stripping reaction analogous to that shown in equation (8) is carried out, the copper remains in the resin phase. The reason for this is the fact that the stable precipitate CuCN is formed (equation 3), and only two moles of cyanide are released per mole of copper. When this reaction is carried

out on copper cyanide that is loaded onto an anion exchange resin, the two moles of cyanide are liberated, but the CuCN precipitate remains trapped in the resin pores, and net copper elution efficiency is zero.



This fairly unique chemistry has been turned to advantage in the AuGMENT process, wherein CuCN is intentionally precipitated in the pores of a conventional strong base resin and, in this form, produces a regenerated resin that is an efficient adsorbent for free cyanide ions and soluble copper cyanide.

Similar processes had been developed previously to recover free cyanide with CuCN precipitated in the pores of an anion

exchange resin, by essentially maintaining the concentration of copper in the resin at steady state. However, these processes were unable to handle copper cyanide in the feed, as they did not incorporate a cost-effective method of eluting copper from the resin. This problem has now been overcome in the AuGMENT process, wherein copper cyanide is eluted from the resin with a strong copper cyanide solution at a relatively high CN:Cu molar ratio (~4:1). Elution is coupled with electrolysis, and the AuGMENT process produces cathode copper.

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