

METHODS OF NEUTRALIZING CYANIDE
IN MINING WASTES AND WASTE WATERS

by

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ABSTRACT

The widespread use of cyanide by the mining industry for the recovery of gold from low grade ore has created a number of environmental problems. One problem is the presence of residual cyanide and cyanide complexes in mining wastes and waste waters. There are, however, a number of methods available for the neutralization of residual cyanide and cyanide complexes. These techniques make use of physical, chemical and biological processes. Each of these methods has its own advantages and disadvantages. Often a method can only be used to treat either tailings, solutions containing tailings or solutions alone.

Many of the methods used in neutralization of residual cyanide and cyanide complexes are examined in this paper. The characteristics of each method, and the conditions under which they should be used, are discussed. Although there are many methods available for the neutralization of cyanide and cyanide complexes in waste solutions, only the alkaline chlorination method, or plain rinse water, is used in the treatment of heap leach piles. In the treatment of tailings and solutions from tank leaching the hydrogen peroxide, Degussa, INCO and complexation/conversion processes can be used. In the treatment of solutions alone processes such as the Kastone, oxidation, ozonation, natural degradation, biodegradation, acidification/volatilization, adsorption, reverse osmosis, and ion exchange can be used. Following the discussion of each method is a table listing ten important parameters which can be used for comparison purposes when evaluating the various techniques. Hopefully this paper will help direct future decisions as to which method is preferable for a specific site or need.

INTRODUCTION

The use of cyanide solutions has proven to be an economical means of extracting metals, particularly gold, from low grade ores. This has lead to the widespread use of cyanide by the gold mining industry. Cyanide is applied as a spray solution to heaps of ore or mixed with the gold ore in cyanide extraction tanks. As a result of these uses residual cyanide and cyanide complexes are found in mining wastes and waste waters.

Cyanide poses unique environmental problems. These problems are associated in part with the different forms cyanide takes. The toxicity of cyanide will vary with the form taken and with the environment in which it is found. The specific type of organism encountered will also affect the level at which cyanide is toxic.

The reaction between cyanide and ore will be dependent on mineralogy. Various types of cyanide waste products and solutions will form, requiring specific neutralization methods. It is the purpose of this paper to outline the methods available for neutralization of cyanide and cyanide complexes in mining wastes and waste waters. The advantages and disadvantages of each method will be discussed. Through use of the tables which immediately follow each discussion,

comparisons may be made between techniques. In this way the different methods of cyanide neutralization can be examined and the best technique selected for use under any existing environmental condition.

LITERATURE REVIEW

Cyanide

The term "cyanide" refers to all chemical groups and compounds having the cyanide ion ($\text{C}\equiv\text{N}^-$) present as a functional unit (Fuller 1977). Cyanide in solution takes the form of free cyanide, hydrogen cyanide, simple cyanides and complex cyanides (EPA 1980, Stanton et al. 1986). Free cyanide (CN^-) is a negatively charged, diatomic ion in solution. Free cyanide and hydrogen cyanide (HCN) exist in equal concentrations in solution at a pH of 9.36 and a temperature of 20 C°. There is an increasing concentration of hydrogen cyanide in solution as the pH, and to a much lesser extent, temperature are lowered (EPA 1986).

A "simple cyanide" is an alkali that is bonded to the cyanide ion, for example sodium, to form sodium cyanide (NaCN), or a metal that is bonded to the cyanide ion, for example zinc, to form zinc cyanide (ZnCN_2). "Complex metal cyanides" form when both an alkali, sodium, and a metal, zinc, are bonded to the cyanide ion forming a compound with the chemical formula of $\text{Na}_2\text{Zn}(\text{CN})_4$ (McGivney and Shelton 1985). The simple metal cyanides are very insoluble, but form soluble complex metal cyanides in the presence of an alkali, or form hydrogen cyanide gas when in contact with acid (Fuller 1977). On the basis of stability the metal

cyanides are grouped into categories of weak complexes, among them zinc and cadmium cyanides, moderately strong complexes, among them copper, nickel and silver cyanides, and strong complexes composed of iron, cobalt and gold cyanides (EPA 1986).

Toxicity of Cyanide

The maximum recommended contamination level for cyanide is 0.01 mg/l in drinking water with a rejection for treatment of raw water supplies set at 0.2 mg/l (EPA 1980). The National Academy of Science and National Academy of Engineering (1973) suggested that levels of total cyanide should be no greater than 0.005 mg/l at any time in the marine environment. Towill et al. (1978) suggested that the cyanide level be variable depending on the marine species present and amount of free cyanide only. The threshold limit for cyanide toxicity to biological activity in fresh water systems varies with water quality, temperature, type and size of the organism (Fuller 1977, 1985), water pH, oxygen content of the water, and species acclimation (Huiatt 1985).

The toxicity of cyanide is due to its strong affinity for metals. Cyanide forms stable complexes with ferric iron, inhibiting the essential metabolic function of iron as an electron carrier and the ferricytochrome oxidase enzyme (Stanton et al. 1986). This results in asphyxiation at the

cellular level due to the inability of tissue to utilize oxygen (Towill et al. 1978). Lethal levels of cyanide for human adults are 1 to 3 mg/kg of body weight if ingested, 118 to 355 mg/m³ if inhaled and 100 mg/kg of body weight if adsorbed (Huiatt 1985).

The soil loading rate is the primary factor determining cyanide toxicity to microorganisms or the possibility of movement into groundwater (Fuller 1985). Cyanide is toxic to many microorganisms with 1 mg/l being lethal to some forms of bacteria (Towill et al. 1978). The limit of tolerance for effective anaerobic biodegradation has been suggested by Fuller (1985) to be 2 mg/l of cyanide.

The major effect of cyanide on plants is reduction of the respiration rate resulting from inhibition of the cytochrome oxidase enzyme. Ion transport, translocation, production of adenosine triphosphate (ATP) and other metabolic processes eventually fail after respiration ceases. Cyanide has also been found to produce chromosomal aberrations in some plant species (Towill et al. 1978).

Fish, particularly trout, are among the most sensitive of the higher organisms to cyanide (Stanton et al. 1986). Sodium cyanide causes oxygen deficiency in tissues through inhibition of the cytochrome oxidase enzymes. If prolonged this can cause permanent damage or death (Cardwell et al. 1976). Cyanide in the form of the cyanide ion or as hydrogen cyanide at levels as low as 0.01 mg/l can rapidly

and permanently affect the swimming ability of salmonids even in well oxidized water (Doudoroff 1976, EPA 1980).

Binary mixtures, for example zinc bonded to hydrogen cyanide or ammonia bonded to hydrogen cyanide, usually have an additive effect on fish toxicity (Smith et al. 1979).

Concentrations of cyanide and hydrogen cyanide above 0.2 mg/l are fatal to most fish while concentrations of 0.03 to 0.2 mg/l of cyanide are fatal to juveniles and some of the more sensitive fish species (EPA 1980, Stanton et al. 1986). Low water temperature can depress the lethal threshold of cyanide down to 0.02 mg/l (Doudoroff 1976). Cyanide concentrations of 0.01 to 0.1 mg/l were found to be lethal to most game fish (Towill et al. 1978). Criteria for protecting freshwater aquatic life have been set with a 24 hour average cyanide limit of 0.0035 mg/l with the concentration of cyanide not to exceed 0.052 mg/l at any time (EPA 1980).

In a test of a number of freshwater species fathead minnows were found to be the most sensitive fish to sodium cyanide followed by bluegills, brook trout, channel catfish and goldfish (Cardwell et al. 1976). In a separate study fish eggs were found to be tolerant to hydrogen cyanide while fry and juvenile fish were found to be least tolerant. The toxicity of hydrogen cyanide increased inversely with temperature and oxygen content for all juvenile species (Smith et al. 1979).

Cyanide Movement

Cyanide is a reactive and short lived compound (EPA 1986). Soils with a high pH, free calcium carbonate (Stanton et al. 1986), low clay content (EPA 1986), or having clays with a low anionic exchange capacity were found to increase the mobility of cyanide (Fuller 1977, Huiatt 1985). A thick soil allows mobility as does the lack of iron oxides. In addition, cyanide mobility is increased in soils under anaerobic conditions (Fuller 1977, EPA 1986).

The movement of cyanide from soils into and out of surface water is increased by higher pH and lower temperatures (Huiatt 1985). Movement will also depend on the type of metals present and the resulting metal cyanide complexes formed. Properties of the water body (depth, surface area, amount of turbulence and aeration) will affect movement as will quantities of organic and inorganic suspended matter. A reduction in the interaction with sediment will increase mobility (EPA 1986).

The movement of cyanide in ground water is similarly influenced by pH, low temperature, concentration and type of metals present and subsequent formation of metal cyanide complexes. Aeration and the interaction with soil or rock particles will decrease mobility (EPA 1986).

Metal cyanide complexes composed of iron, copper, zinc, nickel, cobalt and cadmium, commonly found at gold and

silver mines, decompose and release cyanide at varying rates (Huiatt 1985). Zinc and cadmium complexes are the least stable and decompose to release free cyanide during the ore rinsing process. Strong complexes formed with iron and cobalt are only slightly soluble and release only small amounts of free cyanide (EPA 1986).

Heap Leaching

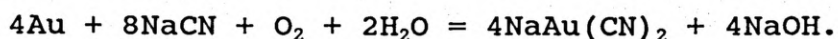
Heap leaching is a process which uses sodium cyanide to economically recover precious metals in low grade ores. Cyanide is sprayed over the heap in the form of a dilute solution of sodium cyanide. An impermeable pad under the heap collects the solution containing the precious metals (Von Michaelis 1985). Pad liners are made of either clays and synthetic materials or asphalt (EPA 1986, Stanton et al. 1986). The precious metals are recovered from the solution by either carbon adsorption or by zinc precipitation (Von Michaelis 1985). Adsorption of the precious metals onto activated carbon is the preferred method since zinc precipitation is less efficient and has higher costs (Heinen et al. 1978).

There are two basic methods of heap leaching, short and long term. The short term method treats 900 to 9000 metric tons (1,000 to 10,000 short tons) of ore in a pile 1.2 to 2.4 m (4 to 8 ft.) high on permanent pads. The ore is crushed until it is between 0.6 to 1.9 cm (1/4 to 3/4

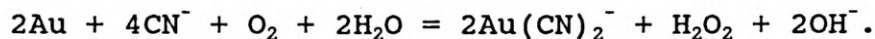
in.) in diameter. The leach cycle continues for 7 to 30 days before the ore is removed from the pad (EPA 1986). The long term method treats 9,000 to 1.80 million metric tons (10,000 to two million short tons) of ore in piles 3 to 21 m (10 to 70 ft.) high (Stanton et al. 1986). The average size of the ore is less than 15 cm (6 in.). The leach cycle may continue for a number of months, or even years, after which the processed ore is simply left in place on the pad (Heinen et al. 1978).

Sodium cyanide in the form of a dissolved solid in water is placed on the ore pile through direct pumping, or by a mechanical feed system, at a rate of 200 to 3000 l/day/m² of ore. Consumption of the sodium cyanide solution is at a rate of 0.5 to 1 g of solution per 2000 g of ore (Stanton et al. 1986, Watson 1987). The solution concentration ranges from 250 to 700 mg/l sodium cyanide, or 125 to 350 mg/l of free cyanide (Stanton et al. 1986, EPA 1986). The amount of sodium cyanide used in the processing of the ore depends on the concentration of the cyanide consuming constituents in the material, that is the metals iron, copper, and zinc and the sulfides (EPA 1986). The solution pH is maintained at 10.3 for optimum processing (Stanton et al. 1986).

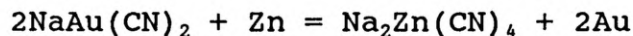
The gold cyanidation process is written as:



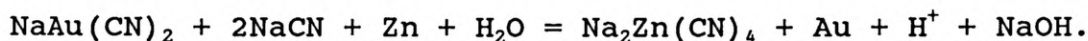
The dissolution of gold and complexation with cyanide is written as:



The precipitation step is written as:



or:



Tank Leaching

Tank leaching, or flotation, is another process for recovering precious metals in low grade ores. This process is used when a portion of the gold has formed compounds with sulfides (pyrite and pyrrohotite), with arsenides (arseno pyrite), or when it occurs as gold telluride (Huiatt et al. 1983). The amount of cyanide consumed and the reaction equations are similar to those for heap leaching except that carbon adsorption is used for the recovery of gold instead of zinc.

At the Golden Sunlight Mine at Whitehall, Montana the ore is reduced by grinding until 65 percent is less than 0.15 mm. Other mines may grind the ore finer until 65 to 80 percent is less than 0.07 mm. The crushed ore at the Whitehall, Montana mine is cycled through tanks, each with a capacity of 1.5 million liters (400,000 gal), over a period

of 48 hours. Coarse sand is then removed by hydrocycloning, after which the gold bearing solution is routed to carbon-in-pulp tanks where the gold-cyanide complex is adsorbed onto activated carbon (Lofftus 1989).

In tank leaching there is no separation of the cyanide solution from the tailings before the precious metals are removed from the ore. Subsequently, after the precious metals are recovered both the cyanide solution and the tailings go to the waste pond together without the possibility of recycling the cyanide contained in the solution (Von Michaelis 1985).

Treatment Problems

One of the major difficulties in the treatment of residual cyanide is identifying the type of cyanide species that exist on the surface of the spent ore and in the solution (Huiatt et al. 1983). The content and form that the residual cyanide takes in heap leach tailings and in solution depends on ore mineralogy, ore pH, permeability of the tailings, thickness of the tailings, concentration of the cyanide solution, solubility and dissociation rate of the metal cyanide complexes, temperature, type of application and rinsing solution used, and the rate of cyanide release from the tailings (EPA 1986). Cyanide may be physically or chemically adsorbed onto tailings mineral surfaces and/or it may react with metallic and nonmetallic

elements in the tailings to produce cyano complexes and cyanates on the mineral surfaces or in interstitial solutions (Huiatt et al. 1983).

Flotation tailings often have associated with them tightly bound, stable complexes. An almost insoluble metal hexacyanoferrate precipitate forms, while simple cyanides are present in an extremely low amount and may not be detectable. The complex metallocyanides found in flotation tailings persist only to varying degrees in solution (Huiatt et al. 1983).

There are a number of treatment processes available that can neutralize cyanide and cyanide complexes remaining in heap leach tailings, in tank leach tailings and in solutions during processing of the ore or after the mining operation is completed (EPA 1986). The methods of cyanide neutralization are discussed in the following section. Neutralization of heap leach piles will be discussed first. This will be followed by a discussion of methods of neutralization of tank leaching wastes and finally those methods that apply only to solutions will be reviewed.

METHODS OF CYANIDE NEUTRALIZATION

In the treatment of heap leach piles the tailings are normally rinsed with water or an alkaline chlorine solution as a preliminary step to begin the degradation of residual cyanide (EPA 1986). The methods of treatment available for the neutralization of tailings/solutions from tank leaching consist of hydrogen peroxide, Degussa, INCO and complexation/conversion processes. For the treatment of solutions containing residual cyanide and cyanide complexes the Kastone process, oxidation, ozonation, natural degradation, biodegradation, acidification/volatilization, adsorption, reverse osmosis and ion exchange can be employed. These methods of neutralization of heap leach piles, tank leach tailings/solutions and solutions alone are discussed in this section. A table that lists ten important parameters that can be used for comparison purposes follows each discussion.

Alkaline Chlorination

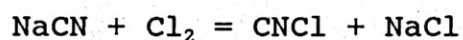
Alkaline chlorination is the most highly developed, or commonly practiced, of all the currently available methods for the treatment of residual cyanide in any type of carrier

in terms of experience and ease of use (Huiatt et al. 1983). In this treatment the cyanide ion is oxidized to carbon dioxide and nitrogen. Total detoxification of simple cyanide as well as cadmium and zinc complexes is possible. Nickel, cobalt, silver and gold complexes do not dissociate readily and require more time and excess chlorine. Iron cyanides do not dissociate with this method and are left untreated (McGivney and Shelton 1985, Schiller 1983).

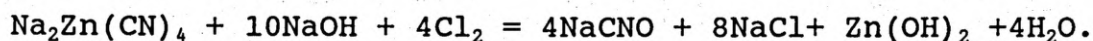
Chlorine in solution, calcium or sodium hypochlorite is sprayed over the heap in the same manner used to apply the sodium cyanide solution. The pH must be elevated if free cyanide is to be oxidized (Stanton et al. 1986). Lime is used for pH control (Scott 1985). The process destroys cyanide, hydrogen cyanide, and cyanide released from metal cyanide complexes (EPA 1986). The complete oxidation of cyanide theoretically requires 6.8 mg of chlorine per milligram of cyanide, while only 4.9 mg of chlorine are required per milligram of thiocyanate (Schmidt et al. 1981). In addition to chlorine, 6.2 mg of sodium hydroxide will be required per milligram of cyanide (Murphy and Nesbitt 1964). Since chlorine can be as toxic to fish as cyanide an accurate system for controlling the amount of chlorine to be added must be used (Tyler et al. 1951). It has been found that 15 to 20 percent excess hypochlorite must be added to improve efficiency. This extra amount of hypochlorite will double the amount of cyanide destroyed and will also destroy

cyanogen chloride (CNCl) that forms (Palla and Spicher 1971).

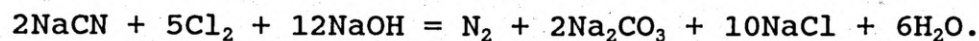
Two stages are required in the treatment process (EPA 1986). In the first stage cyanide undergoes oxidation and hydrolysis at a minimum pH of 10.5 in a two step process. The first step is almost instantaneous while the second step requires between five to ten minutes for completion (EPA 1985, Schmidt et al. 1981). The first stage of the reaction is written as:



Metal cyanide complexes are oxidized during the first stage of the process as shown below for zinc cyanide complexes:

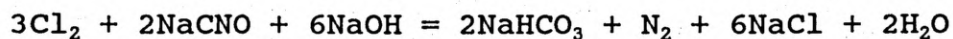


The overall reaction for the first stage can be written as:



Cyanate formed during the first stage of the process is then treated by oxidizing the cyanate to nitrogen and bicarbonate. The second stage of the treatment is carried out at a lowered pH of about 8.5 as shown below in the

overall reaction (EPA 1985, 1986, Schmidt et al. 1981). The second stage reaction:



takes several hours for completion (E.I. du Pont 1985).

The overall reaction is slow, especially if appreciable quantities of heavy metals are present and have reacted with the cyanide solution (Table 1) (Towill et al. 1978). When the treatment process is complete the effluent draining from the heap pile is discharged to a waste pond for a retention time of about 15 days. Cyanide removal is 98.7 to 99.9 percent (Schmidt et al. 1981, Scott 1985).

Table 1. Ten parameters to be used for comparison between alkaline chlorination and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Iron cyanides.	10, 14, 29, 42, 44.
Types of chemicals used in treatment.	Chlorine in solution, calcium or sodium hypochlorite and sodium hydroxide.	21, 47.
Toxic chemicals used in treatment.	Chlorine and sodium hydroxide.	21, 47.
Removal efficiency of the treatment.	Cyanide removal is 98 to 99 percent.	43, 44.

Table 1. Continued

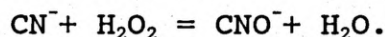
Parameter	Characteristic	References
By-products formed during treatment.	Cyanogen chloride ^a and ammonia. ^b	a:5, 11. b:49.
Optimum pH for treatment.	During the first stage 10.5 and then 8.5 during the second stage of the reaction.	11, 14, 43, 44, 48.
Length of treatment time.	Normally two hours, ^a for the chemical reaction, but longer when heavy metals are present ^b .	a:11. b:32, 43, 48, 49.
Cyanide and metal recovery after treatment.	Cyanide and metals. ^a Arsenic is precipitated in stage two. ^b	a:43, 44. b:23, 44, 47, 51.
Ponding requirement.	Fifteen days is required for a more complete degradation.	44.
Notes:	A problem is the high cost of reagents involved. ^a Automation is possible. ^b	a:20, 42. b:11, 20, 44.

Hydrogen Peroxide

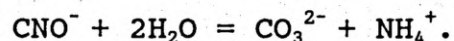
Hydrogen peroxide is used for the treatment of free cyanide and weak cyanide complexes in tank leach tailings and solutions. No undesirable by-products are formed (Table 2), nor are additional chemicals added which may ultimately be detrimental to the environment (EPA 1986). The rates of reaction are slow even in the presence of excess hydrogen peroxide (Stanton et al. 1986). This method destroys cyanide, hydrogen cyanide, and copper, zinc and nickel

cyanide complexes. Metals are precipitated as hydroxides with thiocyanate left untreated. If copper is added iron cyanide complexes may be precipitated as well (Huiatt et al. 1983). Cyanide undergoes oxidation and hydrolysis at the start of the reaction with the residual cyanide only undergoing oxidation (Masson 1907).

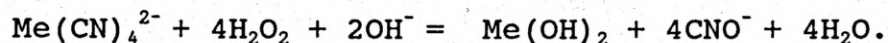
The reaction may be written as:



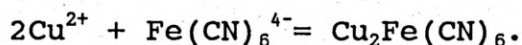
The cyanate formed under oxidation then undergoes hydrolysis to form ammonia and carbonate ions:



The reaction for the precipitation of metals is:



Complex iron cyanides are too stable to be oxidized but they may be precipitated by the addition of copper as shown below:



The residual peroxide remaining after cyanide removal decomposes to oxygen gas and water. However, this stage does not occur unless the initial ratio of peroxide to cyanide has exceeded a ratio of about 4 to 1 (Masson 1907). The reduction of the cyanide concentration in solution from

50 mg/l to less than 0.5 mg/l requires over eight hours even when the initial molar ratio of hydrogen peroxide to cyanide is as great as 5 to 1 (Stanton et al. 1986).

The products of oxidation of cyanide are cyanate along with ammonium carbonates. Cyanate is the primary product. A portion of the cyanide is converted by hydrolysis without oxidation to produce carbonates, formate and ammonia (Masson 1907). After neutralization is completed the solution may be evaporated or sprayed onto an environmentally suitable area (EPA 1986).

Table 2. Ten parameters to be used for comparison between hydrogen peroxide and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Iron cyanides and thiocyanate.	21.
Types of chemicals used in treatment.	Hydrogen peroxide. ^a Copper is used as a catalyst for precipitation of ferrocyanides. ^b	a:21. b:14, 21.
Toxic chemicals used in treatment.	Hydrogen peroxide.	14.
Removal efficiency of the treatment.	The cyanide concentration can be reduced to 0.5 mg/l.	47.

Table 2. Continued

Parameter	Characteristic	References
By-products formed during treatment.	Copper ferrocyanide, carbonates cyanate and metal hydroxides.	14.
Optimum pH for treatment.	Seven to nine.	47.
Length of treatment time.	Two to four hours is normal, ^a but up to eight hours is possible. ^b	a:11, 22. b:22, 47.
Cyanide and metal recovery after treatment.	Copper ferrocyanide, ^a and metal hydroxides. ^b	a:21. b:14.
Ponding requirement.	After chemical treatment the effluent is either evaporated or sprayed over a suitable area.	14.
Notes:		

Degussa Process

The Degussa process is a modification of the hydrogen peroxide treatment of tank leach tailings and solutions. Unlike the hydrogen peroxide method the Degussa process is very efficient in the use of neutralizing chemicals. In this process the concentration of hydrogen peroxide can be quickly elevated or lowered to efficiently react with cyanide and other oxidizable substances, for example sulfides, thiocyanates, and metal ions. In order to determine the amount of hydrogen peroxide required a

continuous automatic titration is carried out in a small side stream. The Degussa process takes on importance by adjusting the amount of hydrogen peroxide added to the effluent flow within minutes, based on the cyanide concentration and amount of other oxidizable substances. The amount of hydrogen peroxide required is reduced by fine side stream control making this process a feasible neutralization technology (Knorre and Griffiths 1985).

No toxic by-products are formed during the reaction (Table 3), and no additional salts are added to the effluent. Any excess of oxidizing agent decomposes into water and oxygen. Hydrogen peroxide oxidizes cyanide to cyanate at a pH of 10.5 to 11.0. The cyanate then undergoes hydrolysis to form ammonium and carbonate. The reaction equations are identical to those found when using the hydrogen peroxide method (Knorre and Griffiths 1985).

The rate of dissociation of complex metal cyanides depends on the complexes formed, and to some extent the amount of excess hydrogen peroxide added. As cyanide forms complexes, metals are precipitated as hydroxides (Knorre and Griffiths 1985). Complex iron cyanides are precipitated by heavy metal ions (such as copper) in the pH range of natural waters.

After hydrogen peroxide has been added and the initial reaction is over the tailings are pumped to a leach tank for detoxification. The retention time in the tanks is about

two hours. The tailings are then cycloned to separate the tailings from the solution and the overflow released. The concentration of free and weakly bonded cyanide is reduced to less than 0.5 mg/l. When an excess of hydrogen peroxide is used this concentration can be reduced to 0.1 mg/l. Although the consumption of hydrogen peroxide varies widely it normally is in the range of 0.4 to 1.0 l of a 70 percent solution of hydrogen peroxide per cubic meter of tailings (Knorre and Griffiths 1985).

Table 3. Ten parameters to be used for comparison between the Degussa process and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Iron cyanides.	22.
Types of chemicals used in treatment.	Hydrogen peroxide.	22.
Toxic chemicals used in treatment.	Hydrogen peroxide.	22.
Removal efficiency of the treatment.	Cyanide is reduced to 0.1 to 0.5 mg/l.	22.
By-products formed during treatment.	Carbonate, ammonia, metal hydroxides and iron cyanides.	22.

Table 3. Continued

Parameter	Characteristic	References
Optimum pH for treatment.	Ten and a half to eleven.	22.
Length of treatment time.	Two hours.	22, 47.
Cyanide and metal recovery after treatment.	Iron cyanides and metal hydroxides.	22.
Ponding requirement.	Leach tanks are required.	22.
Notes:	Each cubic meter of ore to be treated will require 0.4 to 1.0 liters of a 70 percent solution of hydrogen peroxide.	19.

INCO Process

The INCO process was developed by the International Nickel Company. Cyanide and metal cyanides are rapidly removed by oxidizing leach tank tailings and solution with a mixture of sulfur dioxide and air. The process is carried out at a pH of 7 to 10 (Devuyst et al. 1982) and uses a small amount of copper (50 mg/l minimum) as a catalyst (Huiatt et al. 1983). The INCO process is more cost efficient than alkaline chlorination. This is due to the cyanide oxidation reaction taking place first, thereby reducing the amount of reactant taken up in degrading

sulfidic minerals such as thiocyanate (only about 10 to 20 percent of thiocyanate is oxidized) (Devuyst et al. 1985).

Complete removal of cyanide is possible, most of it is oxidized to cyanate, while iron cyanides are removed through precipitation as copper or zinc ferrocyanides (EPA 1986, Huiatt et al. 1983). Other metals are precipitated as metal hydroxides, and along with calcium sulfate are directed to the tailings pond (Devuyst et al. 1985). The INCO process can be carried out in either a continuous or batch treatment (Devuyst et al. 1982). The process is rapid, 10 to 30 minutes (Schiller 1983), simple to operate and comparatively inexpensive (Huiatt et al. 1983). The reaction may be written as:



Cyanide levels of several hundred mg/l can be reduced to less than 1 mg/l (Schiller 1983). Metals such as copper, iron, nickel and zinc are also reduced to less than 1 mg/l. Tailings slurries consume about 7 g of sulfur dioxide per gram of total cyanide at a pH of 9 (Table 4) (Huiatt et al. 1983). Solutions alone consume about 2.5 g of sulfur dioxide per gram of total cyanide (Devuyst et al. 1982).

Sulfur dioxide can be supplied for the process in a number of forms: as sulfur dioxide, elemental sulfur from roaster ovens or sodium sulfites (Devuyst et al. 1985).

Normally a mixture of 2 to 5 percent of sulfur dioxide in air is bubbled through the waste (Schiller 1983).

Table 4. Ten parameters to be used for comparison between the INCO process and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Iron cyanides, thiocyanate and cyanate.	5, 6, 14, 20, 21, 44.
Types of chemicals used in treatment.	Sulfur dioxide (2.5 to 5 percent) and a minimum of 50 mg/l of copper to act as a catalyst.	5, 21, 42.
Toxic chemicals used in treatment.	Sulfur dioxide.	5, 21, 42.
Removal efficiency of the treatment.	Several hundred mg/l of cyanide are reduced to a level of 0.5 to 1.0 mg/l. ^a Three to 7 g of sulfur dioxide are required per gram of total cyanide reduced. ^b	a:42, 44. b:5, 6, 21, 44.
By-products formed during treatment.	Cyanate, copper and zinc ferrocyanides and metal hydroxides.	5, 6, 21.
Optimum pH for treatment.	Nine is optimum, but the range is 7 to 10.	5, 6, 20, 21, 44.
Length of treatment time.	Ten to 30 minutes.	42.
Cyanide and metal recovery after treatment.	Copper or zinc ferrocyanide are removed by precipitation. Metals precipitate out as hydroxides.	5, 14, 21, 44.

Table 4. Continued

Parameter	Characteristic	References
Ponding requirement.	The tailings waste pond is used to hold hydroxides and calcium sulfate residues.	5.
Notes:	Two problems are found, sludge formation and the quantity of chemicals required.	5.

Complexation/Conversion

Complexation/conversion is used upon tank leach tailings and solutions to create less toxic and less soluble forms of cyanide, for example ferrocyanide and ferricyanide (Stanton et al. 1986). The addition of ferrous sulfate to tank tailings and solutions containing cyanide and complex cyanides of zinc and copper converts most of the cyanide to ferrocyanide at a pH of 7.5 to 10.5. This process is one of the oldest methods of cyanide disposal (Huiatt et al. 1983) and is commonly used in Europe but not in the USA (Towill et al. 1978). Cyanide can be reduced by 88 to 96 percent, requiring 16 moles of ferrous sulfate per mole of cyanide. This method may only be effective on highly concentrated cyanide solutions (Table 5) and then only when close control of the solution pH is maintained (Huiatt et al. 1983).

Cyanide reacts with ferrous sulfide at a pH of 7.5 with a retention time of 15 minutes. The ferrous sulfide to cyanide ratio is maintained at 3 to 1. The tailings and

solution may be discharged into a tailings waste pond where further adsorption continues. Other treatment methods must be used to obtain solutions of a high enough quality for discharge (Scott 1985).

Thiocyanate is less toxic and less soluble than cyanide and forms as a reaction product between cyanide and sulfur (EPA 1986, Stanton et al. 1986). In a mixture of peroxide and thiosulfate, cyanide is converted to thiocyanate at a pH of 7 to 10. Cyanide can be reduced from 5 mg/l to less than 0.02 mg/l in 2 to 4 hours. Free cyanide, or complexes that are less stable than iron cyanides, are all subject to conversion (Huiatt et al. 1983).

If sulfide or thiosulfate is present cyanide reacts to form thiocyanate when sulfide minerals are oxidized. Metal thiocyanate complexes may also form when free cyanide is absent. Most metal thiocyanate complexes are usually insoluble, but if they dissolve they form either an alkali or a heavy metal ion and either a ferrocyanide or ferricyanide complex (EPA 1986).

Cyanide reacts with water to form ammonia and formate. In an alkaline solution the by-products are formate salts and volatile ammonia. In an acidic solution the by-products are formic acid and ammonium salts. These reactions occur only slowly (Stanton et al. 1986).

Cyanide also reacts with sugars in the form of open chain aldoses to form cyanohydrins which hydrolyze to form aldonic acids (Raef et al. 1974). The reaction occurs above pH 8 and is optimum at a pH of 11. The by-products of the reaction are biodegradable (Raef et al. 1977a, 1977b).

Possible sources of aldose carbohydrates are wastes from textile mills, canneries, breweries, sugar beet plants, cereal grain processing plants and pulp or paper mills. The mixing of aldose carbohydrates and cyanide waste streams at a high pH can be used as a pretreatment step for biological oxidation (Raef et al. 1977a, 1977b).

Table 5. Ten parameters to be used for comparison between complexation/conversion and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Iron cyanides.	20, 21, 47.
Types of chemicals used in treatment.	Ferrous sulfate, ferrous sulfide, sulfur ^a aldoses. ^b	a: 8, 42, 44, 47, 49. b: 35, 36, 37.
Toxic chemicals used in treatment.		

Table 5. Continued

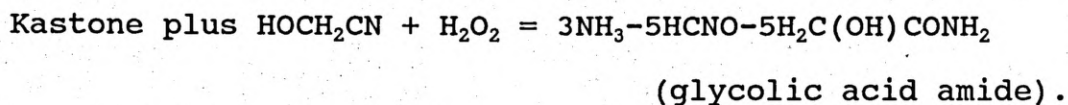
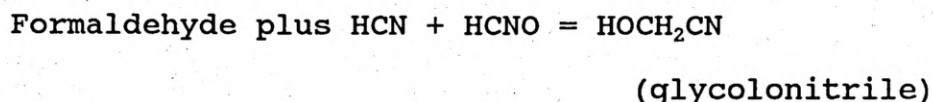
Parameter	Characteristic	References
Removal efficiency of the treatment.	Ferrous sulfate removes 88 to 96 percent of the cyanide while sulfur reduces cyanide from 5 mg/l to 0.02 mg/l. ^a High concentrations of aldoses must be used. ^b	a:21. b:35.
By-products formed during treatment.	Ferrocyanide and thiocyanate. ^a The by-products of aldoses are biodegradable. ^b	a:11, 14, 21, 47. b:35, 36, 37.
Optimum pH for treatment.	For ferrous sulfate 7.5 to 10.5. For ferrous sulfide 7.5, and 7 to 10 for sulfur. ^a Optimum pH for aldoses is 11, but the range is from 8 to 11. ^b	a:11, 21, 44. b:35, 36, 37.
Length of treatment time.	Ferrous sulfide requires 15 minutes and sulfur 2 to 4 hours.	21.
Cyanide and metal recovery after treatment.	Metal thiocyanate and cyanide complexes form with the use of ferrous sulfate and sulfur.	14.
Ponding requirement.	Ponding is required to reach acceptable effluent quality.	44.
Notes:	Ferrous sulfate is best used when 10 to 100 mg/l of hydrogen cyanide is present.	21, 47.

Kastone Process

This treatment may be used to treat waste liquids. The solution is adjusted to a pH of 11 (10.5-11.5) and formaldehyde added as needed. Kastone (a Dupont product) is

then mixed with the solution. The solution must be agitated either mechanically or with air. Since the reaction is temperature dependent dilute wastes would have to be warmed to 38 to 54 C° (100 to 130 F°). However, heating the solution is less economical than adding 10 to 20 percent excess Kastone to the solution to shorten the reaction time of one half to one hour with agitation (E.I. du Pont 1985).

The reaction may be written as:



As Huiatt et al. (1983) described the process, Kastone uses a formulation containing 41 percent hydrogen peroxide with trace amounts of catalysts and stabilizers in conjunction with formaldehyde. The cyanide wastes are heated (Table 6) and then treated with two to three parts of a 37 percent solution of formaldehyde per part sodium cyanide. Three to four parts of the peroxygen compound (Kastone) is then added and the solution agitated for one hour (E.I. du Pont 1979, 1985). Copper is added as a catalyst at a rate of 25 to 100 mg/l (E.I. du Pont 1984a).

The principle products from the reaction are cyanates, ammonia and glycolic acid amide. Both cyanate and glycolic

acid amide are biodegradable. Cyanate can be readily hydrolyzed in acid solutions to form ammonia (E.I. du Pont 1985). Acid hydrolysis may be required since complete destruction of cyanates does not occur (Huiatt et al. 1983). Kastone reacts with less than 15 percent of the thiocyanate present, therefore, this would be a desirable process for sulfidic ores if the operator wishes to maintain high thiocyanate concentrations in the treated waste liquid (E.I. du Pont 1984a).

Table 6. Ten parameters to be used for comparison between the Kastone process and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Thiocyanate and iron cyanides.	20, 21.
Types of chemicals used in treatment.	Hydrogen peroxide and formaldehyde. Copper, 25 to 100 mg/l, is used as a catalyst.	9, 11.
Toxic chemicals used in treatment.	Hydrogen peroxide and formaldehyde.	9, 11, 21.
Removal efficiency of the treatment.	The cyanate which is not destroyed will require acid hydrolysis for complete degradation.	11, 21.

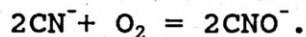
Table 6. Continued

Parameter	Characteristic	References
By-products formed during treatment.	Cyanates, ammonia and glycolic acid amide.	11, 21.
Optimum pH for treatment.	Ten and a half to eleven.	11.
Length of treatment time.	One half to one hour with agitation.	11, 21.
Cyanide and metal recovery after treatment.	Iron cyanide, thiocyanate and residual copper.	9, 20.
Ponding requirement.		
Notes:	Wastes must be heated to 38-54 C° or 10 to 20 percent excess Kastone must be used along with one hour of agitation.	11, 21.

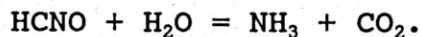
Oxidation

Oxidation may be the most economical method for removal of cyanide from water. Removal of cyanide can be up to 99 percent (E.I. du Pont 1985, EPA 1985). Another advantage of the oxidation method is that it does not make use of caustic and/or toxic chemicals (Table 7) (Weber and Corapcioglu 1981). Although the oxidation method has long been used the full process reactions are not yet well

understood (Stanton et al. 1986). The reaction may be written as:



In water, cyanic acid is converted by hydrolysis to cyanate (EPA 1986). Cyanate can in turn be hydrolyzed to ammonia and carbon dioxide (Huiatt et al. 1983, Palla and Spicher 1971), with the reaction written as:



Ammonia forms when cyanate is hydrolyzed and is subsequently further oxidized to form nitrate (EPA 1986). The reactions are pH dependent with conversion of cyanide to cyanate occurring at an optimum pH of 10 to 12.5 and hydrolysis of cyanate at a pH of 7 to 9. Normally, the pH is set at 8.5 which allows both reactions to proceed, one after the other (Huiatt et al. 1983, Palla and Spicher 1971). At pH 8.5 the reaction will take about one hour. It is important not to let the hydrogen ion concentration level drop below pH 6 or a toxic and explosive gas, nitrogen trichloride (NCl_3), forms (Palla and Spicher 1971).

Table 7. Ten parameters to be used for comparison between oxidation and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Iron cyanides	21, 43.
Types of chemicals used in treatment.	Oxygen and chlorine. ^a Copper is used as a catalyst on a 1 to 1 weight basis with cyanide. ^b	a:14, 47. b:2.
Toxic chemicals used in treatment.	Chlorine ^a or sodium hypochlorite may be used. ^b	a:13. b:34.
Removal efficiency of the treatment.	Up to 99 percent of cyanide is removed with chlorine oxidation.	12, 48.
By-products formed during treatment.	Cyanate, formate, carbonate, ^a ammonium carbonate, ^b ammonia ^c , and carbon dioxide. ^d	a:8, 27. b:21, 27. c:14, 21, 48. d:8, 14.
Optimum pH for treatment.	Up to 8.5. ^a The reaction is accelerated at a lower pH, but must be kept above a pH of 6. ^b	a:14. b:2, 8, 13, 14, 21.
Length of treatment time.	One half to one hour, ^a and 15 to 20 minutes with agitation. ^b	a:21, 34. b:48.

Table 7. Continued

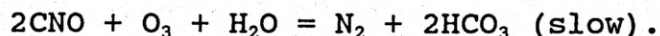
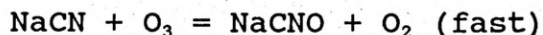
Parameter	Characteristic	References
Cyanide and recovery after treatment.	Metal hydroxides.	2, 34.
Ponding requirement.		
Notes:	A sludge equal to 5 percent of the total volume of water forms.	21, 34.

Ozonation

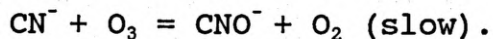
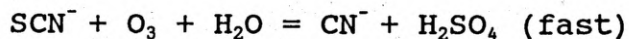
Ozonation is an economical alternative to alkaline chlorination for solutions, (Rice and Browning 1980, Towill et al. 1978), rapidly destroying cyanide and thiocyanate (Rowley and Otto 1980). Hydrogen cyanide as well as the weakly disassociable metallic cyanides (zinc, cadmium and copper) are also degraded. Ozone can be electrically generated on site from air or oxygen and is a more effective oxidizer than chlorine. Additionally, there are no toxic by-products (Table 8) and ozone can be handled with less risk (Huiatt et al. 1983).

Oxidation of cyanide by ozone will form cyanate (Gurol et al. 1985), which is only one thousandth as toxic as cyanide (Hendrickson and Daignault 1973). Complete destruction of cyanide in water requires 1.3 moles of ozone to 1 mole of cyanide for cyanide concentrations over 5 mg/l

with the rate of reaction decreasing for more dilute cyanide concentrations (E.I. du Pont 1985, EPA 1985). Three moles of ozone are required to convert one mole of thiocyanate to cyanate or ammonia. Seven moles of ozone are required to convert one mole of thiocyanate to nitrate (Layne et al. 1985). At the start of the reaction the pH is held at 11.0 or 12.0. Oxidation of the cyanate will be almost complete before the pH drops below 8.0 (Murphy and Nesbitt 1964, Rice and Browning 1980, Rowley and Otto 1980, Tyler et al. 1951). The reaction for the oxidation of cyanide by ozone may be written as:



The reaction for the oxidation of thiocyanate by ozone may be written as:



Additional treatments may be required, for example ultraviolet light, to reduce complex iron cyanides to less than 0.1 mg/l (Rowley and Otto 1980). Because of the need for additional treatments with many waste solutions the ozonation method may not be suitable for all cyanide wastes (Towill et al. 1978).

Table 8. Ten parameters to be used for comparison between ozonation and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Iron cyanide.	17, 20, 21, 24, 28.
Types of chemicals used in treatment.	One to 1.3 parts ozone to 1.0 part of cyanide is required, ^a and 3 parts ozone to 1 part of thiocyanate is required to form cyanate or ammonia, and 7 parts ozone to 1 part of thiocyanate to form to nitrate. ^b	a:13, 24, 28, 50. b:24.
Toxic chemicals used in treatment.	None.	24.
Removal efficiency of the treatment.	Cyanide can be reduced to 0.1 mg/l, and then other methods of treatment, such as UV radiation are required.	21, 28, 41.
By-products formed during treatment.	Metal hydroxides.	41.
Optimum pH for treatment.	The starting pH of 11 will be reduced to 7.6 by the end of the process.	32, 39, 41, 50.
Length of treatment time.	An immediate reaction takes place, that is mass transfer controlled.	17, 24, 39.
Cyanide and metal recovery after treatment.	Metal hydroxides.	32, 39, 41, 50.
Ponding requirement.		

Table 8. Continued

Parameter	Characteristic	References
Notes:	UV radiation is required to reduce complex iron cyanides to less than 0.1 mg/l.	21, 39, 41.

Natural Degradation

Natural degradation is the most widely used method for the treatment of mine waste waters (Scott 1985). Processes included in what is referred to as "natural degradation" include ultraviolet radiation, volatilization, oxidation, acidification, adsorption, and biodegradation (EPA 1986). Ultraviolet radiation has the greatest impact on the destruction of iron cyanides while temperature has the greatest affect on reaction rates. Aeration increases hydrogen cyanide dissolution by an order of magnitude. The rate of hydrogen cyanide removal is also increased with lower pH, down to a pH of 5 (Simovic et al. 1985). The rate of cyanide degradation (Table 9) depends on cyanide concentration, temperature, type of bacteria present, ultraviolet radiation, aeration, pond conditions (area, depth, turbidity), oxygen availability and solution pH (with an optimum pH of 10).

Under aerobic conditions hydrogen cyanide reacts with oxygen to form cyanate. Cyanate in turn reacts with water to produce carbon dioxide and ammonia (Stanton et al. 1986).

Microorganisms incorporate cyanide and break it down to form carbon dioxide and ammonia (Knowles 1976, Reynolds 1924). However, unless the aerobic system has been acclimated to cyanide a concentration greater than 1 mg/l of cyanide can cause overloading of the microorganisms present and a breakdown in the degradation process (Murphy and Nesbitt 1964). Microorganisms which degrade cyanide include bacteria such as Pseudomonas paucimbilis, Actinomycetaceae of the genus Nocardia, and Bacillus pumilus and fungi such as Stemphylium stearothermophilus (Knowles 1976).

Under anaerobic conditions hydrogen cyanide reacts with sulfur to form thiocyanate. Thiocyanate in turn reacts with water to produce hydrogen sulfide, carbon dioxide and ammonia (Stanton et al. 1986). Microorganisms in an anaerobic system are even more sensitive to high cyanide concentrations than those under aerobic conditions. Under anaerobic conditions the microorganisms may not recover to their previous cyanide removal efficiency (Murphy and Nesbitt 1964).

The cyanide content in waste ponds has been known to decline from 64 to 0.05 mg/l in a matter of months, with a subsequent drop in pH from 10.5 to 7.0. The drop in pH is the result of natural carbonation and hydrolysis of the thiocyanate. Through the processes mentioned natural degradation can be used as an effective pretreatment to reduce final treatment costs (Huiatt et al. 1983).

Table 9. Ten parameters to be used for comparison between natural degradation and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	None.	45.
Types of chemicals used in treatment.	None.	14, 21, 45.
Toxic chemicals used in treatment.	None.	14, 21, 45.
Removal efficiency of the treatment.	Cyanide removal is up to 90 percent, but the effluent is not of acceptable quality.	14, 45.
By-products formed during treatment.	Hydrogen sulfide gas, ^a carbon dioxide and ammonia ^b .	a:14, 44, 47. b:44, 47.
Optimum pH for treatment.	Optimum pH for cyanide is 10.3 and 5 for hydrogen cyanide.	45.
Length of treatment time.	Days to months.	45.
Cyanide and metal recovery after treatment.	Stable complexes combined with cyanide form.	45.
Ponding requirement.	Ponding is required.	21, 45, 47.

Table 9. Continued

Parameter	Characteristic	References
Notes:	UV radiation is required to reduce complex iron cyanides to less than 0.1 mg/l.	21, 39, 41.

Biodegradation

The use of specific microorganisms in the treatment of solution wastes is possible and has the advantages of low treatment costs and no by-product disposal problem (Table 10) (Winter 1962). Organic compounds including cyanide are susceptible to degradation by microbes (Fuller 1977). Microorganisms can remove through oxidation and adsorption cyanide, thiocyanate, and complexed metal cyanides (including iron and copper) (Mudder and Whitlock 1984).

Bacteria, fungi, algae and protozoa exist that are capable of degrading cyanide concentrations up to 15 mg/l (Towill et al. 1978, Ware and Painter 1955). Cyanide is metabolized by these microorganisms to carbon dioxide and ammonia (Huiatt et al. 1983) over a wide pH range and under both aerobic and anaerobic conditions (Towill et al. 1978).

A patented mutant strain of Pseudomonas paucimobillis was tested at the Homestake mine at Lead, South Dakota to treat effluent. The results were equal to or better than that of other commonly used processes and proved to be both effective and cost efficient. Bacteria indigenous to the

waste waters of the Homestake mine area were used as a seed source to produce a number of bacteria species. For conditions at the Homestake mine Pseudomonas paucimobillis showed the greatest promise. No chemicals were added to the waste waters except soda ash as an inorganic source of carbon to aid in nitrification, and phosphorus which was used as a trace nutrient (Mudder and Whitlock 1984).

The use of microorganisms requires water above a minimum temperature of 10 to 18 C° (50 to 65 F°) to allow the biological process to proceed. The Homestake mine accomplished this by blending mine waste water at a temperature of 21 to 29 C° (70 to 85 F°) with tailings impoundment water at a temperature of 1.1 to 21 C° (34 to 70 F°) (Mudder and Whitlock 1984).

This treatment method is capable of removing both cyanide and metals from the effluent and can neutralize solution cyanide concentrations up to 10 mg/l and thiocyanate concentrations up to 70 mg/l. Total cyanide was reduced from 2.0 to 0.30 mg/l while thiocyanate was reduced from 50.0 mg/l to less than 0.10 mg/l (EPA 1986). Whitlock (1987) reported that the system degrades or removes 90 to 98 percent of the cyanide, thiocyanate, toxic heavy metals and ammonia initially present.

Complex metal cyanides composed of copper, nickel, iron and zinc can be removed from solutions to a level less than 0.1 mg/l (Huiatt et al. 1983). The process makes use

of rotating biological contactors on which the microorganisms are located. These rotating disks bring the microorganisms into contact with the effluent to be treated. A biomass build-up takes place on the disk surface. This build-up is routinely removed by reversing the direction of disk rotation and through the use of increased compressed air (Scott 1985, Whitlock 1987). Compressed air is directed from supplemental air diffusers situated near the bottom of the tank which holds the effluent. The solution will reveal 15 to 50 mg/l suspended solids after treatment. Suspended solids of this magnitude must be reduced before discharge. A retention time of four hours will allow the suspended solids to settle out (Whitlock 1987). Eventually this material is pumped into the tailings pond (EPA 1986). A further clarification of the effluent solution may take place through use of sand filters which can reduce suspended solids concentrations to less than 10 mg/l (Whitlock 1987).

Table 10. Ten parameters to be used for comparison between biodegradation and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	None.	15.
Types of chemicals used in treatment.	Soda ash and phosphorous are added as nutrient supplements.	14, 31, 44.

Table 10. Continued

Parameter	Characteristic	References
Toxic chemicals used in treatment.	None.	31.
Removal efficiency of the treatment.	Total cyanide can be reduced from 2.0 to 0.3 mg/l and thiocyanate from 50 to 0.1 mg/l.	14, 22, 56.
By-products formed during treatment.	Hydrogen sulfide gas, nitrates, anions of sulfate, carbonates, ^a ammonia and carbon dioxide. ^b	a:14, 23 31, 44. b:14, 21, 23, 52.
Optimum pH for treatment.	A wide range is possible.	14, 47.
Length of treatment time.	Two and a half hours.	56.
Cyanide and metal recovery after treatment.	Metals, such as copper and zinc, are absorbed by the bacteria.	14.
Ponding requirement.	Metals may be returned to the barren waste pond.	14, 20.
Notes:	Two to 10 mg/l of total cyanide is the optimum level for treatment. ^a The solution to be treated must be at a minimum temperature of 10 to 18 C. ^b	a:1, 20. b:14, 44, 56.

Acidification/Volatilization

The most well known method of acidification according to Scott (1985) is the Mills-Crowe process. The waste

cyanide solution in this process is acidified to a pH of 2 to 3 with sulfuric acid. Volatilized hydrogen cyanide is recovered by absorption in an alkaline solution of sodium hydroxide. The primary purpose of this method is the recovery of cyanide. Acidification according to the Mills-Crowe process will permit recovery of up to 91 percent of the cyanide (Table 11) for later reuse. This method will not achieve discharge water quality standards without other treatments, because the final concentration of cyanide in the effluent may be as high as 1 mg/l (Murphy and Nesbitt 1964). Furthermore, acidification will have no affect on ferrocyanide or thiocyanate present in the solution (Huiatt et al. 1983).

During the treatment process gypsum and calcium carbonate will form in significant quantities and create a sludge problem. Zinc, copper, nickel and iron may also be present in the solution. Neutralization of the acidic solution before discharge will be necessary (Huiatt et al. 1983).

Table 11. Ten parameters to be used for comparison between acidification/volatilization and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Ferrocyanide and thiocyanate.	21, 31.

Table 11. Continued

Parameter	Characteristic	References
Types of chemicals used in treatment.	Sulfuric acid or sulfur dioxide. Sodium hydroxide may be used to capture the cyanide for reuse.	51.
Toxic chemicals used in treatment.	Sulfuric acid.	8, 44.
Removal efficiency of the treatment.	Cyanide removal is 85 percent, with up to 91 percent of cyanide removed if sodium hydroxide is used later in the process.	44.
By-products formed during treatment.	Copper cyanide, ammonium sulfate, gypsum, hydrogen cyanate, various acidic solutions and calcium carbonate.	21.
Optimum pH for treatment	Two to three.	8, 31, 44.
Length of treatment time.	Hours.	14.
Cyanide and metal recovery after treatment.	Cyanide, ^a along with zinc, copper, nickel and iron. ^b	a:31,44. b:21.
Ponding requirement.		
Notes:	Adsorption is required for free cyanide removal. ^a Further neutralization methods will be required. ^b Neutralization of the acidic solution will be necessary. ^c	a:21. b:32, 44. c:8, 21.

Adsorption

Adsorption is based on the temporary bonding of cyanide in solution to another surface (McGivney and Shelton 1985), followed by oxidation (Bucksteeg 1966). Some of the advantages of the adsorption method are low cost of operation, the non-use of any toxic chemicals or the production of toxic by-products (Bernardin 1973).

Both activated carbon and illite clay are able to adsorb cyanide and remove it from the effluent. However, only activated carbon is effective in reducing cyanide to levels acceptable for raw drinking water standards (Table 12) (Fuller 1976). The adsorption capacity of carbon is increased with the use of oxygen and cupric ions (Huiatt et al. 1983). Most complex cyanides are removed and cyanide is oxidized to form carbon dioxide and ammonia. It is very important to resupply the carbon surface with fresh oxygen to maintain adsorption capacities (Weber and Corapcioglu 1981).

Surface-activated cationic organic compounds collect anionic cyanide and complex metal cyanides. Since complex metal cyanides are removed more effectively than cyanide alone, metals may be added to the solution to increase the efficiency of the process (Huiatt et al. 1983). Iron complexes are adsorbed onto the carbon but are not fully oxidized, therefore, further treatment is required (McGivney and Shelton 1985).

Table 12. Ten parameters to be used for comparison between the adsorption process and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Iron cyanides are adsorbed, but not oxidized.	29, 31.
Types of chemicals used in treatment.	Activated carbon and illite clay. ^a Copper is used as a catalyst on a 1 to 1 weight basis. ^b	a:25. b:2, 3, 21.
Toxic chemicals used in treatment.	None.	2.
Removal efficiency of the treatment.	One hundred mg/l of activated carbon can adsorb 0.2 to 2 mg/l of cyanide.	2, 11, 42.
By-products formed during treatment.	Carbon dioxide and ammonia.	21, 29.
Optimum pH for treatment.	Four to four and a half.	42.
Length of treatment time.		
Cyanide and metal recovery after treatment.	Cyanide and copper complexes when treated with acid.	2, 14, 21.
Ponding requirement.		

Table 12. Continued

Parameter	Characteristic	References
Notes:	Drinking water quality is possible in the effluent. ^a Automation is possible. The carbon can be reused after treating with acid. ^b	a:25. b:2.

Reverse Osmosis

High pressure, 2.8 to 5.6 million N/m² (400 to 800 psi), is required in reverse osmosis to drive the solution to be treated through semipermeable membranes (McNulty and Hoover 1980). The result is a large volume of permeate solution which has passed through the membrane and a low volume having a high cyanide solution concentration which was unable to pass through the membrane. Up to 95 percent of the wastes are concentrated in the low volume solution resulting in up to 81.6 percent cyanide removal (Table 13). Cyanide that has been removed can be recovered or recycled (Rosehart 1973). This treatment process can provide safe drinking water (EPA 1985). The size of the treatment facility will determine the amount of solution that can be processed (McNulty and Hoover 1980).

A problem in the reverse osmosis process is the narrow acceptable solution pH range required by the membrane (McNulty and Hoover 1980). Scaling by calcium and other salts may also occur and cause fouling of the membrane

(Rosehart 1973, Weathington 1988). Other techniques must be used if further treatment of the concentrated cyanide solution is required (EPA 1985).

Table 13. Ten parameters to be used for comparison between reverse osmosis and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	The cyanide fraction is separated out of solution.	8, 13, 40, 54.
Types of chemicals used in treatment.		
Toxic chemicals used in treatment.		
Removal efficiency of the treatment.	Cyanide removal is 29 to 82 percent.	13, 40.
By-products formed during treatment.	Cyanide and calcium ions form.	40.
Optimum pH for treatment.	Two and a half to seven.	30.
Length of treatment time.	Hours.	40.
Cyanide and metal recovery after treatment.	Cyanide and calcium ions.	8, 40.

Table 13. Continued

Parameter	Characteristic	References
Ponding requirement.		
Notes:	The concentrated cyanide solution formed must also be treated. ^a Drinking water quality can be obtained. ^b	a:8, 13, 40, 54. b:40.

Ion Exchange

The ion exchange method simply replaces one ion in solution with another (Palla and Spicher 1971). An ion exchange facility with a lead column of anionic exchange resin can adsorb over 99 percent of the cyanide in water (Bernardin 1973, EPA 1985). The process operates at an optimum pH of 11. Since the resin does not remove free cyanide effectively, conversion of free cyanide to ferrocyanide by reaction with ferrous hydroxide must be performed (Table 14). Cyanide and metals may be recovered and the cyanide reused (Huiatt et al. 1983) as both cyanide and ferrocyanides are concentrated on the exchange resin (McGivney and Shelton 1985).

Several problems are inherit in the ion exchange method. A concentrated cyanide solution remains after the resin is regenerated and must be treated. Resin poisoning, can occur when exchanged ions become securely attached to the resin and regeneration is no longer possible. Iron

cyanides are a major cause of this phenomenon. (McGivney and Shelton 1985). The occurrence of resin poisoning can be reduced by keeping the cyanide ions in solution below a level of 7 percent of the total anions in solution (Palla and Spicher 1971). Concentrations of thiocyanate can also interfere with the adsorption of cyanide by poisoning the resin (Huiatt et al. 1983, Mudder and Whitlock 1984).

Table 14. Ten parameters to be used for comparison between ion exchange and other neutralization methods.

Parameter	Characteristic	References
Types of cyanide not affected by treatment.	Free cyanide	19, 31, 54.
Types of chemicals used in treatment.	Organic compounds.	21.
Toxic chemicals used in treatment.	None.	25.
Removal efficiency of the treatment.	Up to 99 percent of the cyanide in the water is removed.	2, 13.
By-products formed during treatment.	Ferrocyanide.	21, 32.
Optimum pH for treatment.	Eleven.	21.
Length of treatment time.	The process treats 38 to 379 l/min.	34.

Table 14. Continued

Parameter	Characteristic	References
Cyanide and metal recovery after treatment.	All metal complexes are removed.	7, 29.
Ponding requirement.		
Notes:	A concentrated cyanide solution is formed. Iron cyanide poisoning of the resin is possible.	29.

SUMMARY AND CONCLUSIONS

Many processes and treatments which make use of physical, chemical or biological means to neutralize cyanide have been discussed. These methods can be used alone or in combination. The best treatment method for any one site will vary depending on the form of cyanide present, initial cyanide concentration and cyanide removal efficiency. Other considerations are the final cyanide concentration level to be obtained, the formation of by-products as a result of the treatment and the toxicity of any chemicals used in the neutralization process.

Although many methods are capable of neutralizing cyanide in waste solutions only alkaline chlorination as a treatment process is feasible for heap leach tailings. The treatment of heap leach tailings requires a large volume of neutralizing solution that can be sprayed over the processed ore. There are a number of techniques that can be used to neutralize tank leach tailings/solutions. The hydrogen peroxide and INCO process both provide a fast and efficient method of treatment. The hydrogen peroxide method has an advantage in that any excess degrades into harmless substances and there is no problem of acid formation as with the INCO process.

The neutralization of cyanide solutions offers the greatest number of treatment methods from which to choose. Oxidation and hydrogen peroxide provide ease of use and are efficient and fast methods of cyanide neutralization. There is also the advantage that any excess of chemicals added to the cyanide solution will not cause further problems. Often natural degradation will be incorporated with other treatment methods. This method can significantly reduce the the amount of cyanide that would otherwise require treatment, although time consuming and requiring holding ponds.

In terms of total reclamation there are a number of considerations which must be taken into account. Heap leach piles composed of rock fragments will have texture problems. The tailings ponds will also have textural problems depending on how fine the ore has been ground and the manner in which the coarse sand and finer size fragments have been mixed. The solution in the tailings ponds will often have, depending on the type of cyanide neutralizing treatment chosen, both an elevated electrical conductivity and sodium absorption ratio. The pH of the solution in the tailings ponds can be either high or low, again depending on the treatment chosen for neutralization. During many of the treatment processes a sludge composed of carbonates may form. It is due to the use of lime for pH control.

Research is needed to better understand how these treatment processes can best be used in combinations. Research is also needed to find ways to better treat groundwater that has become contaminated with cyanide. Information about what actions need, and can, be taken in any number of situations would be helpful.

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