# CYANIDE USE AND MANAGEMENT IN THE GOLD INDUSTRY

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## ABSTRACT

Cyanide has been used for the recovery of gold and silver for more than 100 years. The current stage of knowledge of cyanide chemistry and toxicology is such that as long as it is managed properly, cyanide can be used successfully in the mining industry with minimal risk to the environment or human health and safety. Canadian companies use technologies that are based on best practices. These technologies enable them to discharge effluents that comply with provincial cyanide concentration limits, which are among the highest standards in the world. This paper will include: a review of gold milling processes; the chemistry and toxicity of cyanide; effluent treatment processes that are currently being practiced; and discuss the development of an alternative to cyanide.

## INTRODUCTION

Cyanide occurs naturally in various microorganisms and higher plants where it is used as a protective mechanism that makes them an unattractive food source. In some plants it is present in concentrations that would be considered hazardous if they were man made. For example in bamboo tip, concentrations may go as high as 8,000 mg/kg. Cyanide is manufactured, principally in the forms of gaseous hydrogen cyanide and solid sodium and potassium cyanide (Logsdan et al, 1999). About 80% of the world production is used in the production of organic compounds such as nitrile, nylon and acrylic plastics. Other uses range from: use as an anti-caking additive in road salt; as a means of exterminating rodents and insects; and use as the anticancer substance laetrile (Logsdan et al, 1999). The remaining 20% is used to produce sodium cyanide, of which nearly 90% is used in the mining industry to extract gold and silver.

Cyanide has been used for the extraction of gold and silver for more than 100 years. The original patent for the process was obtained by John MacArthur in 1887. The first cyanidation plant was commissioned at the Crown Mine in New Zealand in 1889. Within 20 years of its introduction, worldwide production doubled. The popularity of the cyanidation process is based on its simplicity. At ambient conditions, a dilute solution of sodium or potassium cyanide (about 1 g/L) is capable of dissolving finely disseminated gold particles at concentrations as low as a few grams per tonne. There are alternatives to cyanide leaching (thiourea, thiosulphate, thiocyanate) but none are used commercially and their environmental impact has not been assessed. Some of the work that is presently being performed to develop a process using ammonium thiosulphate will be discussed.

## GOLD PRODUCTION

In 1999 there were about 33 primary gold mines operating in Canada producing a total of 158 tonnes of gold (Keating, 2001). Cyanidation, accounted for about 88% of all Canadian production, the balance being obtained as a by-product of base metal refining (10%) and placer mining (2%).

Current cyanidation processes involve a combination of: crushing / grinding; gravity concentration; flotation; cyanidation; gold recovery using: carbon-in-pulp (CIP), carbon-in-leach (CIL), filtration-zinc precipitation (Merrill-Crowe); electrowinning and refining. In the crushing and grinding stages ore is ground to facilitate dissolution; a typical grind would be 80% -105 μm. Some mills grind the ore in a cyanide solution so that it can attack the freshly exposed gold surfaces. In some cases, preconcentration of the coarse gold by gravity is practiced to improve overall recovery and reduce the size of the cyanidation circuit. A combination of flotation and cyanidation is used when the bulk of the gold is associated with a sulphide, in this case it is common practice to separate the sulphide fraction, and in so doing the gold by froth flotation. The sulphide concentrate would typically represent 10-15% of the original feed and contain up to 99% of the gold which is then fed directly

cyanide can recover 80% of the gold when the ore is ground to 80% -100 μm. For other gold containing ores some pretreatment is required. Roasting is used to burn away carbon that will adsorb or Apreg-rob@ the leached gold. Autoclaving is used to oxidize sulphide and arsenic minerals thereby liberating entrained gold particles. Information on the processing methods used as well as the cyanide destruction techniques in place at some Canadian gold mines are shown in Table 1.



Figure 1: Typical gold processing flow sheet.

## CYANIDATION

Cyanide in solution exists as either free or complexed cyanide. When solid sodium cyanide is dded to solution it dissociates to form the sodium and CN⁻ ions. The CN⁻ ion then combines with the hydrogen ion to form molecular HCN (Logsdan et al, 1999). Free cyanide normally refers to the combined concentration of these two compounds. In solutions, an equilibrium is set up between these two compounds, the ratio being determined by the pH (Figure 2). Under normal conditions of temperature and pressure, the concentrations of HCN and CN⁻ are equal at pH 9.4; below this pH HCN predominates and above this pH CN⁻ predominates.
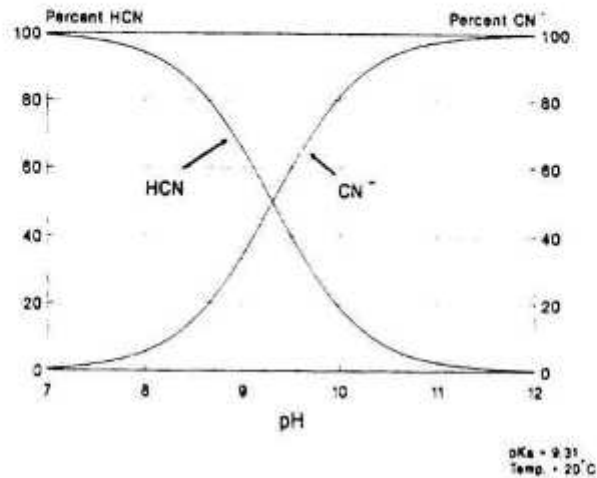


Figure 2: Speciation of cyanide as a function of pH (Higgs, 1992).

Mills typically use solutions of sodium or potassium cyanide in the range of 100 to 500 mg/L to extract gold from the ore under well aerated conditions. Cyanidation is conducted at álkaline pH=s (pH 10-12) which: prevents the loss of HCN, suppresses cyanicides such as zinc and improves the efficiency of the extraction process. Leaching takes place in a series of mechanically agitated tanks for 24-48 hours at about 50-55% solids. The dissolution is believed to be a two stage dissolution which is represented by the overall equation shown below.
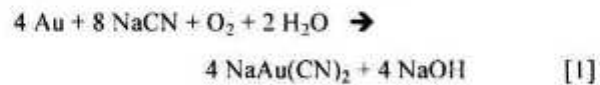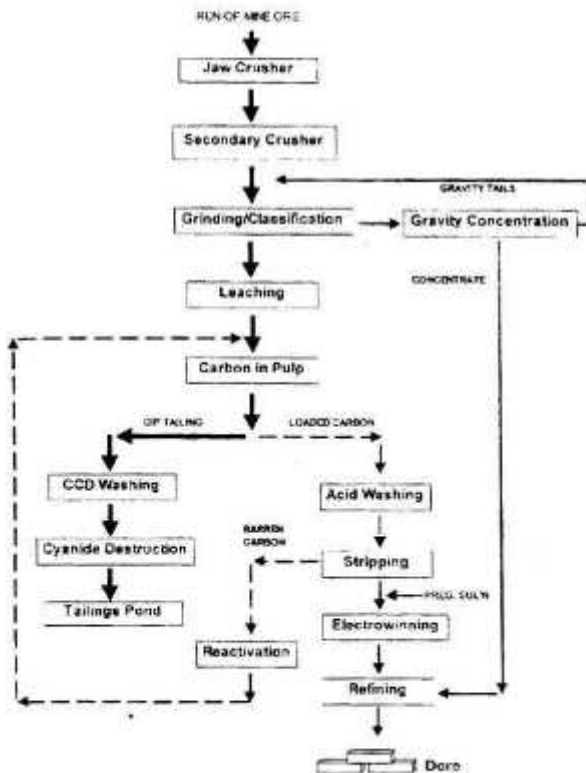
$$4\ Au + 8\ NaCN + O_2 + 2\ H_2O \rightarrow$$

$$4\ NaAu(CN)_2 + 4\ NaOH \qquad [1]$$

Table 1: Milling and effluent treatment practice in Canadian Gold Mines (Adapted from Damjanovic, 2000).

| Mine | Process | Effluent treatment/ Effluent quality |
|---|---|---|
| Barrick Gold, Est Malartic, Quebec | Gravity, flotation, cyanidation, Merrill-Crowe | Inco SO$_2$/air, natural degradation |
| Barrick Gold, Holt McDermott, Ontario | Carbon-In-Leach (CIL) | Natural degradation CN$_F$ <0.001 CN$_T$ 0.01 mg/L CN$_{WAD}$ 0.066 mg/L [2] |
| Battle Mountain Gold, Golden Giant Mine, Ontario | Gravity, cyanidation, Carbon-In-Pulp (CIP) | Hemlo Process CN$_T$ 0.3 [2,3] |

Table 1: Milling and effluent treatment practice in Canadian Gold Mines (Adapted from Damjanovic, 2000).

| Mine | Process | Effluent treatment/ Effluent quality |
|---|---|---|

Table I: Milling and effluent treatment practice in Canadian Gold Mines (Adapted from Damjanovic, 2000).

| Mine | Process | Effluent treatment/ Effluent quality |
|---|---|---|
| Black Hawk Mining Inc., Keystone Gold Mine, Manitoba | Cyanidation, CIP | Natural degradation |
| Cambior, La Mine Doyon, Quebec | Cyanidation, CIP/CIL | Natural degradation $CN_F$ 0.01 mg/L $CN_T$ 0.07 mg/L $CN_{WAD}$ 0.01 mg/L [2,3] |
| Inmet Mining Corp., Trolius, Quebec | Gravity, flotation, cyanidation, CIL | Inco $SO_2$/air |
| Kinross Gold Corp., Timmins Operations, Ontario | Gravity, cyanidation, CIP | Hydrogen peroxide, ferric sulphate |
| Placer Dome, Campbell Mine, Ontario | Gravity, flotation, pressure oxidation, Merrill-Crowe, CIP | Inco $SO_2$/air, natural degradation $CN_F$ 0.25 mg/L |
| Placer Dome, Dome Mine, Ontario [1] | Gravity, cyanidation, CIP | Inco $SO_2$/air |
| Placer Dome, Musselwhite Mine, Ontario | Gravity, cyanidation, CIP | Inco $SO_2$/air, natural degradation $CN_T$ 0.022 mg/L $CN_{WAD}$ 0.008 mg/L [2] |
| Richmont Mines, Nugget Pond Division, Newfoundland | Cyanidation, CIP | Inco $SO_2$/air |
| Royal Oak Mines, Pamour Mine, Ontario | Flotation, cyanidation, Merrill-Crowe | Natural degradation |
| TVX Gold Inc., New Brittania Mine, Manitoba | Cyanidation, CIP | Natural degradation, ferric sulphate |

| Mine | Process | Effluent treatment/ Effluent quality |
|---|---|---|
| Williams Operating Corp., Williams Mine, Ontario | Cyanidation, CIP | Natural degradation $CN_T$ 0.019 mg/L $CN_{WAD}$ 0.007 mg/L [2,3] |
| Viceroy Minerals Corp., Brewery Creek Mine, Yukon | Cyanidation heap leach, CIP | Zero discharge |

[1] Yeomans and Yaschyshyn, 2001

[2] Melis et al, 1998

[3] Melis, 2000

In solution the cyanide and any metals present may become linked in the form of metallic-cyanide complexes which results in excessive reagent consumption and may also interfere with the dissolution or subsequent precipitation processes. It is important to determine the quantity and composition of these complexes in order to ensure the proper selection of the destruction technique that is able to chemically break down these complexes and then destroy the cyanide.

## EFFLUENTS

The effluents from the gold milling process, either with or without prior treatment for cyanide removal, are directed to a tailings pond where solids settle out and are retained. The clear, decant water, with or without further treatment, is then discharged to the receiving waters. Common constituents of gold mill effluents contain: free cyanide, simple compounds, weak complexes and strong complexes. In Table II these are listed in order of increasing stability. The stabilities and relative concentrations in solution will be a factor in the selection of the treatment method (McNamara and Ritcey, 1988).

The metallic complexes are products of relatively insoluble materials and free $CN^-$ in solution, the stronger complexes form as more excess $CN^-$ is available in solution. Iron cyanides are very stable in the absence of light but in the presence of light readily break down. Some of the other compounds that are formed in the process are: thiocyanate (CNS), which occurs in the preparation or leaching stages, it breaks down under UV

light and can be degraded biologically; cyanate (CNO) which is formed by the oxidation of cyanide in leaching or as a result of cyanide destruction process; ammonia ($NH_3$) and formate which are formed at room temperature when CN reacts with water. A typical analysis of an effluent is given in Table III.

Table II: Cyanide compounds in solution in order of increasing stability.

| Compound | Chemical formula | Comments |
|---|---|---|
| Free cyanide | $CN^-$, HCN | Very soluble; equilibrium determined by pH |
| Simple compounds | NaCN, KCN, $Ca(CN)_2$ | Readily soluble |
|  | $Zn(CN)_2$, $Cd(CN)_2$, CuCN, $Ni(CN)_2$, AgCN | Relatively insoluble but do dissolve |
| Weak complexes | $Zn(CN)_4^{2-}$ $Cd(CN)_3^-$ $Cd(CN)_4^{2-}$ |  |
| Moderately strong complexes | $Cu(CN)_2^-$ $Cu(CN)_3^{2-}$ $Ni(CN)_4^{2-}$ $Ag(CN)_2^-$ |  |
| Strong complexes | $Fe(CN)_6^{4-}$ $Co(CN)_6^{4-}$ $Au(CN)_2^-$ |  |

Table III: Typical analyses of gold mill effluent (Scott, 1993).

| Component | Concentration (mg/L) |
|---|---|
| $CN^-$ | 50 - 2000 |
| CNS | 42 - 1900 |
| $S_2O_3$ | 856 |
| As | 0 - 115 |
| Cu | 0.1 - 300 |
| Fe | 0.1 - 100 |
| Pb | 0 - 0.1 |
| Mo | 0 - 4.7 |
| Ni | 0.3 - 35 |
| Sb | 0 - 93 |
| Zn | 13 - 740 |

# REGULATIONS

Presently the Canadian Metal Mining Liquid Effluent Regulations (MMLER) provides the minimum discharge standards for all mines with the exception of gold mines and mines that have been in operation since 1977. Due to this exemption, there are currently no federal regulated levels for cyanide. Proposed changes to these regulations will likely include all mines and place an upper limit of 1.0 mg/L for total cyanide. They will also require that the effluent be non-acutely toxic to rainbow trout. Mines in Canada are also subject to provincial requirements which do include an upper limit for cyanide. Some of the requirements for the different provincial jurisdictions are provided in Table IV below. Also included in the table are selected international effluent discharges standards applicable to mining operations.

Table IV: Effluent discharge limits for total and WAD cyanide (Senes, 1999).

| Jurisdiction | Total Cyanide (mg/L) | WAD cyanide (mg/L) |
|---|---|---|
| Ontario, Canada | 1 [1] |  |
| Quebec, Canada | 1.5 |  |
| British Columbia, Canada | 0.1-0.5 [2] |  |
| Yukon, Canada | 0.05-0.5 [3] | 0.1 - 0.2 [3] |
| Chile | 1 [4] |  |
| South Africa | 0.5 [5] |  |
| World Bank | 1 [6] | 0.5 [6] |
| Tasmania | 0.05, 0.2 [7] |  |

NOTES:

[1] Ontario Regulation, 560/94, values are typical in Certificates of Approval

[2] Pollution Control Objectives for the Mining, Smelting and Related Industries of British Columbia, range of values apply to discharges into marine and fresh waters, all values are dissolved values in the receiving environment

[3] Range of values from 4 licenses held by the Yukon Territory Water Board

[4] Discharge to water ways

[5] General Effluent Standards, separate standards exist depending on the end use (Pulles et al, 1996).

[6] Guidelines for Base Metal and Iron Ore Mining

[7] Discharge to fresh water and marine environment.

The inclusion of a toxicity component represents a shift in focus of regulations from placing limits to measuring the impact on the receiving environment. Current regulatory measures of toxicity relate to the acute lethality of effluents to fish as measured by the 96 hour bioassay method. In this test, 50% of the fish exposed to 100% of the effluent must survive for 96 hours. The toxicity is often expressed as $LC_{50}$, that is the concentration of a component in an effluent that kills 50% of the test fish in 96 hours (Scott, 1993). In 1998, the Canadian precious metals industry had a 86% pass rate for this test. The substances most commonly suspected of causing toxicity are ammonia and copper. Other suspected toxicants include: high alkalinity, heavy metals, cyanate and thiocyanate.

The three groups of animals known to be affected by cyanide are: mammals, reptiles and amphibians; migratory birds and waterfowl; and other forms of aquatic life. Reports of cyanide poisoning of the first group are minimal, due to implementation of appropriate containment design and engineering standards. With waterfowl the primary concern is with exposure in open ponds at mining operation; if the ponds are netted or the weak acid dissociable (WAD) cyanide kept below 50 mg/L the risk is minimized (Smith and Mudder, 1995). For the preservation of aquatic life, WAD cyanide (the toxicologically important form of cyanide) can be reduced to acceptable levels via the use of well established chemical, physical and biological treatment processes. Site specific chronic criteria, 0.08-0.10 mg/L WAD cyanide have been developed for the protection of aquatic life and have been implemented in a number of receiving waters in the US and New Zealand.

## EFFLUENT TREATMENT PROCESSES

After gold recovery by carbon adsorption, the resulting barren solution invariably contains both free and complexed cyanide. Degradation products such as: thiocyanate, cyanate and ammonia are also present in the effluent. As mentioned, due to the toxicity of these components it is usually necessary to treat the effluents before they can be discharged into the environment. The most commonly practised techniques for the treatment of cyanide containing effluents are: natural degradation, chemical oxidation, biological oxidation and recycle or recovery. The process employed at a site is chosen on the basis of site specific factors such as: the level and type of contaminant (i.e. simple, complexed), the form of the effluent (i.e. clarified, slurry) and the final effluent quality desired.

## Natural Degradation

Until the 1980's natural degradation was the only process that was used to destroy cyanide in gold mill effluents. Even with the advent of newly developed chemical methods, natural degradation remains the most commonly used treatment technique either alone or in combination with chemical methods. In this process the cyanide and dissociated metal complexes are broken down by natural processes that occur through prolonged exposure to the environment in tailings ponds. A number of physical, chemical and biological mechanisms are involved in the overall removal of cyanide in this method, but volatilization and metallo-cyanide dissociation are the main ones controlling the process (Simovic and Snodgrass, 1989). Other factors that are also involved are: pH depression, dissociation, photolysis, chemical and biological oxidation, precipitation and absorption (Scott, 1993). Following dissociation of the complexes, the base metals precipitate as hydroxide. If iron cyanide complexes are present, photolysis with sunlight is necessary for their dissociation (ADI, 1994).

The rate at which natural degradation occurs is influenced by a number of factors, including: pH, temperature, ultraviolet radiation, aeration, turbidity, and the pond conditions (e.g. area, depth, retention time). The effect of surface area was evident at Hemlo Gold=s Giant Mine in Northern Ontario. At this site the surface area of the tailings pond was increased from 23.3 acres in 1987 to 43.9 acres in 1988 with a corresponding decrease in depth (Konigsmann et al, 1989). This produced a significant effect on the final effluent concentrations of CN and the metals over these two years (Table V). Other examples showing the effectiveness of natural degradation are seen in data for Lupin and Holt-McDermott Mines. At the Lupin mine natural degradation is the sole method of cyanide degradation (Scott, 1993), it is accomplished in a series of two ponds whose total retention time is two years. In 1991, the cyanide concentration in the mill discharge was reduced from 166 mg/L cyanide to 0.019 mg/L as a result of the degradation in the ponds. At the Holt-McDermott operation, two settling basins of 75 and 100 Ha are used for natural degradation. Recent results show effective removal of $CN_T$ from 100 mg/L to less than 0.01 mg/L, cyanate and thiocyanate are also reduced significantly in this system (Goode et al, 2001). This even though the ponds are covered with ice for 4 months of the year.

Table V: Effluent quality at Hemlo Gold Golden Giant Mine (Konigsmann et al, 1989)

| | CN | Cu | Fe | Ni |
|---------|------|-----|------|-----|
| Tailings | 88.3 | 8.5 | 22.3 | 5.8 |
| 1987 | 6.1 | 3.1 | 0.7 | 2.3 |
| 1988 | 0.7 | 0.2 | 0.3 | 0.3 |

Some of the advantages of a natural degradation system are that it is relatively inexpensive and can be developed in conjunction with existing tailings ponds. If properly designed it could also result in the removal of contaminants such as ammonia and iron cyanide complexes. The most significant disadvantage for Canadian operations is that during the colder months natural degradation is practically non-existent. This means that if an operation relies only on this process then a water retention time of nine to ten months is needed to ensure that most of the cyanide is degraded. Another disadvantage of this method is that while natural degradation is occurring, the waste may pose a threat to humans and animals.

Some of these factors were taken into account by researchers at Environment Canada who developed a predictive mathematical model (Simovic and Snodgrass, 1989). This model can be used to design ponds for cyanide containing effluents and to predict the change in concentration occurring in a tailings pond and holding ponds as a result of natural processes. It was tested using data from real ponds and was shown to provide statistically sound predictions, at least within the 95% confidence interval of the predicted value.

## Chemical Oxidation

The two most commonly used chemical oxidation methods for the degradation of cyanide are those using $SO_2$ and $H_2O_2$.

In $SO_2$ processes, cyanide in solution is oxidized to cyanate using sulphur dioxide or ferrous sulphate and air in the presence of copper (U.S. EPA, 1994) according to the reaction below:

$$CN^- + SO_2 + O_2 + H_2O \rightarrow CNO^- + H_2SO_4 \qquad [2]$$

The acid formed in this reaction is neutralized with lime. Two patented processes exist using this concept, one by Inco and the other by Noranda.

Inco Limited has developed and patented an $SO_2$/air process for the destruction of cyanide in 1982. The process is patented and requires the payment of a royalty fee to Inco when it is applied. This has become the most

widely used chemical method for the destruction of cyanide in Canada and in fact there are about 45 sites that are licensed worldwide. It is applicable to the treatment of both slurries and clear solutions. In this process the cyanide ion and the cyanide component of metal complexes are oxidized to cyanate by a mixture of $SO_2$ or sodium bisulphite and air in the presence of a copper catalyst at a controlled pH. The theoretical requirement is 2.64 g $SO_2$/g CN (WAD), with actual dosages required ranging from 3 to 5 g/g for clear barren solutions and 4-7 g/g for slurries (U.S. EPA, 1994). Copper sulphate is added at a concentration of approximately 50 mg/L and the pH is controlled to about 8-10. Reaction times vary from 20-90 minutes. At one site 10 mg/L cyanide is removed using the feed pipeline as the reactor, in this case the retention time is only 6 minutes (Yeomans and Yaschyshyn, 2001). Iron cyanide complexes are removed through the formation of copper, zinc or nickel ferrocyanide precipitates (Senes, 1999a). Cost estimates for implementation of the Inco process were provided in Senes (1999b) for the treatment of 2.6 million m$^3$ of wastewater per year; the capital cost was in the range of $1.8 million (Cdn) and the operating cost was $0.10 (Cdn) /m$^3$. This process is generally able to reduce the total cyanide, dissolved iron, nickel and zinc concentrations to less than 1 mg/L, although copper concentrations may exceed this and may have to be removed using other means. At one site copper is removed through the addition of EDTA (Yeomans and Yaschyshyn, 2001). Another area of concern is that although cyanate is thought to be 3,000 to 5,000 times less toxic than cyanide it may further oxidize to form ammonia, which is toxic to freshwater fish. In this case the toxicity can be reduced by the addition of carbon dioxide to reduce the pH and thus convert the ammonia to its less toxic form. Performance data from sites employing the air/$SO_2$ process are given in Table VI.

Table VI: Typical treatment results (Robbins, 1996)

| Company | Effluent type | | |
|---------|---------------|--------|-------|
| | | before | After |
| Colosseum | Slurry | 375 | 0.4 |
| Casa Berardi | Slurry | 250 | 1.0 |
| Golden Bear | Slurry | 200 | 1.0 |
| McCoy/Cove | Slurry | 250 | 5.0 |
| Nickel Plate | Slurry | 250 | 5.0 |
| McBean (barren) | Solution | 370 | 0.2 |
| Mineral Hill (barren) | solution | 350 | 0.5 |
| Stock (pond) | solution | 15 | 1.0 |

Noranda Inc., holds a patent for a similar destruction process for tailings effluent, it has been tested and is presently in place at their Golden Giant Mine in Ontario (Damjanovic, 2000). The process was developed as a result of a site specific need to control antimony and molybdenum (Konigsmann et al, 1989). In the Noranda process, copper and ferrous sulphate are added to the effluent; in the presence of hydroxide ions the ferrous iron is oxidized to ferric oxide while the cupric ion is reduced to cuprous ions which removes the free cyanide as insoluble precipitates. This removal of cyanide ions from solution shifts the equilibrium of the cyanide complexes to produce more free cyanide. Residual cyanide is oxidized by the addition of hydrogen peroxide. This process has only been applied this site. Some effluent data from this process are presented in Table VII.

Table VII: Influent and effluent assays for the Hemlo Process (Konigsman et al., 1989).

|       | Influent | Effluent |
|-------|----------|----------|
| pH    | 9.10     | 9.81     |
| $CN_T$ | 23.20   | 0.13     |
| Cu    | 4.10     | 0.50     |
| Fe    | 5.20     | 0.11     |
| Ni    | 4.80     | 0.08     |
| Sb    | 7.70     | 1.00     |
| Mo    | 1.20     | 0.20     |
| CNS   | 44.40    | 24.20    |

Hydrogen peroxide in the presence of a copper catalyst can be used to convert cyanide to cyanate in much the same way as sulphur dioxide is used in the Inco $SO_2$/air process. Theoretically one mole of hydrogen peroxide will oxidize one mole of cyanide, according to the reaction below:

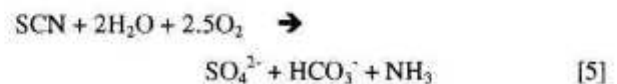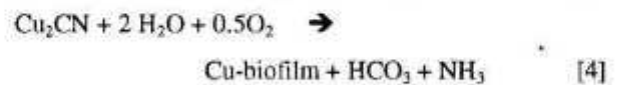$$CN^- + H_2O_2 \rightarrow CNO^- + H2O \qquad [3]$$

In practice higher concentrations are required to achieve faster reaction rates. Any dissolved metals complexes such as those containing copper, nickel or zinc are precipitated as hydroxides. Iron cyanide complexes are not oxidized by peroxide, these will be precipitated as cupric ferrocyanide. In this case though sufficient copper must be available to act as both a catalyst for oxidation and as a precipitant for ferrocyanide (ADI, 1994). The peroxide can be directly dosed into the tailings pond. Since peroxide decomposes rapidly in the presence of solids it is not economical for the treatment of slurries. Equipment requirements for the hydrogen peroxide process are similar to those required for the Inco process. The process is carried out in conventional stirred tanks, at pH 10-11 for 45 minutes to 2 hours with a peroxide to cyanide ratio of 4-5/1 being used (ADI, 1994). The major

advantage of this process is that no by products that might cause toxicity are left after the reaction takes place. Peroxide has been proven effective at a number of operations and its effectiveness is controlled by variable reagent addition in response to varying effluent compositions. On the negative side it has not been proven effective on slurries and added safety precautions are needed in this case since hydrogen peroxide is a strong oxidizer, and can give rise to violent explosions if in contact with combustible material (U.S. EPA, 1994).

**Biological Treatment**

Microbial action either naturally occurring or in an engineered reactor, results in the transformation of cyanide into ammonia. Any metals that are present in the form of cyanide complexes are released and absorbed by the biomass and thiocyanates are converted to sulfate, according to the following reactions (U.S. EPA, 1994):

$$Cu_2CN + 2 H_2O + 0.5O_2 \rightarrow$$
$$Cu\text{-biofilm} + HCO_3 + NH_3 \qquad [4]$$

$$SCN + 2H_2O + 2.5O_2 \rightarrow$$
$$SO_4^{2-} + HCO_3^- + NH_3 \qquad [5]$$

If the proper conditions are in place, further microbial action will convert the ammonia to nitrate:

$$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + 2H^+ + H_2O \qquad [6]$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \qquad [7]$$
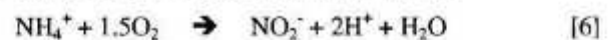
The first such plant to utilize these naturally occurring reactions to degrade cyanide solutions was the Homestake Mine in South Dakota. The treatment plant consists of 48 rotating biological contactors (RBC=s); 24 for cyanide degradation and 24 for ammonia conversion (Senes, 1999). The RBC consists of a series of disks mounted on a rotating shaft with the disks being partially submerged in a trough. The rotating shaft alternately contacts the biomass with the wastewater and the atmosphere. Addition of small amounts of phosphoric acid are needed as a nutrient for the microorganisms. After the ammonia is converted to nitrate, metals and biomass are removed by the addition of ferric chloride and a flocculant. The plant in South Dakota treats and discharges 21,000 $m^3$ per day into a cold water trout fishery (Whitlock, 1995). The average effluent treatment removal experienced in the plant is: 99-100% thiocyanate; 96-98% total cyanide; 98-100% WAD CN; 95-99% copper; and 98-100% conversion of ammonia to nitrate (Whitlock, 1995). Permit values that have to be attained at this site are: 0.10 mg/L WAD CN, 0.13 mg/L Cu, 1.0 mg/L ammonia (Whitlock, 1990). At the time it was build, in 1984, the capital costs were 2/3 the cost of

a conventional treatment plant; the operating costs are $US 0.11 /m$^3$ of water treated (Whitlock, 1995).

A second biological plant has been installed at Homestake=s Nickel Plate mine in British Columbia when it was closed in 1996 (Given and Meyer, 1998). It was put in place in order to treat the tailings pond water prior to discharge therefore the flow to the plant can be controlled without worry of process upsets if the mill were operating. The process involves a combined aerobic and anaerobic biological process for the removal of residual cyanide, thiocyanate, ammonia and nitrate coupled with a High Density Sludge-ferric sulphate process for the removal of arsenic and any other residual metals (Given and Meyer, 1998). The plant was initially operated to treat 1090 m$^3$/day and then slowly increased to 2450 m$^3$/day; the average operating cost is 8.60 $(Cdn)/m$^3$.

These two examples have shown successful application of this technology, it would not likely be applicable to most sites in Canada though because of its reduced performance in the colder climates and seasonal variations of flow rate and water quality (Senes, 1999).

## CYANIDE RECOVERY PROCESSES

Although generally effective, the cyanide destruction processes present both economic and environmental drawbacks (Riveros et al, 1998). Mining companies spend a considerable amount of money both destroying and replacing cyanide. In addition, cyanate, a byproduct of most chemical oxidation processes degrades to ammonia which is highly toxic to fish. Alternatively, cyanide can be recovered from effluents for reuse in the leaching circuit.

The AVR (Acidification - Volatilization - Reneutralization) process is probably the best known method to recover cyanide. In this process the pH of the effluent is reduced to pH 2 to 3 by the addition of sulphuric acid to form HCN. The reduction in pH causes any metallo-cyanide complexes present in the solution to dissociate releasing more HCN while the metals precipitate. The solution is then contacted countercurrently in a packed column with a stream of air; due to the difficulty in volatilizing the HCN, volumes of air about 300-500 times the liquid flow rate are necessary.

The HCN in the air stream is then reabsorbed in a second column by countercurrently contacting it with caustic soda thereby forming sodium cyanide which can be returned to the leaching circuit. The AVR process was used by Hudson Bay Mining and Smelting in Manitoba from 1935 to 1975. This plant incorporated the basic

concepts that have been used in subsequent plants, namely: volatilization in countercurrent columns; air recycling; and the absorption of HCN in lime slurry (Riveros et al, 1998). The Golconda Minerals= Plant in Tasmania improved on the safety aspects by using a negative pressure, ensuring that any leakage would be inward (Kitney, 1988; 1989).

In recent years, the mining industry has been processing more copper rich gold ores resulting in higher cyanide consumptions because of the formation of copper cyanide complexes which in turn results in higher treatment costs. It has been shown (Riveros et al, 1998) that effluents containing as high as 979 mg/L copper and 1893 WAD (weak acid dissociated) cyanide could be treated using an AVR process; in these tests, 90% of the copper was precipitated and easily separated from the solution.

A variation of the original AVR process is known as the Cyanisorb process which was proposed by Mudder and Gladstone (1989). To reduce the acid consumption the solutions were acidified to pH=s varying from 6 to 9.5. Unlike the AVR process this process can treat slurries and thus costs associated with solid / liquid separation are eliminated. This process is presently being used at two operations: the Golden Cross mine in Waihi, New Zealand and the NERCO DeLamar mine in Idaho (Senes, 1999). The Golden Cross plant treats 2180 t/day of a 34% solids slurry; approximately 90% of the cyanide is recovered and the final effluent contains 20 mg/L cyanide. Capital costs for this plant were estimated at $3.7 million (1994 US$); while operating costs were 0.88$ (US)/t ore or about 0.48 $(US)/m$^3$ of water treated (Senes, 1999). One drawback of this process is that since it is operated at neutral pH=s it would not be able to recover cyanide from most metallocyanide complexes, notably those of copper, zinc and iron.

Vitrokele is another process that has been shown to be able to recover cyanide from slurries or clarified solutions. It has been tested in several laboratories and field sites but no commercial plant have been constructed. In this process, an ion exchange resin binds cyanide and metallocyanide complexes. The loaded resin is then eluted in two steps: in the first it is contacted with zinc tetracyanide to remove the metals and in the second with sulphuric acid to remove the free cyanide. The metal containing solution is then acidified with acid for zinc recovery by ion exchange followed by copper precipitation using sodium sulphide or hydrosulphide. The cyanide solution can then be treated with conventional AVR to recover the cyanide. The biggest concern with this process is its long term stability and the resistance of the resin to attrition and fouling (ADI, 1994).

The major advantage of these processes is that cyanide can be recovered for reuse which may be important in remote locations where the cost of cyanide may be very high. Studies in New Zealand have indicated that the AVR process could generate an operating profit, however at the time of the study, cyanide costs in New Zealand were 3-5 times higher than those in the US (U.S. EPA, 1994). Another benefit of the process is that it does not generate any byproducts such as cyanate, ammonia or chloroamines). The major draw back is that the process is complex and requires strict safety precautions because of the evolution of HCN which is highly toxic and thus can present a serious risk to workers in such a plant. With proper precautions, such as operating the system under a negative pressure and having adequate monitoring systems in place, these risks can be reduced.

## ALTERNATIVE TO CYANIDE

While cyanide remains the lixiviant of choice due to its efficiency and low costs, it does pose risks to the environment. The risks involved have been brought to light by the spill of cyanide containing tailings from the Omai Gold Mine in Guyana in 1995 and more recently at the Baia Mare mine in Hungary. As a result of incidents like these some jurisdictions have prohibited the application of cyanide to recover gold (e.g. California, Colorado, Japan and Turkey). In addition, there are other technical problems associated with the use of cyanide. Namely high consumption in copper containing ores and the difficulty in the recovery of gold from refractory ores. As a result of this there have been several projects initiated to develop an alternative to cyanide. The most promising of these is thiosulphate.

In addition to being less toxic and relatively cheap, thiosulphate forms a stable anionic complex with gold but is less reactive to other metals (Yen et al, 2001). However, the chemistry is more complex and many of the mechanisms involved are not fully understood. Thiosulphate leaching requires three components: ammonium thiosulphate, ammonium hydroxide and cupric ion (copper sulphate) (Yen et al, 2001). The thiosulphate dissolves and stabilizes the gold in solution, while the ammonia and copper increase the kinetics, it is thought that the cupric ion acts as a catalyst. The ammonia is needed to stabilize the cupric ion as a cupric tetraamine complex. The overall reaction is thought to be as follows (Hiskey and Atluri, 1998):

$$4 Au + 8 S_2O_3^{2-} + O_2 + 2H_2O \rightarrow$$

$$4 Au(S_2O_3)_2^{3-} + 4 OH^- \qquad [8]$$
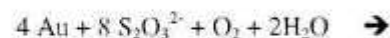
There has been extensive work on the use of thiosulphate as an alternative lixiviant, most of the work has been carried out at the lab scale on mild refractory ores under a wide range of leaching conditions, such as: 0.03 - 4.0 M $(NH_4)_4S_2O_3$, 0.09 - 4.0 M $NH_4OH$, 0.001 - 0.1 M $Cu^{2+}$ and pH 7 -11. Problems encountered thus far are: high reagent consumption; materials selection; and evolution of ammonia in the air. The high reagent requirements at present make this process uneconomical compared to cyanidation and thus more research is required in this area. Recovery of the gold from solution is also another area that is receiving much attention; cementation seems to be the best process, but work is continuing in the areas of ion exchange and solvent extraction.

## CONCLUSIONS

The cyanide leach process has dominated the gold leach industry for the most part of the twentieth century and will likely continue to do so for some years to come. The process is simple, efficient and usually very forgiving under non-optimum conditions (Fleming, 1998). There is justifiable concern over its use since it is a toxic substance and can be lethal if it is injested in sufficient amounts. Over the past two decades though mining companies have made significant advances in the handling and treatment of cyanide waste solutions. In particular the Canadian industry, as described in this report, uses a variety of methods to efficiently destroy cyanide in order to meet regulations that ensure there are no impacts to the environment by effluent discharges.

More often now there are ores that are being discovered that require large amounts of cyanide to leach, these are being avoided for the most part. As resources become more scarce, this may force industry to more fully develop cyanide recovery and recycle processes. Recent public and regulatory pressures may also lead to the development of alternative lixiviants such as thiosulphate.

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