A REVIEW OF COPPER CYANIDE RECOVERY FOR THE CYANIDATION OF COPPER CONTAINING GOLD ORES

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ABSTRACT

With the depletion of simple cyanide treatable ores, many gold producers are today processing gold ores with increasing soluble copper. Typically, the result of this is a requirement for cyanide destruction to prevent the discharge of copper cyanide into tailings storage facilities. This imposes a significant financial cost to producers from the additional cyanide used to solubilise the copper and the cost of cyanide destruction reagents. Therefore, the recovery of copper as a valuable by-product and the recycle of cyanide to the leach circuit have the potential for significant economic and environmental benefits. This includes enabling the treatment of gold ores with even higher soluble copper. Over the years, a variety of processes have been developed or proposed to recover the copper and/or cyanide including acidification based technologies such as AVR and SART, direct electrowinning, activated carbon, ion exchange resins, solvent extraction, polychelating polymers, and membrane technologies. In this paper, these processes are critically reviewed and compared with particular focus on the advantages and limitations in the challenge of recovering and separating copper from cyanide. Ultimately, there is no universal process solution and the choice is highly dependent on the nature of the stream to be treated and integration with the whole plant.

CYANIDATION OF COPPER CONTAINING GOLD ORES

Due to the dwindling resources of simple cyanide extractable gold deposits, a large proportion of the gold processed in the 21st century will be recovered from complex gold ores, many of which will contain copper minerals. It has been estimated that about 20 % of all gold deposits have significant copper mineralization commonly associated with chalcopyrite, tetrahedrite, tennantite, as well as bornite and chalcocite in certain ores (1). Table 1 summarises some of the important copper mineral solubilities in cyanide solutions. It can be seen that the majority of copper minerals including copper oxides, carbonates, sulfides (with the exception of chalcopyrite) and native copper are highly soluble in cyanide solutions. These copper containing minerals are problematic because, when ores containing such minerals are leached with cyanide to recover the gold, copper also dissolves to form stable copper cyanide complexes. The dissolution of copper consumes a substantial quantity of cyanide and thus if not recovered imposes a significant financial cost on the gold mines. The presence of copper also causes other problems such as competition with gold to adsorb on carbon unless sufficient free cyanide concentration is maintained, depletion of gold electrowinning cell efficiency, and gold losses by cementation onto copper minerals. Ores containing greater than 0.5 % reactive copper are generally considered uneconomical to process via conventional cyanidation due to the high reagent cost.

Table 1: Solubility of Copper Minerals in ~0.1 % NaCN Solutions (2)

Mineral	**Formula**	**Copper dissolution (%)**	
		@ 23 °C	**@ 45 °C**
Azurite	$2CuCO_3.Cu(OH)_2$	94.5	100
Malachite	$CuCO_3.Cu(OH)_2$	90.2	100
Chalcocite	Cu_2S	90.2	100
Native Copper	Cu	90.0	100
Cuprite	Cu_2O	85.5	100
Bornite	$FeS.2Cu_2S.CuS$	70.0	100
Enargite	$3CuS.As_2S_5$	65.8	75.1
Tetrahedrite	$4Cu_2S.Sb_2S_3$	21.9	43.7
Chalcopyrite	$CuFeS_2$	5.6	5.6

A significant concern which arises when processing copper containing ores is the discharge of these copper cyanide complexes to tailings storage facilities (TSF). This is because most metal cyanide complexes, including copper, are highly toxic to most forms of life. It is well documented that bird, animal and fish deaths have occurred as a result of gold mines using cyanide(3). Publicised examples include the cyanide spills due to the collapse of tailings dams at Omai in Guyana and Baia Mare in Romania. Copper cyanide complexes are very problematic since they are much more stable than free cyanide ions. The Romanian disaster serves to highlight this problem as copper cyanide complexes were traced for some 2000 km to the mouth of the Danube River (4). Therefore, in complying with the new International Cyanide Management Institute Code (5), the concentration of WAD (weak acid dissociable) cyanide species (which includes copper cyanides) discharged to the TSF is limited to 50 mg / L or lower.

Processing Options

Significant research attention has been given to treating copper-gold ores. The processing options developed or proposed over the years can be categorised as:

1. **Ore segregation technologies.** Selective mining has been used to separate low copper containing ores from high copper containing ores. For example, the Red Dome Gold Mine, Australia selectively mines and cyanide leaches ores containing less than 0.5 % copper, with the high copper ores being stockpiled for future processing. Flotation to produce high grade copper gold concentrates for smelting is a widely adopted technology for treating primary copper-gold ores. This is practiced in many gold mines across the world including the Telfer Gold Mine, Brown's Creek Mine and Boddington in Australia; Grasberg-Ertsberg in Indonesia; El Indio and Candelaria in Chile; and Phoenix in the United States. Low grade concentrates (e.g. Telfer's pyrite concentrate) and / or flotation tails (e.g. Boddington and Phoenix) may be subjected to cyanide leach.

2. **Selective leaching technologies.** The first option in this category is the selective leaching of copper prior to cyanidation for gold using reagents such as dilute acid, iron(III),

copper(II)/chloride or ammonia (1). These processes, however, are often uneconomical in treating low grade copper ores, particularly sulphide ores, due to the high reagent consumption, potential neutralisation before cyanidation, and issues with the recovery of leached copper. Another option is either to choose a reagent which is selective for gold over copper minerals or to choose reagent mixtures and conditions that render the copper minerals insoluble. There have been a number of studies into the application of the copper/ammonia/ cyanide process for the treatment of copper-containing ores (6, 7). It has been shown that the addition of ammonia to the cyanide solution results in a lower cyanide consumption and an increased selectivity of gold leaching over copper. The rate of gold leaching in this system is, however, apparently slower than that with free cyanide and the use of ammonia has its own occupational health and environmental concerns; within Australia, ammonia is also reportable under the National Pollution Inventory. Other selective approaches include leaching with Br_2 by the K-process (8) and leaching with thiourea (9, 10, 11), though neither of these processes have been adopted commercially.

3. **Copper cyanide destruction technologies.** The most widely adopted method for the treatment of cyanidation tails is the Inco SO_2/air process (12). This process involves the use of SO_2, which reacts together with oxygen and copper cyanide complexes, resulting in cyanide oxidation to cyanate. At the end of the reaction, copper is precipitated out as copper hydroxide. Alternative destruction processes include alkaline chlorination, hydrogen peroxide (Degussa process), Caro's acid, electrochemical oxidation, biodegradation, ultrasonic and photolysis. Among these, alkaline chlorination, hydrogen peroxide, Caro's acid and biodegradation are the major processes which have been applied in industry.

4. **Copper cyanide recovery technologies.** The recovery of copper and cyanide potentially offers both economic and environmental benefits and hence may be a more attractive option than destruction. Over the years, a variety of processes have been developed or proposed to recover the copper and/or cyanide. These include the acidification based technologies such as AVR and SART, direct electrowinning, activated carbon, ion exchange resins, solvent extraction, polychelating polymers and membrane technologies. More details on each of these technologies are described within this paper.

A number of review papers have been published on each of these processing options. Selective leaching and flotation technologies have been reviewed in detail by Muir et al. (1). Young has reviewed the methods of cyanide remediation by separation and destruction for cyanide management purposes (13). Jay reviewed some of the copper cyanide destruction and recovery processes with a bias towards the polychelating polymer process (14).

Copper Cyanide Chemistry

In a copper cyanide aqueous system, there exist various copper and cyanide species whose equilibrium can be described by the following reactions (15):

$$Cu^{+} + CN^{-} \leftrightarrow CuCN_{(s)} \tag{1}$$

$$CuCN + CN^{-} \leftrightarrow CuCN_2^{-} \tag{2}$$

$$CuCN_2^{-} + CN^{-} \leftrightarrow CuCN_3^{2-} \tag{3}$$

$$CuCN_3^{2-} + CN^{-} \leftrightarrow CuCN_4^{3-} \tag{4}$$

$$H^{+} + CN^{-} \leftrightarrow HCN_{(l)} \leftrightarrow HCN_{(g)} \tag{5}$$

Figure 1 shows the Eh-pH diagram for the copper-cyanide-water system. As can be seen, there is a large area of predominance of $Cu(CN)_3^{2-}$ under typical gold cyanidation conditions. However, in the presence of hypersaline waters, as typically found in the Eastern Goldfields of Western Australia, it has been shown (16) that the predominant species is $Cu(CN)_4^{3-}$. Figure 2 shows the speciation of copper cyanide complexes as a function of pH, whilst Figure 3 shows the influence of free cyanide. It is clear that $Cu(CN)_3^{2-}$ dominates at alkaline pH (Figure 2) and in the presence of free cyanide (Figure 3). The formation of $Cu(CN)_2^{-}$ is favoured at low pH and at very low free cyanide concentrations (cyanide to copper ratios below 3), whereas $Cu(CN)_4^{3-}$ forms at high pH and high cyanide concentration. Thus, depending on the conditions (e.g. pH and free cyanide concentration), all or any of the three aqueous copper species will be present. The proportion of the different species present in a solution of known pH, temperature, ionic strength, copper and cyanide concentration can be calculated using the stability constants for the various species formed (15, 17), a process often referred to as copper cyanide speciation calculation.

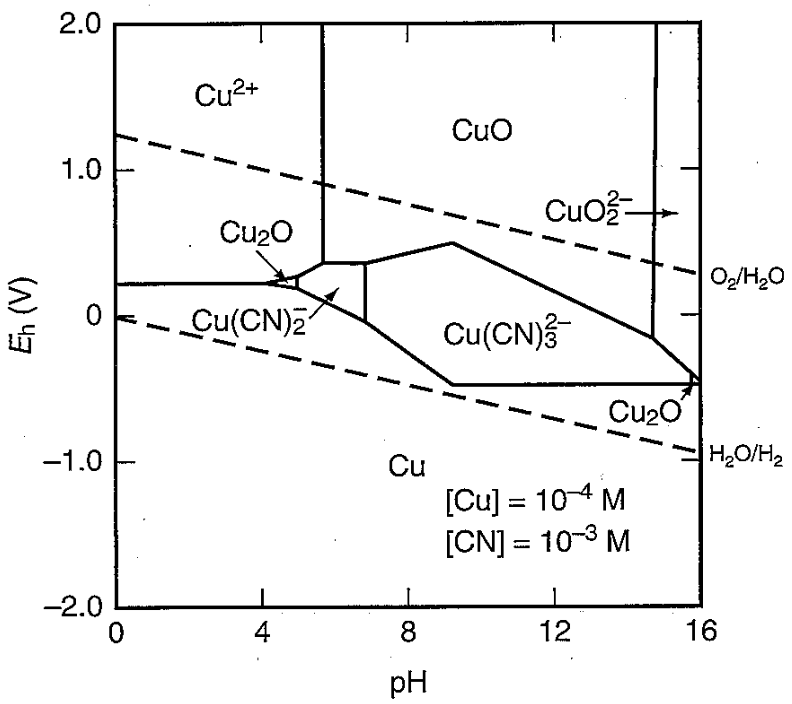

Figure 1: E_h-pH diagram for the Cu-CN-H_2O system at 25 °C (18).

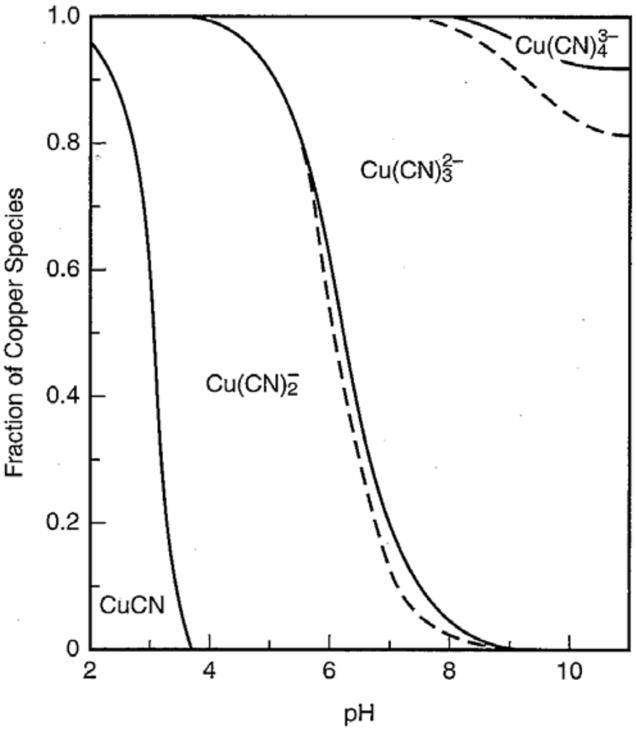

Figure 2: Influence of pH on the distribution of copper-cyanide species, where $[CN]_{total}$ = 220 mg / L, $[Cu]_{total}$ = 22 mg / L, $[Zn]_{total}$ = 0 mg / L (dash lines) or 80 mg / L (solid lines) (2).

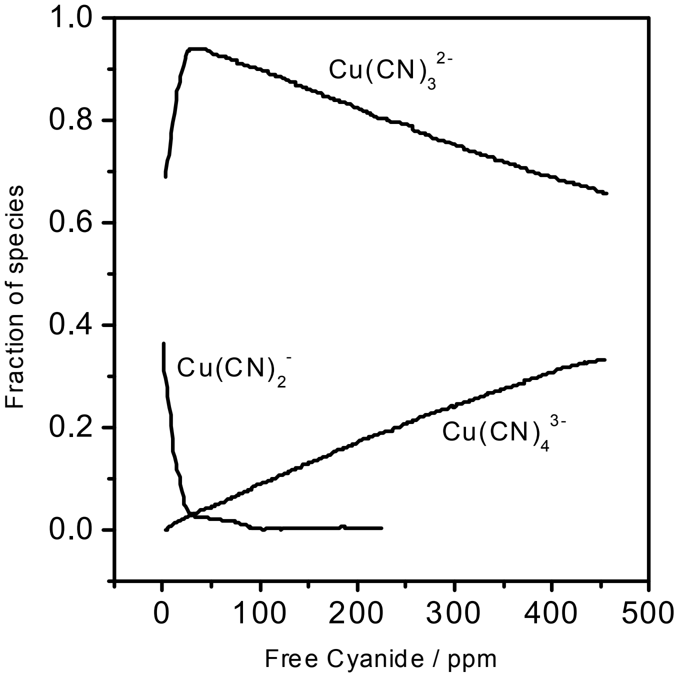

Figure 3: Influence of free cyanide on the distribution of copper-cyanide species at pH 10 and 10 mg / L copper (19).

The high consumption of cyanide during the cyanidation of copper-gold ores is due to one or more of the following factors:

1. Copper forms complexes of high coordination numbers with cyanide (Reaction 2-4), $Cu(CN)_3^{2-}$ in particular.

2. Cyanide is oxidised by oxygen to cyanate via Reaction 6 (catalysed by copper, particularly in the presence of activated carbon (1)).

3. For the case of Cu(II) containing ores, additional cyanide oxidation to cyanate occurs as a result of Cu(II) reduction during dissolution.

4. Copper containing gold ores are commonly associated with sulfides, some of which can readily undergo oxidation and react with the cyanide to form thiocyanate via Reaction 7.

$$3CN^- + 2O_2 + H_2O \rightarrow 3CNO^- + 2OH^- \qquad (6)$$

$$CN^- + S^{2-} \rightarrow SCN^- + 2e^- \qquad (7)$$

COPPER CYANIDE RECOVERY FROM SLURRIES

The technologies for recovering copper and cyanide separately are only applicable to clear solutions and thus are not suitable for the direct treatment of tailings from CIL/CIP processes. These technologies are discussed in the next section. Thus, to recover copper and cyanide from cyanidation slurries either:

1. solid/liquid separation is required to produce a clear solution from which copper and cyanide can be recovered, or

2. adsorption onto a recoverable material (e.g. activated carbon or ion exchange resin) is required to remove copper cyanide from the slurry.

Solid/Liquid Separation

The physical separation of solids from solution can be achieved using such processes as filtration, thickeners and counter current decantation (CCD). These processes have the following issues but are sometimes used to obtain a clarified solution for further processing via e.g. SART:

- high capital and operating costs,
- large footprint for thickeners/CCD's, and/or
- water balance issues with the use of CCD.

Copper Cyanide Recovery by Adsorption

A number of investigations have been conducted into the use of various materials for the adsorption and recovery of copper cyanide and processes developed based on these. Nevertheless, none of the approaches outlined below have achieved widespread application. An important aspect of these adsorbents is that free cyanide ions are not recovered to any appreciable extent due to the poor adsorption/selectivity of free cyanide ions. Hence, several of the approaches below incorporate the addition or recycle of metal, metal salts or metal ions to complex the free cyanide ions and facilitate the recovery of free cyanide.

Activated carbon

Activated carbon has been widely used in gold industry for recovering gold in the cyanidation process since the 1970's. In treating copper-gold ores, a high free cyanide concentration is commonly maintained to encourage the selective adsorption of gold over copper onto carbon. Copper cyanides also adsorb onto activated carbon via an ion pairing mechanism with cations, such as Ca^{2+} (2), with their adsorption affinity following the order: $Cu(CN)_2^-$ > $Cu(CN)_3^{2-}$ >> $Cu(CN)_4^{3-}$ (17, 20). Thus, maintaining a high free cyanide concentration reduces the concentration of the more strongly adsorbed copper di-cyanide and tri-cyanide complexes. The increased copper cyanide adsorption at low cyanide concentrations, which is troublesome for gold adsorption, is utilised in the following processes for the recovery of copper and cyanide.

Pre CIL/CIP (Sceresini Process): This process is based on the principle of removing the copper cyanide complexes early in the leaching process by restricting the addition of cyanide such that the reactive copper minerals dissolve with little or no free cyanide remaining in the leach solution (21, 22). This establishes a chemical environment which minimises the leaching of the precious metals and enhances the adsorption kinetics for copper cyanides on activated carbon. Further cyanide is subsequently added to the copper depleted leach slurry in a CIP or CIL circuit where leaching and adsorption can proceed under typical cyanidation conditions. The copper loaded carbon is eluted using moderate strength cyanide solution at ambient temperature. Cold stripping enhances the selectivity of copper elution over the elution of gold and silver. The gold and silver loading accumulates and thus the eluted carbon is periodically diverted to the gold elution circuit to recover the precious metals. The carbon eluate is then acidified to precipitate the copper as CuCN which is subsequently digested to produce copper sulfate as a saleable product. The digestion of CuCN is discussed in detail below.

The Scerisini process offers a means of reducing the copper entering the gold leaching and adsorption circuit and in turn reduces the level of free cyanide required to leach the gold and to minimise the competitive adsorption of copper. In addition, the recovery of copper in a saleable form delivers extra revenue. This process, however, may not be as effective in treating ores containing slow leaching copper minerals such as chalcopyrite. In addition, there will always be some residual copper and cyanide in the discharge from CIP/CIL circuit that requires further treatment. A full scale demonstration plant was operated at the Mt. Gibson Gold mine in Australia for a period of time before being shut down due to "an interruption to the continuity of copper bearing ore supply" (21).

Post CIL/CIP: A copper cyanide recovery process using activated carbon has been proposed by the authors in which the copper cyanide is recovered following rather than prior to CIL/CIP (23, 24). To enable the effective recovery of copper cyanide using activated carbon, copper powder is used to complex free cyanide and convert $Cu(CN)_4^{3-}$ and the majority of $Cu(CN)_3^{2-}$ to the more readily adsorbed $CuCN_2^-$ complex. Thus, free cyanide is also recovered as copper cyanide. Metallic copper readily dissolves in free cyanide and $Cu(CN)_3^{2-}$ solutions to achieve a final CN:Cu ratio well below 3 (23). An increase in pH due to oxygen reduction during copper dissolution can cause copper to precipitate as $Cu(OH)_2$. Precipitation, however, is not observed if the copper dissolution is conducted in the presence of carbon due to the simultaneous adsorption of copper cyanide onto carbon decreasing the solution copper concentration. The copper loaded carbon can be effectively eluted with distilled water following a pre-soak with high cyanide + 0.2 M sodium hydroxide (25). The cyanide in the pre-soak is controlled such that the resulting highly concentrated copper cyanide eluate contains a minimal cyanide-to-copper ratio of ~3.5, which minimises the subsequent processing costs and recycle of cyanide to elute the copper loaded carbon. It is proposed that the process utilises electrowinning to recover the copper (discussed below) and thus provides a source for recycling copper to complex free cyanide in the copper cyanide recovery step. Alternatively, the SART process could be used.

This Cu-CN-carbon process is capable of recovering both free cyanide and copper cyanide. The metallic copper added to complex the free cyanide and to reduce the overall CN:Cu ratio, however, acts as a recovering media that has to be recovered and recycled. This imposes an additional burden on the carbon adsorption and elution circuit and the copper electrowinning circuit.

Ion exchange resins

Ion exchange resin processes have been used to recover gold from cyanide leach slurries and liquors for well over half a century in the former USSR, and have attracted interest in the western world since the late 1980's. Strong base ion exchange resins have been used to adsorb metal cyanide complexes with little selectivity. Typically, the strongly adsorbed precious metals, such as gold and silver, can be separated from the base metals during elution. An elution process for strong-base anion exchange resins is described by Lukey et al. (26) and involves the selective elution of copper and iron using sodium cyanide solution followed by the elution of zinc and nickel using sulphuric acid solution and then acidic thiourea to remove the gold and silver. Alternatively, thiocyanate or zinc cyanide can be used to elute the gold cyanide complex (27, 28). Due to the challenges involved in elution of the strongly adsorbed precious metals, work has also been conducted to develop gold selective resins (29-33).

As the environmental guidelines imposed on the gold industry have become increasingly stringent in recent times, the use of ion exchange resins for cyanide management has received considerable attention. This has resulted in the development of several technologies utilising resins to recover metal cyanides, particularly for the processing of copper-gold ores.

Augment process: Processes have been developed to recover free cyanide using anion exchange resins with CuCN precipitated in the pores, where the cyanide is eluted as HCN using an acid eluant (34, 35). This essentially maintained the concentration of copper in the resin at steady state. These processes, however, were unable to handle copper cyanide in the feed as they did not incorporate a method of eluting copper from the resin. This problem has been overcome by Fleming and others (36-38), resulting in the Augment process. In the Augment process, CuCN is intentionally precipitated in the pores of a strong base resin during the resin regeneration step (described below) and the regenerated resin is used to adsorb both free cyanide and copper cyanides. The maximum possible ion exchange copper loading on the resin is achieved when a CN:Cu stoichiometry of 2:1 is attained, since only one resin site ($-N^+R_3$) is required to adsorb the $Cu(CN)_2^-$ complex compared to two resin sites for $Cu(CN)_3^{2-}$ and three resin sites for $Cu(CN)_4^{3-}$. The stoichiometry of the loading reaction for a CN:Cu ratio of 5:1 in the feed solution is defined as:

$$\begin{aligned} &2(\circledR{-}NR_3^+)_2SO_4^{2-}(CuCN) + Cu(CN)_3^{2-} + 2CN^- \\ &\quad \rightarrow 2\circledR{-}NR_3^+\,Cu(CN)_2^- + (\circledR{-}NR_3^+)_2CuCN_3^{2-} + 2SO_4^{2-} \end{aligned} \qquad (8)$$

where the symbol ® represents the resin matrix.

From the stoichiometry of the loading reaction it is clear that maximum copper recovery is achieved when the CN:Cu ratio in the feed solution is 3:1 (50 % of resin capacity; copper adsorbed mainly as $Cu(CN)_2^-$ on resin and little $Cu(CN)_3^{2-}$). The copper recovery decreases as the CN:Cu ratio in the feed solution increases, approaching zero net copper extraction when the CN:Cu ratio is greater than 6:1; this latter situation can be accommodated by a 2-stage loading process (36). The loaded resin is treated with a concentrated copper cyanide solution at a CN:Cu ratio of ~4:1. During this process, $Cu(CN)_2^-$ on the resin is converted to $Cu(CN)_3^{2-}$, resulting in a partial elution of copper. As one $Cu(CN)_2^-$ ion occupies one adsorption site whilst one $Cu(CN)_3^{2-}$ ion occupies two adsorption sites, this elution process achieves a maximum of 50 % copper elution efficiency.

$$2\text{®–NR}_3^+\ \text{Cu(CN)}_2^- + \text{Cu(CN)}_3^{2-} + 2\text{CN}^- \rightarrow (\text{®–NR}_3^+)_2\text{Cu(CN)}_3^{2-} + 2\text{Cu(CN)}_3^{2-} \qquad (9)$$

The eluted resin containing mainly $Cu(CN)_3^{2-}$ is then advanced to regeneration before recycling back to adsorption.

$$(\text{®–NR}_3^+)_2\text{Cu(CN)}_3^{2-} + \text{H}_2\text{SO}_4 \rightarrow (\text{®–NR}_3^+)_2\text{SO}_4^{2-}(\text{CuCN}) + 2\text{HCN} \qquad (10)$$

The Augment process has the advantage of efficiently recovering both copper cyanide and free cyanide. It has been demonstrated that this process is quite tolerant to high concentration of thiocyanate (~560 mg / L) and low concentration of iron (~12 mg / L) (36). In treating high iron containing solutions, however, the potential precipitation of $Cu_4Fe(CN)_6$ (or $Zn_2Fe(CN)_6$ if the feed solution contains both zinc and iron) during the resin regeneration with acid can result in the reduction in loading capacity. Also, osmotic shock of resin due to the change in pH with regeneration remains an issue. The Augment process has been tested at pilot plant level but has yet to be fully commercialised.

Vitrokele process: Vitrokele 912 is a particular type of resin which has been developed by Tallon Metal Technologies Inc. for gold processing applications. This resin was successfully applied at Connemara, Zimbabwe for recovering metal cyanides including gold cyanide from heap leaching of an oxidised ore (39). A resin-in-column based process was used to adsorb the metal cyanides from the leach solution, followed by the elution with $Zn(CN)_4^{2-}$. The eluted resin was regenerated using sulphuric acid via Reaction 11 before the next cycle of adsorption.

$$(\text{®–NR}_3^+)_2\text{Zn(CN)}_4^{2-} + 2\text{H}_2\text{SO}_4 \rightarrow (\text{®–NR}_3^+)_2\text{SO}_4^{2-} + \text{ZnSO}_4 + 4\text{HCN} \qquad (11)$$

Pilot plant tests were conducted to demonstrate the recovery of free cyanide from the leach slurry at a North American gold mine and to evaluate the reduction of both free cyanide and metal cyanide levels in a process stream at a gold plant in Europe (39). In these tests, the adsorption occurred in a series of agitated tanks with counter-current transfer of the resin. To recover free cyanide with the Vitrokele resin the elution was conducted with sulphuric acid only. Whilst for the recovery of metal cyanides the resin was eluted with $Zn(CN)_4^{2-}$ and then regenerated with dilute sulphuric acid. In a proposed full plant operation, the eluates from the elution and regeneration would be combined and pH trimmed to precipitate metal cyanides such as CuCN. A cation ion exchange resin bed was proposed to recover the zinc from the decanted liquor, with elution using NaCN to form $Zn(CN)_4^{2-}$ which would be recycled to the elution circuit. Both pilot plant tests were claimed to successfully reduce the WAD cyanide concentration to very low levels (<1 mg / L in most cases). Pilot plant tests with Vitrokele 912 resin were also successfully conducted at Bell Creek Mine, Canada to simultaneously recover both gold and cyanide from leach slurry and at the Hope Brook Gold, Canada to treat the CIP tails for cyanide and copper recovery (40).

The Vitrokele process, however, failed to perform to the expected design criteria when used to treat the pregnant liquors obtained from the vat-leaching of a copper-gold ore at the May Day Mine, Australia in 1997 (41). Due to the high copper content in the pregnant liquor (~200 mg / L) and thus the high loading of copper on resin, a pre-elution step was adopted to selectively elute copper from the loaded resin using a strong cyanide solution (100 g / L NaCN and 10 g / L NaOH) prior to the electro-elution (elution incorporated with simultaneous electrowinning) of gold with zinc cyanide. This pre-elution step produced a copper liquor in a highly concentrated sodium cyanide background, which was then acidified to precipitate copper as CuCN. Apart from the loss of cyanide associated with the CuCN, the AVR circuit had to handle a large quantity of HCN generated from the acidification of the NaCN eluant. The most serious problem, however, was the poor performance of the copper pre-elution (residual copper on resin was more than 50 %) resulting in contamination in the following electro-elution of gold with zinc cyanide and the resin blockage by CuCN during resin regeneration with acid which thus lowered adsorption capacity for subsequent cycles. The uncontrollable handling of copper cyanide and AVR circuits affected almost all other crucial unit operations, resulting in the abandonment of the Vitrokele process. Thus, it is clear that the Vitrokele process is unable to handle solutions containing high copper unless an effective copper selective elution method is developed.

Elutech process: After the failure of Vitrokele process, the May Day Mine changed the resin process to the Elutech process. One key component of this process is the selective elution of copper cyanides using an oxidative eluant comprising of H_2O_2 and H_2SO_4 to produce HCN and

Cu^{2+}, the latter can be further processed using conventional solvent-extraction/electrowinning or precipitation technologies (42, 43).

$$\begin{aligned}&2(\text{®}-NR_3^+)_2Cu(CN)_3^{2-} + 4H_2SO_4 + H_2O_2 \\ &\qquad \rightarrow 2(\text{®}-NR_3^+)_2SO_4^{2-} + 6HCN + 2CuSO_4 + 2H_2O\end{aligned} \tag{12}$$

At the May Day Mine pilot plant trial, commercially available strong base resins were used with a resin-in-column configuration (41). A cycle of operation consisted of an adsorption with little selectivity, an elution with the above oxidative eluant and water wash in between. This elution method was claimed to have a high selectivity for copper, with greater than 99 % copper and less than 0.2 % gold being removed for each cycle. Separation of zinc and copper could also be achieved if required. The eluant was recycled between the resin column and the HCN stripping column to facilitate the immediate HCN scrubbing with air, minimising the oxidation of cyanide to cyanate by residual peroxide. These adsorption/base metal elution cycles were repeated a number of times before the resin was subjected to the electo-elution of gold with zinc cyanide at 60 ^oC. Alternatively, gold could also be eluted using a copper cyanide/sodium cyanide eluant at room temperature incorporated with a gold cementation cell using copper powder.

Although the Elutech process appears to successfully solve the problem of selective elution of copper, issues with this process include:

1. loss of cyanide by oxidation during the oxidative elution,

2. degradation of the resin capacity due to the oxidation of the resin adsorption sites by the oxidant in the presence of Cu^{2+}, and

3. reduction in the net operating capacity of resin bed due to the precipitation of $Cu_2Fe(CN)_6$ in handling high iron solutions (43, 44).

Chloride elution based process: All the above resin processes involve the use of acid for either resin elution or resin regeneration and thus have the potential problems of resin breakage due to osmotic shock and resin blockage due to the formation of copper cyanide and/or copper iron cyanide precipitates. An eluent with pH close to the loading conditions (pH 10-11) would largely be preferred to avoid such problems. Dai et al. (24) investigated a wide range of organic and inorganic eluents and developed a chloride based elution method that delivered satisfactory elution results. This method involved a pre-soak of the loaded resin (commercially available Purolite A500/2788 strong base anion exchange resin) with 1 M NaCN followed by the elution with 4 M NaCl. Close to 90 % of the copper was successfully eluted in only 2 bed volumes, resulting in a small volume of highly concentrated copper eluate which is suitable for downstream processing. The elution mechanisms were suggested to involve:

1. during the pre-soak the conversion of copper cyanide species to the more highly charged $Cu(CN)_4^{3-}$ and $Cu(CN)_3^{2-}$ species which have lower affinity for resin adsorption in the presence of cyanide under high ionic strength conditions,

2. partial elution of copper due to the increased total charge of the copper cyanide species, and

3. the ion-exchange of the higher charged copper cyanide species with Cl^- during the elution.

The eluted resin is in chloride form and is ready for recycling without regeneration. Because no acid is used in this elution method, the resin breakage and blockage problems are thus avoided. One drawback of this process, however, is that the cyanide used for pre-soak will have to be recovered, imposing an extra burden on the cyanide recovery circuit. If thiocyanate is present in the cyanidation tails solutions, it can be minimally or partially recovered using different elution flowsheets (24). The fate of iron cyanide in this process has not been addressed, but it is expected to follow the copper cyanides. The presence of thiocyanate and iron cyanide in the eluate should have little effect on the downstream processing with SART, but their effect on the potential use of electrowinning needs further investigation as does the presence of chloride. Strong base resins are able to effectively recover copper cyanide from solutions containing free cyanide without any solution pre-treatment. However, if the free cyanide is also to be recovered, complexation of the free cyanide by dissolving metallic copper powder before the resin process has been proposed (23).

Summary: The resin processes discussed above are summarised in Table 1 for comparison. In cases where free cyanide is not recovered then a second resin recovery process can be used which utilises $Zn(OH)_2$ to complex with the cyanide to form zinc cyanide (45).

Table 1: Comparison of various resin processes for copper cyanide recovery

Process	Free CN^- recovery	Eluant	Regen. Soln.	Issues	Application Level
Augment	yes/CuCN media	Copper cyanide	H_2SO_4	Osmotic shock; resin blockage	Pilot plant
Vitrokele	limited	NaCN + NaOH	H_2SO_4	Poor copper elution; resin blockage; extra burden in AVR; Osmotic shock	Commercial plant
Elutech	limited	H_2O_2 + H_2SO_4	n/a	Oxidation of cyanide; loss of resin capacity; Osmotic shock	Pilot plant
Chloride	limited	NaCN (Pre-soak) + NaCl	n/a	extra cyanide handling	Lab research

RECOVERY OF COPPER AND CYANIDE

Concentration Processes

Efficiencies and reduced capital costs in recovering the copper and cyanide can be achieved by first concentrating the copper cyanide. Activated carbon and ion exchange resins can be used and were discussed in the preceeding section. Other processes that allow concentration from clear solutions (e.g. from heap leaching) are described below.

Solvent extraction

Solvent extraction offers an alternative to ion exchange resin and activated carbon for concentrating copper from copper cyanide solutions. Processes based on solvent extraction have been proposed to recover copper from cyanide leach solutions. Davis et al. (46) used the Cognis (formerly Henkel) reagent LIX7820, a mixture of a quaternary amine (Aliquat® 336) and 4-nonylphenol, to concentrate copper to 470 - 630 mM from dilute liquors containing less than 16 mM copper and ~65 mM total cyanide, followed by the separation of copper and cyanide using SART. Since Aliquat® 336 is such a strong extractant it is difficult to strip the loaded copper cyanide complexes by changing solution pH (to higher values), the addition of nonylphenol is used to render the extraction with the quaternary ammonium cation pH-dependent. Since nonylphenol is a weak acid (with a pKa value around 10), under low pH conditions, nonylphenol is protonated and the quaternary ammounium compounds extract an anion from the aqueous phase. Under more highly alkaline conditions, nonylphenol starts to be significantly converted to the highly hydro-carbon-soluble phenoxide anion and forms an ion pair with the quaternary ammonium cation. Consequently, the extracted copper cyanide anions will be gradually expelled to the aqueous phased with increasing equilibrium pH due to the competition by the phenoxide anion. The extraction and stripping of copper cyanide complexes therefore occur via an ion-exchange mechanism similar to that of strong base ion exchange resins (47).

$$(Q^+P^-)_{org} + X^- + H_2O \Leftrightarrow (Q^+X^-)_{org} + (PH)_{org} + OH^- \qquad (13)$$

where Q^+ is the quaternary ammonium cation, PH is the protonated form of the nonylphenol, and X^- is the extracted anion e.g. copper cyanide complexes.

Another solvent extraction based process proposed by Dreisinger et al. (48) included the following steps:

1. extraction of copper cyanide complexes from clarified solutions using the Cognis reagent LIX 7950,
2. stripping of copper cyanide from the loaded organic phase using a high pH-copper cyanide rich spent electrolyte,
3. electrowinning of copper from the strip solution in a Du Pont type membrane cell (described below), and
4. recovery of the cyanide from a bleed stream from the electrowinning cell using AVR.

The LIX7950 is a tri-alkylguanidine extractant. The guanidine extractant exhibits a pKa of approximately 12. It is capable of being protonated to form an ion pair with the copper cyanide complexes at pH's below 11 during loading and is converted to the neutral guanidine functionality during alkali stripping resulting in the release of copper cyanide complexes (49).

$$(RG)_{org} + H_2O + X^- \Leftrightarrow (RGH^+X^-)_{org} + OH^- \qquad (14)$$

where RG represents the extractant and RGH^+ is the protonated form of the extractant.

Due to the release of hydroxyl ion into the solution during the extraction stage, it was found that without controlling the pH, the extraction of copper cyanide complexes can be very poor and thus impossible to reduce the copper to low concentrations (50). The pH is typically maintained at close to 10 by the addition of sulphuric acid to improve the extraction of copper. For both LIX 7820 and LIX 7950, the extraction efficiency was found to decrease significantly with increasing copper content (e.g. from 99.8 % for 1.6 mM copper to 64.0 % for 7.9 mM copper for LIX 7950 and from 96.9 % for 1.6 mM copper to 35.2 % for 7.9 mM copper for LIX 7820 under conditions of CN:Cu = 5, aqueous/organic volume ratio A/O = 1 and controlled pH 10.5) (51). The extraction efficiency was also found to decrease with increasing CN:Cu ratio due to the extractants preferentially extracting $Cu(CN)_3^{2-}$ over $Cu(CN)_4^{3-}$ and CN^- (47, 50-51). The decrease in extraction efficiency requires more extraction stages to achieve satisfactory copper recovery. On the other hand, when recovering copper from solutions containing low CN:Cu ratios (e.g. 2.2) the precipitation of CuCN in the organic phase has been noticed (50). These extractants also strongly extract zinc and nickel cyanides, but the extraction of iron cyanide is poor. The presence of thiocyanate in the solution significantly depresses the extraction of copper, e.g. the presence of 50 mM thiocyanate decreased the copper extraction efficiency from ~100 % to ~10 % from a solution containing 4 mM copper (CN:Cu=3) using 10 % v/v LIX 7950 at controlled pH 10.5 (47). The majority of free cyanide is rejected to the raffinate and can be recycled directly. The stripping of loaded copper is simple and effective. Moderately strong NaOH solutions (0.5-1 M) stripped ~90 % copper into a small volume which is suitable for further processing via SART or electrowinning. With SART, however, the acid consumption can be high due to the use of NaOH for stripping. The presence of a small amount of cyanide in the stripping solution favoured the stripping due to the formation of less extractable $Cu(CN)_4^{3-}$ species.

The use of solvent extraction for the recovery of copper from copper cyanide solutions thus faces some challenges. Degradation of expensive organics is always a concern for solvent extraction technologies but has received little research in the application of copper cyanide recovery. The potential contamination of the raffinate by organics may cause problems, e.g. reducing the efficiency of gold recovery by activated carbon, if it is recycled back to the leach circuit. The most significant problem, however, is the low extraction efficiency for the recovery of copper from solutions containing high copper and/or thiocyanate, and the continuous decrease in the extraction efficiency with each stage due to the increase in CN:Cu ratio as the extraction proceeds (decrease in copper content with esentially unchanged free cyanide).

Membranes

A membrane is an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two compartments. Passive transport through membranes occurs as a consequence of a driving force, i.e. a difference in chemical potential by a gradient across the membrane. Such processes include concentration (pervaporation and dialysis), pressure (gas separation, reverse osmosis, nanofiltration, ultrafiltration and microfiltration) or by an electrical field (electrodialysis) (52). Membrane technologies have gained wide applications in the medical technology and water treatment industries, and have started to attract interest in the mining industry. Nevertheless, their application is limited at present due to the need for very clean solutions (free of solids and precipitates).

HWPT EMSTM Process: HW Process Technologies, Inc. (HWPT) has developed an Engineered Membrane Separation (EMSTM) system that enables the recovery of both cyanide and copper from copper cyanide containing solutions (53). Its membrane component separates multi-valent salts (copper and base metal cyanide complexes) from mono-valent salts (cyanide, gold and silver cyanide complexes) via a nanofiltration mechanism (54). The permeate-to-concentrate ratio of this EMSTM treatment is typically 90:10. The nominal 10 % by-volume bleed of 10 fold concentrated copper can be treated for copper recovery via electrowinning or SART. Whilst the 90 % by-volume permeate containing precious metal cyanide complexes and cyanide ions can be subject to precious metal recovery via zinc cementation or a conventional carbon process, followed by the recycling of the residual cyanide.

This process has been tested in a pilot plant using the pregnant leach solution generated from a thin-layer on-off pad heap leach of agglomerated tailings at a mine site in Durango State, Mexico (53). The pilot plant test achieved 85 - 90 % recovery of copper cyanide complexes in the concentrate and greater than 90 % gold recovery in the permeate. Issues with this process are the undesirable loss of some gold to the copper concentrate and the potential for precipitation of calcium salts (mainly $CaSO_4$ and $CaCO_3$) in the concentrate, potentially fouling the membrane; Ca^{2+}, SO_4^{2-} and CO_3^{2-} ions are commonly found in abundance in gold leach solutions from lime addition to control pH, hypersaline process water, CO_2 adsorption from the air, and dissolution from the ore being treated. Although some calcium is precipitated out during the lime addition and leaching stages and the solution is filtered before entering the membrane circuit, further precipitation of residual calcium is likely as a result of the approximately order-of-magnitude concentration of calcium ions during the EMSTM process. Therefore, in the pilot plant test the clarified solution was processed through a standard sodium-cycle softener resin process to lower the calcium concentration to ~ 150 mg / L prior to the EMSTM process.

Acidification Processes

Acidification processes take advantage of the protonation of cyanide at low pH to form hydrogen cyanide via Reaction 5. This protonation of cyanide means that as the pH is reduced, the cyanide in copper cyanide complexes is released via the reverse of Reactions 1 to 4.

Copper precipitation

Sufficient acid addition ultimately results in the formation of a copper cyanide precipitate (CuCN). Thus, in this situation some cyanide remains complexed with the precipitated copper. Other precipitates can also form depending on the solution composition as shown in Reactions 15 and 16.

$$\mathrm{Cu(CN)_3^{2-} + SCN^- + 3H^+ \rightarrow CuSCN + 3HCN} \qquad (15)$$

$$\mathrm{4Cu(CN)_3^{2-} + 2Fe(CN)_6^{4-} + 16H^+ + O_2 \rightarrow 2Cu_2Fe(CN)_6 + 12HCN + 2H_2O} \qquad (16)$$

The composition of the final precipitate depends on pH, HCN removal, iron concentration, and thiocyanate concentration in the solution. The pH required to form each of the major precipitate constituents is: less than 4 to form $Cu_2Fe(CN)_6$, around 3 to form CuCN, and less than 2 to form CuSCN (55). This is provided HCN is constantly removed from solution via volatilisation (see below), otherwise the pH required for each precipitate is reduced. Also without volatilisation $Cu_4Fe(CN)_6$ can form instead of $Cu_2Fe(CN)_6$ as the oxidation of copper by oxygen is likely to be limited (56). The formation of CuSCN and $Cu_2Fe(CN)_6$ is preferable over the formation of CuCN. This is because cyanide in the form of SCN^- and $Fe(CN)_6^{4-}$ is considered unrecoverable. Hence for every mole of these species formed one extra mole of cyanide is recovered compared to when CuCN is formed.

As the copper precipitate CuCN contains cyanide, there is a loss of cyanide and problems marketing the precipitate as saleable copper. Sceresini and Richardson (21) propose a digestion method that can overcome this issue, releasing hydrogen cyanide and oxidising copper to give copper (II) sulfate according to Reaction 21. The CuCN precipitate is filtered and thoroughly washed to achieve a very low chloride level prior to the digestion with sulphuric acid and oxygen at about 75 ^{o}C for ~8 hours to produce copper sulfate solution for direct sale or for producing copper cathode via electrowinning. The HCN gas liberated during digestion is scrubbed by lime and recycled. This technique has been used at Mt Gibson for treating CuCN generated from the Sceresini process (described earlier). Sceresini (57) stated that while the process is effective, a sulfidisation technique (discussed further below) was more effective for maximising cyanide recovery.

$$4CuCN + 4H_2SO_4 + O_2 \rightarrow 4CuSO_4 + 4HCN + 2H_2O \qquad (17)$$

CANMET also propose a thermal decomposition but under reducing conditions to release cyanide species from copper iron cyanide double salts (58). Specific details of the process, however, are not mentioned and the limitation of the technique to copper iron double salts is likely to make this process not applicable in many cases.

Volatilisation

Volatilisation processes take advantage of the volatility of hydrogen cyanide (HCN). They work by bubbling air through acidified solution to remove hydrogen cyanide gas via Reaction 18. The hydrogen cyanide gas is then adsorbed into an alkaline solution, normally lime, as per Reaction 19. This means cyanide is both separated from the solution and concentrated, potentially up to the solubility limit of calcium cyanide. Several industrial processes exist based on this concept including the acidification, volatilisation, and reneutralisation (AVR) process; the Cyanide Recovery Process (CRP); and the Cyanisorb process.

$$HCN(aq) + air \rightarrow HCN(g) + air \qquad (18)$$

$$2HCN + Ca(OH)_2 \rightarrow Ca(CN)_2 + H_2O \qquad (19)$$

The reactions leading to the formation of hydrocyanic acid are rapid, with volatilisation being the rate limiting step in the process (56, 59). Volatilisation is also a high energy process which is made worse if low residual cyanide is required (58, 60). To help overcome the slow kinetics of volatilisation and reduce energy consumption, packed towers can be used to facilitate breakdown of gas bubbles and increase the surface area for diffusion of hydrogen cyanide from the liquid to gas phase. The Cyanide Recovery Process (CRP) and the Cyanisorb process are both based on this concept.

In addition to better reactor design, process variables have been shown to have varying effects on the volatilisation of HCN. Several authors have shown that the volatilisation time required can be reduced by using increased air flow rates (61, 62). It is also known that lowering pH can reduce volatilisation time for free and WAD cyanide species (63). The same work showed a 40 % increase in cyanide recovery when the temperature is raised from 15 °C to 25 °C. Work by Vapur et al. (61), however, shows only a 3 - 4 % increase in cyanide recovery between 10 °C and 30 °C. These two works differed mainly in the use of a packed column by Vapur et al. (61) and suggests a possible interaction effect between the factors of temperature and reactor design.

While AVR type technology can also be used for slurries to recover the cyanide, the copper is precipitated as copper cyanide which is not recoverable and is discharged to the tailings which can have environmental implications. The processing of slurries is also more difficult with the volatilisation from a pulp requiring a significantly longer residence time to remove the hydrogen cyanide from solution. Fleming and Trang (56) found that the cyanide recovered in 120 minutes from the volatilisation stage reduced from 96.5 % for a solution to 54 % for a pulp. Work conducted by Vapur et al. (61) achieved 97.3 % recovery of cyanide from a pulp in 90 minutes again highlighting the importance of the gas/slurry contact. A limitation reported in all studies with slurries is increased acid consumption due to acid consuming constituents in the solids.

Gas Membranes

The mechanism of using a hydrophobic gas membrane to recover cyanide from cyanide containing solutions is as follows: a hydrophobic microporous membrane, e.g. polypropylene (PP) or polytetrafluoroethylene (PTFE), is used to separate two aqueous streams: the cyanide containing stream and the cyanide stripping stream (e.g. NaOH). The membrane pores remain gas-filled (air) as long as the pressure difference between these two aqueous phases is less than the breakthrough pressure. Upon acidification of the cyanide containing stream the volatile $HCN_{(aq.)}$ is generated, which volatilises and diffuses across the gas layer into the strip solution where it reacts with NaOH to form NaCN. This process involves the following mass transfer steps:

1. $HCN_{(aq.)}$ diffuses through the boundary layer (liquid film) from the bulk of the feed to the feed-membrane interface,

2. HCN volatilises at the feed-membrane interface and diffuses through the air in the membrane pores from the feed side to the stripping side, and

3. HCN is adsorbed by stripping solution and immediately reacts with NaOH at the membrane-stripping interface.

The overall mass transfer resistance is thus the sum of the resistance of the three individual mass transfer steps. It has been found that the membrane resistance and stripping film resistance are negligible compared to the feed liquid film resistance (64). Based on Fick's first law, the following equation has been derived to describe this mass transfer process (65):

$$\ln\left(\frac{[HCN]_{F,0}}{[HCN]_{F,t}}\right) = \left(\frac{KA}{V_{F,0}}\right)t \tag{20}$$

where $[HCN]_{F,0}$ and $[HCN]_{F,t}$ are the initial HCN concentration in the bulk feed and the HCN concentration at time t respectively, K is the overall mass transfer coefficient, A is the membrane area and $V_{F,0}$ is the initial feed volume.

This gas membrane process has been used to recover cyanide from industrial wastewater streams (64). It also has the potential to be used in the recovery of cyanide in the gold industry. However, because it requires acidification of a clarified stream, this process can be better used as a sub-process of a comprehensive copper cyanide recovery flowsheet, for example as a sub-process for the ion exchange processes that use acid elution, to recover HCN (see ion exchange section). The authors have also studied gas membranes as a sub-process for the simultaneous recovery of HCN during the low pH electrowinning of copper from copper cyanide solutions (unpublished data). The recovery of HCN was found to be very effective but some issues were also identified with the simultaneous recovery approach, including:

1. precipitation of CuCN in the copper cyanide stream due to the extraction of HCN by the gas membrane,

2. loss of the pH buffer, acetate (as HAc), to the caustic stream at pH 5 at which the electrowinning was carried out, and

3. continuous dilution of the copper cyanide stream by the vapour transferred across from the caustic stream due to the osmotic distillation effect with highly saline solutions such as NaCl resin eluates (see ion exchange section).

All these problems can be avoided or alleviated by adopting a sequential recovery approach by which cyanide is recovered following the electrowinning of copper and pH adjustment to 6 - 8 at which acetate is in the form of NaAc but cyanide is in the form of HCN.

Sulfidisation

Like AVR, sulfidisation processes involve acidifying the solution, but use sulfide to precipitate Cu_2S instead of producing CuCN. Such processes use sulfide ions from reagents such as Na_2S, NaSH, or H_2S to produce a copper sulfide precipitate as shown in Reaction 21.

$$2Cu(CN)_3^{2-} + S^{2-} + 6H^+ \rightarrow Cu_2S + 6HCN \tag{21}$$

Two processes exist which exploit this chemistry and only differ in terms of the precipitate handling. They are the Metallgeselshaft Natural Resources (MNR) process (66) and the sulfidisation, acidification, recycle, and thickening (SART) process. The MNR process uses only filtration for post precipitation dewatering, requiring large filtration machines as the slurry can be as low as 0.5 %

solids. The SART process instead thickens the slurry to 10 – 15 % facilitating more than a 100 times decrease in slurry volume and hence filter size (55, 59). The SART process also uses some of the thickened slurry as seed during precipitation, promoting crystal growth.

Reaction 21 is rapid and goes to near completion with stoichiometric sulfide addition at pH less than 5. This gives sulfidisation processes several advantages over volatilisation processes such as reduced residence time and increased cyanide recovery. Further, MacPhail et al. (59) showed reduced acid consumption for SART compared to AVR along with increased copper recoveries. As cyanide is not separated from other aqueous species after SART is performed, SCN^- and iron cyanides can build up in the circuit (56, 59). Cyanate does not build up as it is destroyed during acidification.

To offset the impact of a positive water balance if CCD is used to generate a clear solution feed to SART, several authors have proposed using volatilisation in conjunction with sulfidisation (56, 67). The work by Fleming and Trang (56), however, shows that this cannot be done during sulfidisation due to loss of sulfide as hydrogen sulfide gas. Their results showed a 25 times increase in cyanide in the precipitate as less sulfide was available to react with copper. Volatilisation could be performed on the recycle stream after sulfidisation as was initially proposed for Newcrest's Telfer Operation (67). Alternatively copper cyanide could be removed and concentrated from the tailings stream in other ways as discussed previously in this paper.

Sulfide itself can also cause problems in sulfidisation processes. MacPhail et al. (59) have reported that thiocyanate forms during SART, attributing this to the addition of sulfide to the solution before it is acidified. Sulfide and cyanide, however, do not react quickly without a catalyst making the reagent addition order unlikely to be the cause of the observed thiocyanate increase. Sulfide is also a problem if overdosed as excess sulfide in SART will be returned to the leach circuit along with the recovered cyanide. Within the leach circuit the excess sulfide ions will have the time and catalysts to form thiocyanate, resulting in a reduction in usable cyanide recovered (68). Excess sulfide may also result in the generation of hydrogen sulfide gas.

Finally, as an alternative for importing or generating Na_2S or NaSH for use in SART, it is possible to use biogenically produced H_2S (69). Known as biogenic sulfide the authors claim it offers lower costs than transporting sulfide to the plant or current onsite generation technology. The use of H_2S also means acid consumption can be reduced due to the availability of the two protons from the hydrogen sulfide gas. However, there are limited details on this process and there are only a few commercial installations, some of which feed a SART process.

Scaling

A potential problem with the above acidification based technologies is scaling. The use of sulfuric acid on solutions having high calcium concentrations can cause the formation of scale (70). This is due to sulfate and calcium reacting to form gypsum. Further, if reneutralisation is required after acidification, further gypsum can form if lime is used (60, 68). Prevention of scale is possible through the use of other acids but these are more expensive and often cause additional problems. Generally, scale problems are treated by periodic shutdowns for descaling. For some equipment, however, scale cleaning may be difficult making such processes undesirable.

Electrowinning

The mechanism by which copper deposits from its cyanide complexed forms to reduced copper metal on the electrode surface is not well understood, with several different mechanisms having been proposed which are summarised by Dudek and Fedkiw (71). The potential electrochemical reactions involved in copper cyanide electrowinning are summarised below, including the oxidation of cyanide (72) and copper cyanide complexes (73) at the anode.

Cathode reactions:

$$\mathrm{Cu(CN)_3^{2-} + e^- \rightarrow Cu + 3CN^-} \qquad (E^0 = -1.09\ \mathrm{V}) \qquad (22)$$

$$\mathrm{Cu(CN)_2^{-} + e^- \rightarrow Cu + 2CN^-} \qquad (E^0 = -0.43\ \mathrm{V}) \qquad (23)$$

$$\mathrm{2H_2O + 2e^- \rightarrow H_2 + 2OH^-} \qquad (E^0 = -0.83\ \mathrm{V}) \qquad (24)$$

Anode reactions:

$$4OH^{-} \rightarrow O_2 + 2H_2O + 4e^{-} \qquad (E^0 = 0.40\ V) \qquad (25)$$

$$CN^{-} + 2OH^{-} \rightarrow CNO^{-} + H_2O + 2e^{-} \qquad (E^0 = -0.97\ V) \qquad (26)$$

$$Cu(CN)_3^{2-} + 8OH^{-} \rightarrow 3CNO^{-} + Cu(OH)_2 + 3H_2O + 7e^{-} \qquad (27)$$

where E^0 is the standard reaction potential at 25 °C.

Alkaline conditions

Direct electrowinning has been used in the electroplating industry to recover copper and destroy the cyanide from spent copper-cyanide electroplating solutions via the above reactions (72, 74). In the gold industry, however, the recovery of both copper and cyanide is desirable and therefore a membrane cell has been proposed to avoid the anodic destruction of cyanide ions released during the cathodic reduction of copper cyanide complexes, thus enabling its recycle to the leaching process. This patented process is commonly referred to as the DuPont process named after the DuPont ion exchange membrane used in the process (75). In this process, the leachate (cyanidation tails solution) from leaching copper-gold ores using a molar ratio of CN:Cu > 3:1 is pumped at a high flow rate through the cathode compartment to electrodeposit the copper on high surface area cathodes (e.g. steel wool, stainless steel wool, stainless steel knitted mesh and aluminum wool) in the cell. A cation exchange membrane is used to separate the cathode compartment from the anode compartment and thus to diminish the anodic oxidation of cyanide ions. Recommended also is the use of sulfide, thiourea, thiocyanate, benzothiazole or thiosulphate to reduce hydrogen evolution at the cathode by blocking/poisoning the catalytic sites.

The direct electrowinning of copper from gold plant waste streams has also been studied by other researchers using similar membrane electrowinning cells (76-78). The electrowinning of copper from alkaline cyanide solutions often suffers from low current efficiencies and high energy consumption due to the electroactive species being $Cu(CN)_3^{2-}$ under alkaline conditions, whose standard reduction potential is more negative than that of hydrogen evolution (Reaction 22 and 24). The electroactivity of the aqueous copper cyanide species is in line with the standard reduction potentials and follows the order of $Cu(CN)_2^{-} > Cu(CN)_3^{2-} > Cu(CN)_4^{3-}$ (77). Even if the initial solution mainly contains $Cu(CN)_2^{-}$, the most electroactive copper cyanide species, the current efficiency drops sharply initially as the copper is deposited from solution due to the increase in the CN:Cu ratio from the released cyanide ions shifting the copper cyanide speciation to $Cu(CN)_3^{2-}$, a less electroactive species.

Table 2 summarises the results from various electrowinning investigations conducted. Importantly, only high current efficiencies are achieved at high copper concentrations and thus the process becomes less efficient at higher percentage copper recoveries. Lu et al. (77) used a graphite felt cathode which has high surface area and a relatively high over-potential for hydrogen evolution and were thus able to achieved higher current efficiency. An option to increase the current efficiency has been described by Dreisinger et al. (50) which takes a bleed stream from the electrowinning cell for cyanide recovery by the AVR process with the CuCN precipitate returned to the electrowinning process to lower the CN:Cu ratio and thus to encourage the formation of $Cu(CN)_2^{-}$. The use of elevated temperature also improves the current efficiency, however the hydrolysis of cyanide ions is accelerated and becomes significant at temperatures above 50 °C (79, 80).

Table 2: Copper electrowinning performances from alkaline copper cyanide solutions.

Researcher	**Cu (mM)**	**CN:Cu**	**Temp. (°C)**	**Current density (A m^{-2})**	**Cu recovery (%) / time (h)**	**Current efficiency (%)**	**Power consumption (kWh kg^{-1})**
Lemos et al. (2006)	~10	3.5	ambient	0.185	99 / 5	1.5	79
Wang et al. (2009)	195	~4.4	50	7.5	68 / 8	76.5	3
Lu et al. (2002)	15-30	3-9	40	-	40 / -	50-80	1-2
DuPont	~80	2.9	ambient	-	25 / -	82	2.4

Apart from the low current efficiency and high power consumption, the complex design of the membrane cells and the difficulties in handling the membrane deter the application of these technologies. To eliminate the use of a membrane, sulfite has been proposed as a sacrificial species to reduce the anodic destruction of copper cyanide complexes via Reaction 27 during the electrowinning of copper cyanide. This is in anticipation that the dominant anodic reaction would become the oxidation of sulfite to sulfate (81). It has been found, however, that the effect of sulfite on suppressing the anodic oxidation of copper cyanide decreases with increasing the CN:Cu ratio due to the shift in the discharged species from $Cu(CN)_3^{2-}$ to $Cu(CN)_4^{3-}$. Under optimum conditions (CN:Cu = 3 - 3.2, $[SO_3^{2-}]$ = 0.4 - 0.6 M and temperature = 50 - 60 ^oC), 80 - 90 % anodic current efficiency of sulfite was achieved, with the rest being the destruction of copper cyanide complexes.

Acidic conditions

The problem of low current efficiency and high energy consumption with copper electrowinning from alkaline cyanide solutions can potentially be solved by conducting the electrowinning at low pH to increase the concentration of the most electroactive species, $Cu(CN)_2^-$ (Figure 2), and thus minimise the hydrogen evolution side reaction (82). Another advantage of electrowinning the copper at low pH is that the cyanide ion released during electrowinning will form HCN when there is sufficient H^+ available in the solution. Thus, there is little change in the speciation of the remaining copper cyanide in solution, which occurs in alkaline solutions due to the increasing ionic cyanide to copper ratio. The optimum pH for electrowinning was found to be pH 5 and an acetate solution was used as a pH buffer to minimise the interfacial pH change at the electrode surface, which significantly enhances the electrowinning performance. A current efficiency of 90 – 100 % and an average energy consumption of 0.85 – 1.00 kWh $(kg\ Cu)^{-1}$ were achieved using this low pH electrowinning method with a membrane cell, which outperforms all the alkaline electrowinning methods employed by other researchers (Table 2). The released cyanide is protonated ($HCN_{(l)}$) and has the potential to be simultaneously recovered by a hydrophobic gas membrane contactor (65), which was described previously.

Electrochemical studies have found that in acidic solutions, the anodic oxidation of free cyanide (in HCN form) is substantially more difficult than the oxidation of cyanide ions in alkaline solutions (via Reaction 26) and can hardly be differentiated from the oxygen evolution curve (82). This gives some prospect to eliminate the use of a membrane in the electrowinning of copper from acidified solutions if the dominant anodic reaction is oxygen evolution. Unfortunately, although the anodic oxidation of HCN was difficult, the oxidation of $Cu(CN)_2^-$ was found to occur at ~ 550 mV (SHE), a potential significantly more negative than oxygen evolution, and thus would be the dominant anodic reaction in a non-membrane electrowinning cell, destroying cyanide and precipitating copper as CuO. The authors have also investigated potential anode materials to encourage oxygen evolution over the oxidation of $Cu(CN)_2^-$ and the addition of a sacrificial species to replace or suppress the oxidation of $Cu(CN)_2^-$, but without success.

Polychelating polymers

It has been found that particular non-toxic, long-chain water-soluble polymers containing significant concentrations of nitrogen, oxygen and/or sulphur groups are capable of complexing with anionic metal cyanide species. If the charge density of the polymer is sufficiently high, the metal may be displaced from the accompanying cyanide ions (copper atoms more strongly co-ordinate with the lone pair of electrons present at N, S and O sites within the polychelating polymer than to the cyanide ions) (14, 83). This forms the basis for the copper cyanide recovery with polychelating polymers.

$$Cu(CN^-)_x + (P)H \Leftrightarrow Cu(P) + x(CN^-) + H^+ \qquad (28)$$

$$Cu(CN^-)_x + (P)Na \Leftrightarrow Cu(P) + x(CN^-) + Na^+ \qquad (29)$$

where P, PH and PNa are the polychelating polymer, its protonated form and sodium salt form respectively.

In a patented process Smith and Robinson (83) used branched chain poly(ethyleneimine) polymers in which the ratio of primary to secondary to tertiary amines is approximately 1:2:1. Whilst Jay (84) used poly(alkyleneimine) polymers which are grafted polymers and/or grafted and crosslinked polymers containing primary, secondary, tertiary and possible quaternary amine functionality. Due to the oxidation by oxygen in the solution both Cu(I) and Cu(II) valency states have been found to exist in the copper-polychelator speciation. Membrane ultrafiltration was used to separate the copper-polychelator complex (retentate) from the cyanide ions (permeate). The cyanide was directly recycled to the leach circuit; whilst the copper was recovered by conventional electrowinning directly from the polychelated copper polymer solution, releasing the polychelator for recycling (14).

$$\text{Anode: } Cu(P) \Rightarrow Cu^{2+} + (P) + 2e^{-} \tag{30}$$

$$\text{Cathode: } Cu^{2+} + 2e^{-} \Rightarrow Cu^{0} \tag{31}$$

Alternatively, the copper can be stripped from the polymer using dilute acid or competing chelating agents for further processing e.g. precipitation (83):

$$Cu(P) + H^{+} \Rightarrow H(P) + Cu^{+} \tag{32}$$

$$Cu(P) + L \Rightarrow (P) + CuL \tag{33}$$

There are some potential issues with this technology. The contamination of foreign metal ions such as iron can significantly affect the current efficiency of copper electrowinning via the Fe^{2+}/ Fe^{3+} redox couple. In treating a whole tailings stream, the use of membrane ultrafiltration to separate the polychelator and copper complexes from cyanide ions can be energy intensive and costly. Therefore, this technology may be more suitable for the separation of copper from cyanide ions where the copper cyanide has been concentrated by activated carbon, ion exchange resin or solvent extraction (14). To enable the use of this technology to recover metal cyanides from leach slurries rather than clarified solutions, Jay incorporated the poly(alkyleneimine) polymers into a solid polymer (insoluble) and proposed a polymer-in-pulp process in which copper is recovered via polychelation and cyanide is potentially released simultaneously (84). However, these processes are yet to be tested industrially.

CONCLUSIONS

The recovery of both copper and the recycle of cyanide in treating copper - gold ores by cyanidation potentially has both economic and environmental benefits. Various processes have been developed or proposed which all require a clarified feed solution. For the recovery from CIL and CIP cyanidation tails, either physical separation of the solution from the slurry or adsorption of copper cyanide onto a recoverable adsorbent is required. The adsorption processes using activated carbon or ion exchange resins are typically more attractive from a capital cost and operating point of view than physical separation using filters or thickeners with CCD.

1. The resin technologies enjoy fast adsorption kinetics and little influence from the cyanide-to-copper ratio. However, there remain some challenges including their high cost, small bead size, low resistance to osmotic shock, reduced adsorption efficiency in hypersaline solutions and a number of potential issues with the individual resin processes as detailed in Table 1.

2. The activated carbon based copper cyanide recovery processes are relatively low cost and have good compatibility with the existing gold plants (i.e. using the existing reagents/materials, facilities and proven process flowsheets, thus requiring minimal plant modification and familiar technology). Unlike the ion exchange resin based technologies, thiocyanate and iron cyanide have little effect on the carbon processes due to their poor adsorption on carbon. Hypersaline process water is detrimental for resin processes but beneficial for carbon processes in assisting adsorption via ion pair formation. One concern with carbon processes is the potential oxidation of cyanide to cyanate by oxygen particularly in the presence of both carbon and copper (85). Therefore, the situations where cyanide, oxygen, copper and carbon co-exist should be avoided as much as possible in the overall process flowsheet.

Table 3 summarises the advantages and limitations of activated carbon in recovering copper from copper cyanide solutions in comparison with ion exchange resins.

Table 3: Comparison of activated carbon and ion-exchange resin in recovering copper cyanides

Factor Process	Loading mechanism	Loading limit	Low CN:Cu ratio	SCN^- / $Fe(CN)_6^{4-}$ competition	Potential cyanide recovery	Potential cyanide oxidation	Hyper-saline solution	Cost	Risk
Carbon	Ion pairing	Freundlich isotherm	essential	weak	yes	yes	beneficial	low	low
Resin	Ion exchange	IX capacity	non-essential	strong	yes	no	detrimental	high	high

For clear solutions solvent extraction offers an alternative to activated carbon or ion exchange resins to concentrate copper cyanide, but faces some challenges such as the degradation of organics, the low efficiency for extracting copper from solutions containing high copper and / or thiocyanate and the decrease in extraction efficiency with extraction stages due to the increase in CN:Cu ratio.

Technologies developed or proposed to separate and recover copper and cyanide from clear solutions include the acidification based technologies such as AVR and SART, direct electrowinning, polychelating polymers and membrane technologies.

1. Acidification based technologies such as AVR and SART are favoured by the industry due to their simplicity in chemistry and effectiveness and robustness in recovering the copper and/or cyanide. However, there are known efficiency issues with these processes and the CuCN or Cu_2S product must be readily saleable.

2. The direct electrowinning of copper from alkaline copper cyanide solutions normally suffers from low current efficiency and high power consumption. Electrowinning from acidic solutions has the potential to significantly improve the current efficiency and reduce the power consumption, but is more suitable for concentrated copper solutions (e.g. carbon or resin eluate) to avoid acidification of the whole tailings stream. The anodic destruction of cyanide is a major issue with the electrowinning technology and thus requires the use of a membrane electrowinning cell which discourages the application of this technology.

3. Polychelating polymers have the advantage of directly separating copper from its cyanide complexes. However, the subsequent separation of copper loaded polychelator using membrane ultrafiltration can be energy intensive. Polymer-in-pulp using insoluble polymers incorporated with polychelating functions appears to be promising, but more research is required to further develop this technology and demonstrate it at the pilot scale.

4. Membrane technologies have advanced very quickly in recent years and are expected to have application within the gold industry in the near future and particularly in the recovery of copper and cyanide. The gas membrane technology is likely to be integrated into the overall flowsheet to recover and concentrate cyanide from acidified clear solutions.

Thus, a combination of the above processes is required to achieve copper and cyanide recovery. For example to avoid the clarification of the whole stream, ion exchange resins or activated carbon can be used to concentrate the copper and/or cyanide from the slurry to produce a small volume of highly concentrated solution suitable for separation and recovery of the copper and cyanide via processes like SART or electrowinning and a gas membrane. There is no universal process solution and the choice is highly dependent on the nature of the stream to be treated and integration with the whole plant.

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