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FATE AND EFFECTS OF CYANIDE FROM GOLD AND SILVER MINING

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September 1985

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1.0 INTRODUCTION

Cyanide has for many years been recognized as a very effective and economical tool in various chemical and physiochemical processes. Industrial applications including petrochemical, metal electroplating, and/or finishing, photographic processing, ore extraction, coke, and iron and steel manufacturing, have often resulted in contamination of surface waters.

This report summarizes recent literature on the application of cyanide in the gold and silver mining industry (Section 2); cyanide chemistry and waste treatment (Section 3); behavior and fate of cyanide in the environment (Section 4); and cyanide toxicity (Section 5).

2.0 GOLD AND SILVER MINERALOGY

The ease with which gold and silver ores can be processed using heap-leach cyanidation depends upon the physical and chemical properties of the mineral, the chemistry of the interfacing metals in the ore, and the nature of the gangue minerals. McQuiston and Shoemaker (1975) devised a useful classification for gold ores, an abbreviated summary of which follows:

- Native or free gold ores in which the gold is in its elemental state and not locked in other sulfide minerals
- Gold associated with iron sulfides as discrete particles separate from, attached to, or disseminated within sulfides
- Gold tellurides, including calaverite, krennerite and slyvanite
- Gold in other minerals including arsenic, antimony, copper porphyries, carbon compounds, lead and zinc

Of these ores, those suitable for cyanide heap-leaching are native and certain sulfide ores. Among the properties making extraction by leaching possible are, 1) the size of the gold particles is extremely small, 2) the host rock is porous to cyanide solution and retains this porosity throughout the leach cycle, 3) the ore is relatively free of "cyanicides" which destroy cyanide or otherwise interfere with the dissolution process, and 4) the ore does not contain excessive amounts of clayey constituents that will impede solution percolation (Heinen et al., 1978).

Addison (1980) classified silver ores as follows:

- Silver with copper porphyries
- Silver with lead and zinc minerals, occurring as the native metal, as argentite, as sulfo-salts, or as argentiferous galena
- Silver with vein copper minerals, occurring primarily as argentiferous tetrahedrite.
- Silver with cobalt and nickel minerals, occurring as massive native silver together with arsenic, cobalt, nickel, iron, and occasionally, copper
- Silver with minor gold

Of these ores, only silver with minor gold is amenable to direct cyanidation. Cyanidation following flotation can be applied to silver with lead and zinc minerals and silver with cobalt and nickel minerals.

2.1 Leaching Technology

Gold ore can be economically leached at grades about an order of magnitude lower than they are commonly milled. Current leaching operations are producing gold from ores containing as little as 0.03 oz/ton with cutoff grades down to 0.01 oz/ton. Most silver leaching operations are producing from ores containing 1 to 4 oz/ton.

Three major types of leaching systems exist, including heap, dump and in-situ (vat-leaching not considered). In the typical heap-leaching operation, ore is mined or gathered from old mine-waste piles and placed upon prepared pads. The ore may or may not undergo crushing prior to placement on the pad.

If mine waste-rock piles or dumps are judged to contain sufficient mineral value to justify leaching, and the solutions can be controlled without appreciable losses, the pile is dump-leached without preparation. Common in the copper industry, this technique is rarely used for gold operations.

Ore may be leached in-situ (in place) if it conducts fluids flow, with or without blasting. An exposed body of ore may be leached by spraying solution on the surface and collecting it in recovery wells following percolation through the ore. Buried ore bodies require that the solution be injected into the formation through injection wells and collected through adjacent recovery wells. In-situ leaching has been applied to gold recovery sporadically.

Heap-leaching of gold or silver ores typically employs cyanide as a leaching solution. Two types of heap-leach cyanidation are used commercially: short-term leaching of crushed ore and long-term leaching of run-of-mine material (Heinen et al., 1978).

Short-term leaching processes require that the ore be crushed to achieve adequate exposure of the mineral values to the cyanide solution, while maintaining reasonable percolation rates. To achieve this end, ore is typically crushed to minus 3/4 in. or less. The leaching cycle ranges from 7 to 30 days in length.

Long-term leaching is useful in extracting gold from uncrushed, porous, sub-mill-grade material. The material, generated by blasting, may contain large boulders, but is generally minus 6 in. in size. Leaching of the heaps continues until it is no longer profitable, perhaps for years.

Preparation for heap-leaching of ore includes preparation of an impermeable pad, mining or gathering ore from dumps, crushing the ore (optional) and placing the ore on the pad. Ore pads are typically situated on flat terrain graded to provide a gently sloping surface for drainage, on the order of 1 to 4%. The pad site is lined with an impervious material to prevent leaching solution losses due to seepage. The liner material used is usually tar, clay, or plastic.

Ore is placed on the pads by scrapers, trucks, front-end loaders, and bulldozers; conveyors and stackers may also be used. The height of each layer or lift of ore may range from 1 to 7 m in height, the average typically falling between 2 and 3 m. Each pad may have a capacity of 900 to 9,000 metric tons.

Following leaching of the first lift, the ore may be removed from the pad, or left in place with the next lift placed on top. Additional lifts may be placed following the next leaching cycle. Whether the ore is removed after each leaching episode is dictated largely by the characteristics of the ore. If the ore is finely crushed, leaching is efficient and a single lift is quickly depleted of mineral values, and the spent material is removed. Operations employing larger sized ores generally use multiple lifts. This allows the solution to extract extra mineral values from the lower lifts until they are depleted, without wasting pad space.

The cyanide leach solutions are applied by spraying from perforated plastic pipes, by sprinkling using plastic sprinkler heads, or by ponding. In the case of the former two methods, rates of application range from 200 to 3000 l/sq m of surface area daily. In ponding operations, the impoundment is maintained at a depth of several inches as the solution percolates downward. Solution strengths for commercial applications typically range from 150 to 2500 g of sodium cyanide (NaCN) per metric ton of solution. The higher strengths are generally used on ores with high silver content.

As the cyanide solution percolates through the heap, the mineral values in the ore are dissolved. The pregnant cyanide effluent drains off the impermeable pad into a holding pond or tank. The pond, lined to minimize seepage losses, functions as a surge pond and as a settling basin for particles contained in the pregnant solution.

The principle upon which heap-leach cyanidation is based is that weak alkaline cyanide solutions preferentially dissolve gold and silver contained in ore (Heinen et al. 1978). The mechanism of action involves two reactions:

$$4Au + 8NaCN + O_2 + 2H_2O \longrightarrow 4NaAu(CN)_2 + 4NaOH \qquad (1)$$

$$2Au + 4NaCN + O_2 + 2H_2O \rightarrow 2NaAu(CN)_2 + H_2O + 2NaOH \qquad (2)$$

While most of the gold dissolves by the second reaction, a significant proportion undergoes dissolution via reaction one (Huiatt et al. 1982).

An adequate supply of dissolved oxygen is essential for the dissolution of gold, throughout the reaction period. Oxygen is introduced by bubbling air through the leach solution and/or by spraying the solution onto the heap.

Despite its essential nature, absorbed oxygen, in conjunction with carbon dioxide in the air, may result in cyanide losses as shown:

$$2NaCN + O_2 + 4H_2O \rightarrow Na_2CO_3 + (NH_4)_2CO_3 \qquad (3)$$

$$NaCN + CO_2 + H_2O \rightarrow HCN + NaHCO_3 \qquad (4)$$

The rate of gold or silver dissolution is dependent upon the concentration of NaCN and the alkalinity of the solution, the optimum pH being 10.3 (Barsky et al. 1962). A leach solution pH of 9.5 to 11 is maintained through the addition of lime (CaO) or caustic soda (NaOH). This is necessary to minimize decomposition of cyanide by carbon dioxide, which may be substantial in highly oxidized ores, and to neutralize acidic components of the ore responsible for the liberation of hydrocyanic acid (HCN). Excess lime increases cyanide consumption and reduces dissolution rates.

A number of ore constituents may act as "cyanicides", substances which destroy cyanide, or otherwise interfere with the gold dissolution process. Iron sulfide minerals are oxidized to some extent during the leach, resulting in acid formation. These acids are neutralized by the alkali added to the leach solution. Copper minerals may be dissolved by the leach solution, thereby consuming large quantities of NaCN and oxygen. A number of compounds and base metal ions, including realgar (As_2S_2), orpiment (As_2S_3), stibnite (Sb_2S_3), Fe^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+}, act to retard or inhibit gold or silver dissolution.

Naturally occuring carbonaceous materials in sedimentary-type ores act as adsorbents for gold or silver dissolved by cyanide solutions, resulting in premature precipitation. Other organic substances, including flotation reagents, retard cyanidation through the consumption of dissolved oxygen and inhibition of gold or silver recovery from the pregnant solution.

2.2 Flotation Technology

Flotation is practiced when some or all of the gold is trapped in sulfides, such as pyrite and pyrrhotite, in arsenides, such as arsenopyrite, or when it occurs as gold telluride. It is also used almost universally where silver is the metal of principal value (Addison, 1980). The method has permitted the mining of many low grade and complex mineral deposits that, otherwise, would have been unprofitable to exploit. Tailings from the flotation process may be further treated by cyanidation.

The mechanism of flotation involves the attachment of mineral particles to air bubbles which, in turn, are carried to the surface of the ore pulp where they can be removed. If a foaming agent is added which prevents the rising bubbles from bursting upon reaching the surface, a layer of mineral-laden foam forms. This foam can be removed from the surface of the flotation cell to recover the mineral.

The ore is crushed and ground to a consistency fine enough to liberate the mineral values from one another and from the gangue minerals. Minerals are made selectively hyrophobic through the addition of organic, surface-active chemicals called collectors. The selectivity desired is achieved by modulating the role of collectors by additional reagents. Activators enhance mineral adsorption to a collector while depressants prevent adsorption. Those mineral particles made hydrophobic rise with the circulating air bubbles, while hydrophilic particles remain behind in the pulp as tailings.

In the flotation of base metal sulfide ores, cyanide is often used as a depressant. Alkaline cyanides will depress zinc and iron sulfides, as well as copper sulfides if used in excess. Typical concentrations, fed as a 5% solution, range from 50 to 250 g/metric ton of ore (American Cyanimid, 1976).

2.3 Methods of Gold Recovery

Recovery of gold and silver from pregnant heap-leach cyanide solutions is achieved by either of two methods: 1) precipitation with zinc dust, or 2) adsorption on activated carbon in the form of charcoal. The selection of a specific system of recovery will depend upon the specific conditions at a leaching operation and the existing facilities.

2.3.1 Recovery by Zinc Precipitation

Prior to precipitation of gold or silver on zinc, the pregnant solution must be clarified to remove suspended solids. Left in solution, these particulates will coat the zinc dust thereby retarding precipitation. Elimination of dissolved oxygen from the solution is necessary as well, to prevent redissolution of gold following precipitation. Dissolved oxygen reacts with zinc dust to form hydrated zinc oxide. This compound coats the dust, preventing further reaction with the pregnant solution.

Upon addition of the zinc dust to the solution, the precipitation proceeds for both gold and silver, according to the reaction:

$$NaAu(CN)_2 + 2NaCN + Zn + H_2O \dashrightarrow Na_2Zn(CN)_4 + Au + 1/2H_2 + NaOH \quad (5)$$

The speed of the reaction is improved through the addition of lead acetate or lead nitrate to the solution. These soluble salts form a bond with the zinc, resulting in a compound with greater galvanic activity than the zinc alone.

As the zinc should precipitate gold or silver 1 mol/mol, the amount of zinc added to the solution should be proportional to the concentration of gold. In practice, 10 to 100% excess zinc is added to ensure complete recovery. Enough free cyanide must be present to dissolve the zinc, thereby allowing replacement of gold in the alkaline compound and maintaining the solubility of the alkaline compound.

Following precipitation, the solution is forced through Merrill-type pressure filters, leaving the gold and/or silver plus impurities behind. The precipitate is removed from the filter and dried for smelting.

2.3.2 Recovery by Carbon Adsorption

The carbon adsorption process is typically more efficient than zinc precipitation for treating dilute gold cyanide solutions, and dismisses the need for clarification and de-aeration procedures required in zinc recovery. In addition to these simplifications, carbon adsorption entails lower capital and operating costs (Heinen et al. 1978).

The mechanism of carbon adsorption of gold is not fully understood. Adamson (1972) theorized that the gold is adsorbed as the gold cyanide complex Au(CN) through ion exchange. Facts supporting this contention include: 1) CN ions are also adsorbed by the activated carbon, 2) adsorption of Au(CN) ion is not accompanied by adsorption of an equivalent quantity of Ca or Na from solution, and 3) the adsorbed gold can be displaced with OH ions provided by hot alkaline solutions. Davidson (1974) indicated that the gold adsorbed is either in the calcium aurocyanide or hydrogen aurocyanide form, depending on the cyanide solution pH and the concentration and character of the "spectator" cations present.

In the recovery process, the pregnant heap-leach solution is pumped through a series of columns containing activated coconut charcoal. The solution may be percolated downward through a fixed bed of carbon or upward at a rate that maintains the charcoal in a suspended, or fluidized, state. The choice of loading technique is dependent upon the amount of turbidity or slimes in the pregnant solution.

Regardless of the loading technique employed, the columns of charcoal are arranged in countercurrent series. The pregnant solution enters the column containing the most precious metals first, passing into columns with successively less adsorbed metals until emerging as a barren solution from the final column. Charcoal is replaced periodically to maintain maximum recovery efficiency.

The adsorbed precious metals are typically recovered from the loaded columns using the Zadra process. In this process, a hot caustic soda solution (1% NaOH-0.1% NaCN solution at 93°C) is used to strip the charcoal of the mineral values. The gold and/or silver in the strip solution is collected by electrowinning. The charcoal and strip solution are recycled.

2.4 Cyanide in Mineral Extraction Wastes

Wastes resulting from mining and beneficiation processes may be conveniently categorized as air emissions, liquid wastes, and solid wastes. Greber et al. (1979) concluded that air pollution from these operations is not a major environmental concern. Liquid and solid wastes from cyanidation and flotation processes are, however, of concern and are examined below.

2.4.1 Heap-Leach Cyanidation

The holding pond, into which the pregnant cyanide solution drains, should be designed to accommodate this outflow as well as the maximum rainfall and runoff expected for the site. Insufficient pond capacity may lead to discharge of cyanide solution to the watershed during or following leaching operations. If release of solution becomes necessary, e.g., in the event of an abnormal precipitation event, treatment to reduce cyanide levels may be necessary. Methods of treatment of cyanide wastewaters are discussed below.

Heavy-metal cyanide salts may persist in the abandoned heaps for several years. In constrast, Englehardt (1985) measured an 85% loss of free cyanide in an abandoned silver heap leach pile over an 18-month period. From these data, he projected that the cyanide would be completely destroyed in less than four years.

The barren solution emerging from mineral recovery processes contains a variety of cyanide compounds, including free cyanides, simple cyanides of sodium or calcium, complex cyanides of copper, iron, nickel, and zinc, and thiocyanates (Scott 1981). Harrison (1979) reported on the chemical compositions of barren solutions and tailings effluents from several Canadian gold mills (Table 1-1). These data exhibit a marked decline in cyanide and heavy metal concentrations in the tailings impoundments.

2.4.2 Flotation

The cyanide reaction species used in flotation are probably complex iron cyanides ($Fe-Fe[CN_6]$) and copper iron complexes ($Cu-Fe[CN_6]$) (Taggart 1945;

TABLE 1.1. CHEMICAL ANALYSES OF CANADIAN GOLD MILL BARREN SOLUTIONS AND TAILINGS POND EFFLUENTS[a,b,c]

Plant	Solution	Volume[d]	Fe	Ni	Zn	Cu	CN	S.S.	SCN
A	Barren		35.7	2.9	17.9	73	220		180
	Effluent	200,000	0.6	0.4	0.82	2.4	13	17	
B	Barren		21.4	10.0	62.4	6.7	300		54
	Effluent	516,000	8.2	0.7	0.70	1.1	3.3	37	
C	Barren		0.4	1.7	84.1	11	610		400
	Effluent	1,500,000	0.3	0.1	0.20	2.3	6.8	24	
D	Barren		0.1		13.9	6.1	86		42
	Effluent	7,200,000	N/A	0.4	0.19	0.3	0.3	10	
E	Barren		0.1	9	31.0	29	74		50
	Effluent	1,678,000	N/A	0.2	0.13	0.5	1.2	19	
F	Barren		0.8	3.1	12.0	300	310		N/A
	Effluent	915,000	N/A	1.8	0.60	16.0	26.5	53	

a. Table reproduced from Harrison, 1979.

b. Units in mg/l unless otherwise noted.

c. The above analyses are for grab samples taken in 1978. Arsenic was found in the Waste Barren solution from Canadian ores in the range of 0.01 to 0.03 mg/l. The range reported in the final tailings effluent was 0.01 to 212.4 mg/l.

d. Imperial gallons per day (IGPD).

cited in Huiatt et al. 1982). Both of these substances are relatively insoluble in water, the complex cyanides binding strongly to the surface of constituent minerals in the tailings, thereby becoming immobilized.

The EPA (1975) reported concentrations of total cyanides in tailings water from U. S. flotation plants up to 0.03 mg/l. Laboratory studies by the U. S. Bureau of Mines found the bulk of the cyanide from flotation on a porphyry copper ore containing high siliceous gangue associated with the process waste, with small amounts in the concentrate and tailings (Huiatt et al. 1982).

3.0 CYANIDE CHEMISTRY AND WASTE TREATMENT

Cyanides are defined as the class of organic or inorganic compounds containing the CN- group. Any discussion of the treatment, as well as the the toxicology of cyanide-bearing wastes requires some knowledge of the various forms in which cyanide can exist. The chemical speciation of cyanides varies according to source and response to environmental chemicals and physical and biological factors.

3.1 Cyanide Chemistry

The cyanide compounds of interest to the gold and silver industry may be classified as free, simple, and complex cyanides. A fourth class, organic cyanides or nitriles, will not be considered extensively.

3.1.1 Free Cyanides

This class of cyanides includes hydrogen cyanide (HCN) and cyanide ion (CN-). These species share in the equilibrium hydroysis reaction:

$$CN^- + H_2O \longleftrightarrow HCN + OH^- \qquad (1)$$

The reaction is strongly pH dependent (Figure 2-1). At a pH of 9.36, equal to the pK, the concentration of each species is equivalent. Solutions of a more acidic nature favor HCN, with those of pH 8 or less having more than 90% of the free cyanide as HCN.

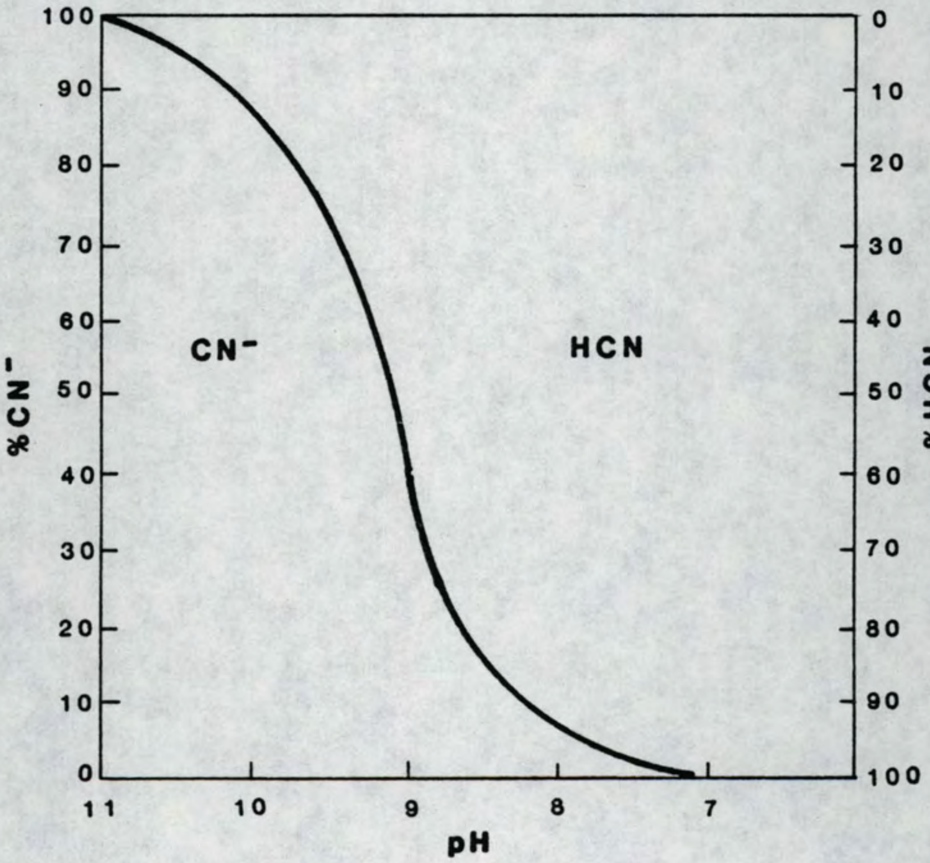


Figure 2-1. Effect of pH on Dissociation of Hydrogen Cyanide

Hydrogen cyanide is a colorless gas or liquid with a boiling point of 25.7°C. It is highly reactive, occurring rarely in nature. In solution HCN will exist in equilibrium with the atmospheric HCN vapor, volatilizing from solution.

3.1.2 Simple Cyanides

This class of compounds is represented by the formula $A(CN)_x$, where A is an alkali (sodium, potassium, ammonium) or a metal, and x, the valence of A, is the number of CN groups (APHA 1980). The formation of simple metal cyanides is favored over complex metal cyanides if the metals are more prevalent than the cyanide.

The simple cyanides exhibit a wide range of solubilities, with soluble compounds, e.g., the alkali cyanides, ionizing to release the cyanide ion:

$$A(CN)_x \longleftrightarrow {}^{A} + xCN- \qquad (2)$$

$$KCN + H_2O \longleftrightarrow KOH + HCN \qquad (3)$$

The rate of reaction is influenced by pH and temperature. The generated cyanide ion undergoes hydroysis to yield HCN at acidic pH (Eq. 1). The simple metal cyanides are insoluble and probably accumulate in the bed sediments (EPA 1979).

3.1.3 Complex Cyanides

Complex alkali-metallic cyanides can generally be represented by the formula $A_yM(CN)_x$, where A is the alkali, y is the number of the alkalies, M is the heavy metal (ferrous or ferric ion, cadmium, copper, nickel, silver, zinc, or others) and x is the number of CN groups (APHA 1980). The value of x is equal to the valence of A taken y times plus the valence of the heavy metal.

The soluble complex cyanides release the radical or complex ion M(CN):

$$A_yM(CN)_x \longleftrightarrow yA^{+x} + M(CN_x)^{-yw} \qquad (4)$$

where w is the oxidation state of A in the original molecule. The complex ion may subsequently undergo dissolution, releasing the cyanide ion.

Ford-Smith (1964) noted 28 elements capable of forming complexes with cyanide, resulting in up to 72 metal-cyanide complexes. Formation occurs in a step-wise fashion (Broderius 1973) as the concentration of cyanide ion in solution increases. Consequently, the higher complexes of a particular metal are in equilibrium with greater cyanide ion concentrations. As an example, copper may be present as $Cu(CN)$, $Cu(CN)_2$, $Cu(CN)_3$ and $Cu(CN)_4$, depending upon the availability of cyanide ion.

3.2 Treatment of Cyanide Wastes

A number of methods exist for treating mill effluents to effect cyanide removal. Ingles and Scott (1981) have organized these into seven major categories (Table 2-1). Each of these processes are discussed below.

3.2.1 Natural Degradation

Given adequate retention time in waste receiving ponds, natural environmental forces may be exploited to reduce the concentration of cyanide effluents. Natural degradation is promoted by volatilization, photodecomposition by sunlight, acidification by carbon dioxide in air, oxidation by oxygen, dilution, sorption on solids, seepage into underlying porous media and biological degradation.

Cyanide removal rates due to natural processes decline in winter as low temperatures and/or the presence of an ice cover inhibit most of the processes listed above. Regardless of these seasonal dynamics, natural processes, while effective as pretreatment to reduce reagent consumption, are not generally capable of effecting complete cyanide destruction.

TABLE 2-1. PROCESSES FOR CYANIDE REMOVAL[a]

Natural Degradation (Lagooning)

- Dilution
- Volatilization
- Biodegradation
- Oxidation
- Metals Precipitation

Oxidation Processes

- Alkaline Chlorination
    - chlorine gas
    - hypochlorites
    - electrolytic (in-situ) generation
- Ozonation
- Hydrogen Peroxide Oxidation
- Inco (sulfur dioxide + air)

Acidification/Volatilization/Reneutralization

Absorption Processes

- Ion Exchange
- Activated Carbon
- Ion Flotation
- Precipitation Flotation

Electrolytic Processes

- Cyanide regeneration
- Cyanide destruction

Conversion to Less Toxic Forms

- Thiocyanate
- Ferrocyanide

Biological Treatment

[a] From Huiatt et al. 1982.

3.2.2 Oxidation Processes

Alkaline chlorination is commonly used to destroy cyanides in waste waters. The oxidation of cyanide may be accomplished using chlorine gas, calcium hypochlorite, or sodium hypochlorite (White 1972).

The reaction occurs in two stages, the first of which results in the production of cyanogen chloride:

$$NaCN + Cl_2 \dashrightarrow CNCl + NaCL \qquad (5)$$

This reaction occurs rapidly, independent of solution pH (White 1972). Cyanogen chloride, though highly toxic, hydrolyzes readily to cyanate under alkaline conditions:

$$CNCl + 2\ NaOH \dashrightarrow NaCNO + NaCL + 2\ H_2O \qquad (6)$$

Two reactions also comprise the second stage of the oxidation process:

$$2\ NaCNO + 3\ Cl_2 + 4\ H_2O \dashrightarrow 3\ Cl_2 + (NH_4)_2\ CO_3 + Na_2CO_3 \qquad (7)$$

$$(NH_4)_2\ CO_3 + 3\ Cl_2 + 6\ NaOH + Na_2\ CO_3 \dashrightarrow$$

$$2\ NaHCO_3 + N_2 + 6\ NaCl + 6\ H_2O \qquad (8)$$

Theoretically, the complete oxidation of cyanide to nitrogen and bicarbonate requires 6.82 g Cl per g CN- removed.

Chlorine requirements are increased significantly if mill effluents contain thiocyanate as this is oxidized to cyanate:

$$SCN- + 4\ Cl_2 + 10\ OH- \dashrightarrow CNO- + SO_4^{2-} + 8\ Cl- + 5\ H_2O \qquad (9)$$

Reagent demand associated with this reaction alone is about 70% of that for the complete oxidation reaction of cyanide.

Alkaline chlorination readily destroys metal cyanide complexes of copper and zinc, the metals precipitating out as hydroxides. Nickel cyanides are more resistant to oxidation. Ferrocyanides are oxidized to ferricyanides which are not destroyed by the chlorination process.

Oxidation of cyanide can also be effected using ozone:

$$NaCN + O_3 \text{-->} NaCNO + O_2 \tag{10}$$

The oxidation to cyanate is rapid, followed by a slower oxidation to nitrogen and carbonate:

$$CNO^- + 3\ O_3 + H_2O \text{-->} 2\ HCO_3^- + N_2 + 3\ O_2 \tag{11}$$

The presence of thiocyanate significantly increases reagent demands of the ozonation process. Thiocyanate is rapidly oxidized to cyanate:

$$SCN^- + 4\ O_3 + 2\ OH^- \text{-->} CNO^- \text{ to } SO_4^{2-} + 4\ O_2 + H_2O \tag{12}$$

The reaction consumes approximately 1.7 times the 1.85 g O_3 required per g CN^- oxidized from cyanide to cyanate.

Ozonation results in rapid oxidation of copper-cyanide complexes. Destruction of nickel and zinc complexes occurs at a slower rate, while cadmium is even more resistant to oxidation. Iron complexes are not destroyed by ozone unless accompanied by elevated temperatures or UV radiation, although ferrocyanide oxidizes to ferricyanide.

Hydrogen peroxide oxidation may be effected using either of two methods. The reactions for each are:

A. With a copper catalyst:

$$CN^- + H_2O_2 \xrightarrow[\text{alkaline solution}]{Cu^{++}} CNO^- + H_2O \tag{13}$$

$$CNO^- + 2\ H_2O \xrightarrow[\text{pH just <7}]{} NH_4^+ + CO_3^{2-} \qquad (14)$$

B. "Kastone" process:

$$HCN + HCHO \xrightarrow{pH=11} HOCH_2\ CN \text{ (glyconitrile)} \qquad (15)$$

$$HOCH_2CN + H_2O_2 \xrightarrow{pH=11} 3\ NH_3 \cdot 5\ HCNO \cdot 5\ H_2C(OH)CONH_2 \qquad (16)$$

(glycolic acid amide)

In the first process, copper ion serves as a catalyst. The Kastone process uses the Kastone Peroxygen Compound (DuPont), a formulation of 41% H_2O_2 with trace amounts of catalysts and stabilizers, in conjunction with formaldehyde.

The hydrogen peroxide processes destroy free cyanide as well as complexes of copper, zinc, and nickel. Cyanide in ferrocyanides can be precipitated by copper. Thiocyanate is not destroyed by these processes.

The INCO (International Nickel Company) process provides for rapid removal of free and complex cyanides through the oxidation of effluents with a mixture of sulfur dioxide and air, using copper as a catalyst. The reaction is described by:

$$CN^- + O_2 + SO_2 + H_2O \rightarrow CNO^- + H_2SO_4 \qquad (17)$$

Thiocyanate is oxidized to cyanate as well:

$$SCN^- + 4\ SO_2 + 4\ O_2 + 5\ H_2O \rightarrow CNO^- + 5\ H_2SO_4 \qquad (18)$$

Due to the considerably slower kinetics of this latter reaction, however, reagent demand is not significantly higher.

The INCO process oxidizes cyanide to cyanate and precipitates metals as metal hydroxides. Iron cyanide complexes remain in the ferrous state and are removed from solution through precipitation of iron compounds in the form of $Me_2Fe(CN)_6$, where Me is Cu, Zn, and Ni.

3.2.3 Acidification/Volatilization/Reneutralization

This treatment relies upon the high volatility of HCN for cyanide recovery. The waste solution is acidified and subsequently exposed to a countercurrent stream of air. The air recovers HCN formed by the acid from cyanide ion and zinc, copper, and nickel complexes of cyanide. The cyanide-laden air stream enters an absorber tower, contacting a weak lime slurry dispersed as a mist. The effluent from the tower is returned to the cyanidation circuit.

The process does not liberate cyanide from ferrocyanide or thiocyanate. Cyanide from the latter species is likely recoverable through the application of a strong oxidant following acidification.

3.2.4 Absorption Processes

Absorption processes for the recovery of cyanide include: ion exchange, activated carbon adsorption, and ion and precipitation flotation. Ion exchange depends upon initial absorption of cyanide complexes by a column of anion exchange resin. This is followed by removal of free cyanide using a column conditioned by precipitation of cuprous cyanide in the resin matrix. The recovery of cyanide is enhanced by prior conversion of free cyanide to ferrocyanide. All metal cyanide complexes are readily absorbed by the exchange resin.

Cyanide is adsorbed by activated carbon and, subsequently, catalytically oxidized. The adsorption capacity of the carbon is increased by the presence of cupric ions in the form of copper cyanides.

Ion flotation utilizes the formation of a froth of air bubbles to carry the substance to be separated out of solution. Collectors employed are ionizable surface-active organic compounds. Metal cyanide complex removal is more effective than removal of cyanide ion, making it desirable to add metal ions to the solution to be treated.

In precipitation flotation, a colloidal precipitate is formed and subsequently floated. Laboratory studies have demonstrated efficient flotation of ferrocyanide, nickelocyanide and cuprocyanide.

3.2.5 Electrolytic Processes

Electroreduction, electrooxidation, and electrochlorination comprise the three methods of electrochemical cyanide recovery. Electroreduction of complex metallocyanides results in metal precipitates and a corresponding quantity of cyanide ion. The regenerated cyanide may be recycled for additional use in cyanidation.

Electrooxidation is used to treat free cyanide and cyanate, oxidizing the cyanide to nitrogen, carbon dioxide, and ammonia. In electrochlorination, NaCl is added to the waste solution, yielding active chlorine. The subsequent reactions are those seen in conventional alkaline chlorination. None of these three technologies are known to be capable of eliminating ferrocyanide.

3.2.6 Conversion to Less Toxic Forms

The toxicity of waste effluents may be reduced through conversion of cyanide to the less toxic thiocyanate and ferrocyanide. Thiosulfate reacts with free cyanides and complex cyanides less stable than iron to yield thiocyanate. Free cyanide, and zinc and copper cyanide complexes may be converted to ferrocyanide through the addition of excess ferrous sulfate. Ferrocyanide may subsequently be removed or decomposed through precipitation or ozonation.

3.2.7 Biological Treatment

A number of microorganisms have been found capable of metabolizing cyanide compounds (Knowles 1976). Homestake Mining Company (Mudder 1975) has performed laboratory pilot studies examining the effectiveness of treating cyanide wastes utilizing this capability. A number of technologies were tested, including activated sludge, biological towers, aerated biological filters and rotating biological contactors.

The treatment processes removed, through oxidation and adsorption, thiocyanate, and free and metal complexed cyanides (including iron cyanide complexes). Reductions of thiocyanate and total cyanide to levels of 1 mg/l or less were achieved by all methods. The most efficient treatment method, activated sludge, failed after a period of 60 d due to accumulation of toxic metals.

3.2.8 Treatment of Solid Wastes

Following cyanide heap-leaching, the heap is generally washed with fresh water to maximize recovery of gold-bearing solution from the solids. The washing step also removes a large portion of free cyanide and heavy-metal cyanide complexes remaining in the heap.

Further reduction of cyanides in the heap may be effected through alkaline chlorination techniques (Stotts 1984). Following leaching, a lime/calcium hypochlorite solution is applied to the heap, using the same distribution system used in mineral extraction. The solution percolates through the pile and is collected in the chlorine pond. The heap effluent is sampled to ensure compliance with free cyanide concentration standards. Failing to meet the standards, the entire procedure is repeated.

The chlorinated tailings are subsequently removed from the leaching pad, spread out in thin lifts (30-60 cm), and left for a minimum of 10 d (Stotts 1984). This period of exposure permits further reduction of cyanide and chlorine through oxidation and volatilization.

Wasserlauf (1983) reported on bench-scale tests examining cyanide detoxification of tailings by alkaline chlorination and sulfur dioxide treatment. Sulfur dioxide treatment resulted in nearly complete removal of cyanide. A cyanide residual of 30 mg/l was present following alkaline chlorination, presumably due iron-cyanide complexes which the method does not destroy (discussed above). Free cyanide levels in the effluent were reduced to less than 1 mg/l by each treatment.

4.0 CYANIDE BEHAVIOR AND FATE

4.1 Photolysis

Two major photochemical processes account for photodegradation of cyanide compounds (Neely 1980). Direct photolysis involves the absorption of light followed by transformation or degradation. In the second process, or indirect photolysis, a sensitizer molecule may act to accelerate the decomposition of chemicals that, by themselves, are not directly photolyzed.

The importance of photolytic reactions will vary with the cyanide species under consideration. Frank and Bard (1977) found HCN to be very resistant to photolysis by wavelengths of light reaching the earth's surface. The same investigators found that, in the presence of titanium dioxide (TiO_2) powder, rates of photocatalytic oxidation of cyanide ion were significant in high intensity artificial sunlight and unfocused sunlight. In the absence of TiO_2 powder, little or no oxidation was noted.

Photodecomposition of metal-cyanide complexes, most notably ferrocyanide $Fe(CN)_6^{4-}$ and ferricyanide $Fe(CN)_6^{3-}$, is better characterized yet incompletely understood. This process is not considered important in solid waste (Huiatt et al. 1982) due to: 1) the low concentration of the two species, 2) extremely low solubility of iron hexacyanoferrates, and 3) lack of exposure to UV light except at the waste pile surface.

The low solubility of the complexes also curtails significant leaching of complex ions into surface waters where photolysis could be important. Nevertheless, aqueous photodegradation is perhaps the only conceivable fate process acting on iron-cyanide complexes (Huiatt et al. 1982).

The mechanism by which photodecomposition occurs for ferricyanide was proposed by Moggi et al. (1966):

$$[Fe(CN_6)]^{3-} \xrightarrow{h\nu} [Fe(CN)_5\ H_2O]^{2-} \xrightarrow{h\nu} \cdots \longrightarrow Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3 \qquad (1)$$

$$[Fe(CN)_5\ H_2O]^{3-} \xrightarrow{h\nu} \cdots \longrightarrow Fe^{2+} + [FeCN_6]^{3-} \xrightarrow{H^+} \text{Prussian Blue} \qquad (2)$$

Given continued exposure to UV light, complete dissociation can occur. Removal of light, prior to complete complex dissociation, results in the recombination of the cyanide ligand with the metal ion.

Lure and Panova (1964; cited in Hendrickson and Daignault 1973) found that, in the presence of sunlight, 75% of the original ferrocyanide concentration in a solution was oxidized in 5 d. Complete removal was effected in 10 to 12 d.

Burdick and Lipschuetz (1948) noted the production of free cyanide due to photolysis of potassium ferrocyanide and ferricyanide for river waters. A 5-hr exposure of 100 mg/l potassium ferrocyanide to sunlight resulted in an increase in cyanide ion from 2.0 to 6.6 mg/l. Schwarz and Tede (1927; cited in Burdick and Lipschuetz, 1948) reported on the production of ferrocyanide, cyanogen, and colloidal ferric hydroxide from potassium ferricyanide decomposed by light. Baudisch and Bass (1922; cited in Burdick and Lipschuetz 1948) suggested a mechanism for the photodecomposition of potassium ferrocyanide to HCN.

In an experiment by the U. S. Air Force Environmental Health Laboratory (Hendrickson and Daignault 1973), a photographic solution containing ferrocyanide killed no fish over a 96-h period in the absence of sunlight. When the solution was exposed to sunlight, a concentration of free cyanide 220 times the lethal concentration was generated in 6 h.

Broderius et al. (1979a; cited in IEC 1979) found that photodecomposition of hexacyanoferrate complexes resulted in 5 moles of HCN per mole of complex, the remaining mole of cyanide being converted to cyanate or cyanogen. A half-life for ferrocyanide of about 20 min. in deionized water (under natural light with concentrations between 0.1 and 1.0 mg/l ferrocyanide) was measured. If it is assumed that this half-life applied equally well to the surface layer of a tailings pond, it appears that photolysis of iron cyanides, during daylight hours, is rapid and the limiting factor in the loss of cyanide from the pond is the transfer rate of HCN from water to air (IEC 1979).

The rate of photolysis, particularly of iron-cyanides, in laboratory experiments is probably more rapid than that seen under natural conditions (Doudoroff 1976). In natural waters, light penetration is limited by turbidity, color, and depth. Broderius et al. (1978; cited in EAI 1979) reported photolysis rates 10 and 30 times less than surface rates at depths of 15 cm and 50 cm, respectively, in natural waters. The intensity and wavelength of light and angle of incidence will also affect the degree of penetration seen. Burdick and Lipschuetz (1948) found maximum cyanide residuals (CN-) of 0.05 and 0.03 ppm, in solutions of less than 100 ppm potassium ferrocyanide, in diffused light and dark, respectively. In direct sunlight, residuals ranged from about 0.5 to 3 ppm.

Asperger et al. (1960) found a pH dependence of photodecomposition, the optimum being a pH of 3.55. These investigators, as well as Broderius and Smith (1980; cited in Huiatt et al. 1982) found more rapid rates of photoaquation of $Fe(CN)_6^{3-}$ to $(Fe(CN)_5\ H_2O)^{2-}$ in cold waters than in warm waters.

Doudoroff (1956) exposed $NaCN\text{-}NiSO_4$ and $NaCN\text{-}CuSO_4$ mixtures to direct sunlight for 6 to 12 h in toxicity tests on fathead minnows, observing no changes in toxicity. These results suggest that photodecomposition is absent or minimal for these complexes.

4.2 Volatilization

As discussed above, HCN has a high vapor pressure and is readily volatilized from solution to the atomosphere. Ludzack and Schafer (1960) reported losses of 14 to 18% of applied cyanide by air stripping (volatilization effected by air forced through the system) in studies on activated sludge degradation of sewage containing 75 mg/l cyanide. The Chester Engineers (1977; cited in Huiatt et al. 1982) found a volatilization rate of 0.021 mg CN/sq ft-hr in still waters for cyanide in the concentration range of 0.1 to 0.5 mg/l. Rates in agitated waters were up to three times greater.

Dodge and Zabban (1952) examined the factors affecting batch volatilization of HCN from NaCN solutions and synthetic Zn and Cu plating wastes. Factors evaluated include pH, cyanide concentration, composition of the solution (i.e., simple or complex cyanides), temperature, presence and rate of aeration/agitation, ratio of surface area to depth in stagnant solutions, interfacial contact area, and bubble size. The conclusions reached included:

- At pH 6.5 and initial cyanide concentrations of 100 to 500 mg/l, reduction of the liquid depth to surface diameter ratio from 1.0 to 0.4 (depth to area reduction by factor of 6.25) resulted in residual HCN concentrations 6 to 7 times lower after 18 h of volatilization in a stagnant beaker.

- For initial NaCN solutions in the range of 10 to 500 mg/l, the rate of loss of HCN from a stagnant beaker was increased by a factor of 3 by decreasing the pH from 6.5-7.0 to 2.2-2.5.

- Gentle mechanical agitation of a NaCN solution, such that no vortex formed, increased the rate of HCN loss.

- Stripping coefficients of 0.029 and 0.18 lb-mole/hr-sq ft-atm were found for gently and violently agitated solutions, respectively, at room temperatures.

Lure and Panova (1964; cited in IEC 1979) studied the loss of cyanide from natural waters by volatilization. Loss was found to increase by a factor of 10 to 14 times upon agitation.

Broderius (1977; cited in EPA 1979) found HCN to be rapidly volatilized from 8 l natural water samples spiked with HCN and left open to the laboratory atmosphere (no wind). The experiment was repeated outdoors, thereby exposing the solutions to moderate winds, and loss rates increased by a factor of 2 to 2.5. Cyanide loss was reduced in spiked solutions not exposed to the atmosphere, indicating volatilization was the predominant process. All experiments used concentrations of cyanide ranging from 25 to 200 ug/l.

Raef et al. (1977a) examined the fate of cyanide, as KCN, in aerobic microbial systems with respect to adsorption, biodegradation, reaction with glucose, and stripping. Using 6 l of a 10 mg/l cyanide solution at 30° C and pH 7.0, a first-order rate of loss was noted when the solution was aerated at a rate of 2 cc/min. The authors concluded that stripping was an important removal process.

4.3 Sorption

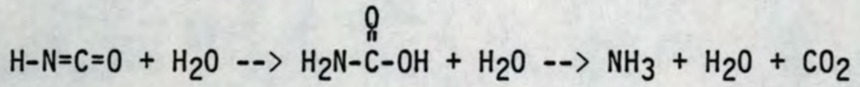
Cyanides can undergo sorption with a variety of materials, including biological solids, soils, and sediments. The EPA (1976) noted the combination of cyanides with organic material resulting in a shorter removal period for natural waters. Raef et al. (1977a) found an absence of cyanide adsorption by nonfloculating bacteria while noting a 12% reduction in cyanide in the presence of floculating cells. Adsorption was assumed to play a minor role in overall cyanide removal in biological treatment plants.

Murrmann and Koutz (1972) found little adsorption of cyanide ions by soils. Cyanide salts of most cations, except for AgCN, are soluble, but likewise, were found to move only a short distance. More extensive migration was precluded as the salts were biologically converted under aerobic conditions to nitrates or underwent complexation with trace metals.

4.4 Chemical Speciation

Hydrogen cyanide can be oxidized to isocyanic acid (HCNO) in the presence of strong oxidizing agents. Hydrolysis can subsequently result in the production of ammonia and carbon dioxide (Hendrickson and Diagnault 1973):

$$HCN + 1/2\ O_2 \text{ --> } HCNO \qquad (3)$$

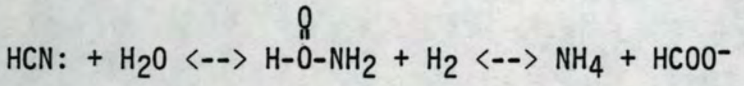


$$H\text{-}N{=}C{=}O + H_2O \text{ --> } H_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH + H_2O \text{ --> } NH_3 + H_2O + CO_2 \qquad (4)$$

The hydrolysis is greatly accelerated at low pH.

Hydolysis can also result in the destruction of HCN (Khorkin et al. 1967; cited in EPA 1979):

$$HCN \text{ <--> } HCN: \qquad (5)$$



$$HCN: + H_2O \text{ <--> } H\text{-}\overset{\overset{O}{\|}}{O}\text{-}NH_2 + H_2 \text{ <--> } NH_4 + HCOO^- \qquad (6)$$

The tautomerization of HCN to HCN: is the rate determining step, the subsequent steps occurring rapidly at room temperature (Kreible and McNally 1929; Kreible and Peiker 1933; Khorkin et al. 1967; all cited in EPA 1979). Hydrolysis is slow at all but the most strongly acidic pH (<1), often requiring several hundred hours to produce measurable hydrolysis.

Hydrolysis of cyanide ion under alkaline conditions results in formate ion and ammonia. Hydrolytic reactions involving HCN and CN- ion are sufficiently slow at environmentally relevant pH as to be non-competitive with volatilization and biodegradation (EPA 1979).

Luthy and Bruce (1979) studied the reaction of free cyanide, as CN-, with sulfur species in aqueous solutions. In solutions characterized by high $[S^{2-}]/[CO_2]$ ratios cyanide may react with polysulfide to produce thiocyanate. Similarly, free cyanide may react with thiosulfate to form thiocyanate, although this mode of formation is much less likely. Both reactions are depicted below:

$$S_xS^{2-} + CN^- \dashrightarrow S_{x-1}\,S^{2-} + SCN^- \qquad (7)$$

$$S_2O_3^{2-} + CN^- \dashrightarrow SO_3^{2-} + SCN^- \qquad (8)$$

Both polysulfide and thiosulfate are oxidation products of sulfides which are abundant in minerals.

These reactions convert a potentially toxic and volatile compound to a relatively non-toxic, strongly ionic species. Screening studies showed that complex cyanides may not be reactive with polysulfides (Luthy and Bruce 1979).

4.5 Bioaccumulation

Free cyanides exhibit little potential for bioaccumulation (Towill et al. 1978; EAI 1979) due their high toxicity, chemical reactivity, and ease of metabolism. Simply, free cyanide is either quickly metabolised or the organism dies.

The bioaccumulation of metal cyanide complexes in fish has been observed by Broderius (1973). Copper cyanide concentrations ranged from undetectable to 303.9 ug/g tissue for various bluegill tissues, with the liver/gall bladder fraction exhibiting maximal bioconcentration. Silver cyanide was accumulated in concentrations up to 168.4 ug/g tissue.

Knowles (1976) has reviewed cyanide production and accumulation by bacteria, fungi, and plants. Castric (1981) reviewed the pathways of bacterial biosynthesis of cyanides, including HCN, from glycine precursors. Biosynthesis is noted to be confined to Chromobacterium violaceum and to members of a closely related group of Pseudomonas spp. Towill et al. (1978) list 31 and 7 species of cyanogenic fungi and bacteria, respectively.

4.6 Biodegradation

Knowles (1976), Towill et al. (1978), and EAI (1979) have reviewed much of the experimental data on biological degradation of cyanide. It is apparent from these publications that numerous microorganisms are capable of metabolizing free cyanide to less toxic forms.

Strobel (1967) noted that cyanide, as KCN, was converted to carbonate and ammonia in non-sterile soils. Raef et al. (1977b) found that biological degradation by bacteria was an important removal mechanism, second only to volatilization. Ware and Painter (1955) isolated a bacterium capable of growing on silica gel medium containing only KCN as a source of carbon and nitrogen.

Pettet and Mills (1954; cited in IEC 1979) found that biodegradation of complex metallocyanides was significant in the presence of toxic heavy metals. At an influent cyanide concentration of 100 mg/l, 80 to 90% of the influent nitrogen from zinc and cadmium cyanides was recovered. This removal rate declined slightly to 75 to 80% for copper and nickel complexes. The extent of cyanide removal was inversely proportional to the solubility of the metal ion, indicating a toxic effect.

Castric (1981) noted that, unlike HCN formation by bacteria, assimilation and subsequent detoxification of HCN is not restricted to closely related microorganisms. Pathways of assimilation are diverse, resulting in the formation of such compounds as beta-cyanoalanine, gamma-cyano-alpha-aminobutyric acid, and hydrogen thiocyanate. Fry and Myers (1981) have delineated a possible mechanism of HCN detoxification by fungal pathogens.

While little or no free cyanide occurs in plants, metabolism of externally added HCN by plants is possible (Towill et al. 1978). This capability was noted in cyanogenic and non-cyanogenic species alike, including sorghum, flax, white clover, barley and pea (Blumenthal et al.; cited in Towill et al. 1978).

Degradation of cyanides by animals is less completely understood (Towill et al. 1978). The existence of rhodanese, an enzyme catalyzing the oxidation of cyanide to thiocyanate, and thiocyanates in certain invertebrates suggests the ability to detoxify free cyanide. Doudoroff (1978) cites data showing that thiosulfate added to water with cyanide reduced cyanide toxicity. It was postulated that the thiosulfate acted to increase the detoxification rate of cyanide to thiocyanate (reaction discussed above). Rhodanese has been isolated in a number of tissues in a variety of mammal species, including dogs, rhesus monkeys, rabbits and rats (Towill et al. 1978).

4.7 Persistence and Degradation of Complex Cyanides

The stability of complex cyanides is extremely variable, depending on the metal involved (Table 3-1). The dissociation constants of the complex cyanides can be used to calculate the amounts of free cyanide that will be released when the complex ions are present in water. These calculations have been summarized by Hyatt (1976; cited in Murphy and Robertson 1979) and are listed in Table 3-2. The low concentrations exemplify the small amount of dissociation seen for most metal-cyanides in the aquatic environment.

The relative persistence of complex metallocyanides depends upon whether the complexes remain as part of the solid tailings phase or remain in the aqueous phase (Huiatt et al. 1982). In the aqueous phase, pH, temperature, dissolved oxygen concentration, UV radiation and availability of other complexing agents are important determinants in complex persistence. Most complexes associated with the tailings remain inert although one, ferric ferricyanide, undergoes degradation, releasing gaseous CO_2, N_2 and traces of other compounds.

Dissociation of complex cyanides involves a number of intermediate steps. Among these steps there may be a rate-limited reaction which prevents rapid dissociation in water. Broderius (1973) found that both the concentration of the complex ion and ph influenced the rate of dissociation at a given temperature. Rates tended to increase either decreasing pH or decreasing total cyanide concentration. The degree of dissociation, as measured by the production of free cyanide, was dependent upon pH as well. At acid pH, the percentage of free cyanides was greatest.

TABLE 3-1. SOME METAL-CYANIDES COMPLEX IONS IN ORDER OF DECREASING STABILITY IN WATER

Name[a]	Formula	Dissociation Content
Hexacyanoferrate (III) or Ferricyanide	$[Fe(CN)_6]^{-3}$	1×10^{-52}
Hexacyanoferrate (II) or Ferrocyanide	$[Fe(CN)_6]^{-4}$	1×10^{-47}
Tetracyanomercurate (II)	$[Hg(CN)_4]$-2	4×10^{-42}
Tricyanocuprate (I)	$[Cu(CN)_3]^{-2}$	5×10^{-28}
Tetracyanonickelate (II)	$[Ni(CN)_4]^{-2}$	1×10^{-22}
Tetracyanocadminate (II)	$[Cd(CN)_4]^{-2}$	1.4×10^{-17}
Tetracyanozincate (II)	$[Zn(CN)_4]^{-2}$	1.3×10^{-17}

A. The Roman numerals indicate the oxidation state of the central metal atom.

TABLE 3-2. DISSOCIATION OF 1 MOLAR AND 10^{-4} MOLAR SOLUTIONS OF METAL CYANIDE COMPLEXES

	Free Cyanide (mg/l) (1 Molar Solution)	Free Cyanide (mg/l) (10^{-4} Molar Solution)
$Cu(CN)_3^{-2}$	5.1×10^{-3}	5×10^{-4}
$Cd(CN)_4^{-2}$	5.8	0.922
$Fe(CN)_6^{-4}$	0.16	1.7×10^{-2}
$Fe(CN)_6^{-3}$	3.2×10^{-2}	9.01×10^{-3}
$Ni(CN)_4^{-2}$	1.4	0.216
$Zn(CN)_4^{-2}$	8.9	1.417
$Hg(CN)_4^{-2}$	1.8×10^{-4}	2.86×10^{-5}

Source: Hyatt 1976; cited in Murphy and Robertson 1979.

When metal ions are introduced into a solution containing a metallocyanide complex, a substitution reaction may occur wherein the complexed metal is replaced by the introduced ion. These reactions are favored if the stability or formation constant of the potential second complex is greater than that of the pre-existing complex. Broderius (1973) noted that, in natural waters, the displaced metal ion is precipitated as an insoluble cyanide, hydroxide, or carbonate.

5.0 TOXICITY OF CYANIDES

The highly toxic nature of cyanides in aquatic environments has been attributed to the presence of undissociated molecules of HCN (Doudoroff 1976). The disparity between HCN and CN-, in terms of toxicity, has been attributed to the difficulty experienced by ionic species in penetrating strongly charged membranes (Doudoroff 1976).

While the toxicity of cyanides has been largely attributed to HCN, Doudoroff (1976) notes that cyanide ion is most likely toxic in its own right. Broderius and Smith (1977) have demonstrated that the cyanide ion contributes to the total toxicity in proportion to its concentration. Ionic concentrations, however, are not expected to be substantial under pH conditions typical of natural waters.

Complex metal-cyanides are not, in and of themselves, particularly toxic. Rather, the toxicity of cyanide complexes is a function of the degree of compound dissociation to free cyanide. Stumm et al. (1954; cited in Doudoroff et al. 1966) noted that the relative toxicities of metal-cyanide complexes, in comparable solutions, increase with increasing stability of the complexes.

5.1 Mechanism of Toxicity

Cyanide may be taken into the body through inhalation, ingestion, or absorption. Once introduced, cyanide as HCN diffuses rapidly. Following penetration of semi-permeable membranes, HCN molecules will be distributed throughout the organism via the general circulation, bringing it to receptor sites where toxic action and/or detoxification occurs. While ionic barriers discriminate against cyanide ion penetration of membranes, once inside the organism it is the cyanide ion that constitutes the reactive agent.

Cyanide toxicity is primarily a result of inhibition of oxygen metabolism by the organism. Cyanide complexes with trivalent iron contained in mitochondrial cytochrome oxidase, thereby preventing oxidation and reduction reactions instrumental in electron transfer from reduced metabolites to molecular oxygen. This failure in tissue utilization of oxygen leads to histotoxic anoxia.

The severity of the outcome of cyanide exposure will depend upon the degree and rate of production of histotoxic anoxia. Towill et al. (1978) note that cytochrome oxidase is completely inhibited by 10^{-8} moles/cc of cyanide. Death, should it occur, results from depression of the central nervous system, the tissue most sensitive to anoxic conditions.

5.2 Toxicity to Invertebrates

The toxicity of cyanides to invertebrates is not well documented. A summary of the results from a number of acute toxicity studies may be found in EPA (1980) and AEC (1973). Most of the species tested exhibit greater tolerance to cyanide than fish species (discussed below). Additionally, a greater variability in sensitivity is seen for the invertebrates.

5.3 Toxicity to Fish

5.3.1 Acute Toxicity

The toxicity of cyanides to fish has been reviewed by Doudoroff (1976), Towill et al. (1978), and Doudoroff (1980). The intent of the discussion that follows is to summarize the important relationships outlined in these documents. For more detailed information, the reader is referred to these reviews.

A number of studies have been performed in which the acute toxicity of cyanides to fish has been assessed. The results of a majority of these have been summarized in EPA (1980) and AEC (1973).

5.3.1.1 Environmental Effects Upon Cyanide Toxicity. A variety of environmental factors, including dissolved oxygen levels, temperature, pH and dissolved minerals, influence the toxicity of cyanides in aquatic environments. Skidmore (1974) found an increase in cyanide toxicity of 140% following a reduction in dissolved oxygen concentration from 10 to 4 ppm. It was postulated that the increased toxicity resulted from higher gill ventilation rates, thereby exposing the organism to more of the poison. Juveniles of several fish species exhibited greater sensitivity to cyanide at dissolved oxygen levels below 5 ug/l (Smith et al. 1979).

Downing (1954) looked at the increase in survival time as a function of dissolved oxygen concentrations in the rainbow trout (Salmo gairdneri). Survival time increased in KCN concentrations between 0.105 and 0.155 ppm cyanide as dissolved oxygen concentrations were increased up to 100% of air saturation value. The effect was most profound at the lowest cyanide concentration.

Data bearing on the effect of temperature on cyanide toxicity have often been contradictory. While a number of studies have indicated an increase in cyanide sensitivity with declining temperatures, several studies have demonstrated just the opposite relation.

Juveniles of several species were found by Smith et al. (1979) to exhibit greater sensitivity to cyanide levels at reduced temperatures. One species, the fathead minnow Pimephales promelas, exhibited increased sensitivity at higher temperatures as well. Smith and Heath (1979) observed a five-fold rise in the 24 h LC50 of the goldfish (Carassius auratus) when water temperature was lowered from 15° to 5°C. A reduced effect was noted for the golden shiner (Notemegonus crysoleucus) while no change in sensitivity with temperature was seen for bluegill (Lepomis macrochirus), rainbow trout and channel catfish (Ictalurus punctatus). Adult mortality of brook trout occurred at the highest cyanide concentrations tested only when water temperature was reduced from 12° to 9°C (Koenst et al. 1977).

Cairns et al. (1975) cite a study by Wuhrman in which an increase in temperature from 5° to 20°C was found to reduce the survival time of trout, minnows and tench by 60%, 75%, and 65%, respectively. Cairns and Scheier

(1963) observed that the concentrations resulting in 100% mortality for bluegill, after 48, 72, and 96 h, were less at 30°C than at 18°C. In an assessment of cyanide as a fish poison, Bridges (1958) noted that lower temperatures extended the time required to kill several species of fish at cyanide concentrations of 1 ppm.

Doudoroff (1976) cited a study performed by the Department of Scientific and Industrial Research of Great Britian (1953) which showed differing effects of temperature on cyanide sensitivity, depending upon the concentration of the toxin. Young rainbow trout were exposed to cyanide concentration ranging from 0.125 to 1.0 mg/l as CN at each of three temperatures ranging from 12° to 22°C. At concentrations of 0.3 mg/l or more, fish died most rapidly at the highest temperature. Temperature had no apparent effect on survival at cyanide concentrations between 0.25 and 0.175 mg/l. Finally, at concentrations ranging from 0.15 to 0.125 mg/l, the trout tended to live longest at the highest temperature.

It is apparent that no clear relationship between temperature and cyanide sensitivity exists. Doudoroff (1976) notes that those studies finding cyanide sensitivity to be proportional to temperature have used relatively high cyanide concentrations, with those studies showing the opposite relation typically employing much lower cyanide concentrations. Cairns et al. (1978) reiterated this idea with the concept of "temperature crossovers."

Doudoroff (1976) speculates that the increase in sensitivity of rainbow trout to slowly lethal levels of cyanide at low temperatures results from a decrease in the rate of detoxification at reduced temperatures. Conversely, when cyanide concentrations are high, the detoxification mechanism is overwhelmed by the influx of cyanide, the rate of death being dependent upon rates of other vital processes within the organism.

The effect of pH on cyanide sensitivity in fish is dependent upon the hydrolytic equilibrium seen between cyanide ion and molecular hydrogen cyanide. Discussed above, this reaction is strongly pH-dependent, with HCN predominating below a pH of 9.0. Given the extremely toxic nature of this species, the increase in cyanide toxicity with decreasing pH is not surprising.

Wuhrmann and Woker found the time to loss of equilibrium by the chub (Squalius cephalus), in sodium cyanide solutions of the same strength, changed with changes in pH. Loss of equilibrium occurred later as pH was increased, up to a point where pH was considered harmful by itself (9.5). Bridges (1958) found the time required to kill largemouth bass (Micropterus salmoides) using NaCN increased from 35-55 min to 80 min in going from a pH of 7.0-7.3 to a pH of 8.9.

Smith et al. (1979) investigated the change in the 96 h LC50 of juvenile fathead minnows at constant temperature (20° C) and dissolved oxygen levels (approximately 7.5 mg/l) over a range of pH from 6.8 to 9.3. The LC50 was fairly constant up to a pH of 8.3 (Figure 1) and appeared to be principallly due to the presence of HCN. Above pH 8.3, the LC50, as HCN, declined while the LC50 as CN- rose. Here, the increasing importance of cyanide ion in determining cyanide toxicity is evident. Doudoroff (1956) showed that young of the same species could withstand more than 1000 times more cyanide combined with nickel ($NaCN-NiSO_4$) at pH 8.0 than at pH 6.5. Reduction of pH by about 3.0 pH unit could result in greater than a ten-fold increase in toxicity.

5.3.1.2 Organismal Properties and Their Effect on Cyanide Toxicity. The sensitivity of fish to cyanide has generally been found to vary with the stage of life-history of the organism (Doudoroff 1976). Smith et al. (1979) found, for a number of warm and coldwater species, that eggs were most tolerant to the acute toxicity of HCN. Newly-hatched fry and juveniles, similar in their sensitivity, were least tolerant. No effect on brook trout (Salvelinus fontinalis) embryo survival was noted for cyanide concentrations up to 77 ug/l, while reduced juvenile survival was seen at concentrations as low as 55 ug/l (Koenst et al. 1977). Kimball et al. (1978) found that bluegill fry survival was adversely affected at 15.6 to 19.4 ug/l HCN. Adult survival was not markedly affected until the start of spawning, at which time reduction in survival was noted at 20.5 ug/l HCN and above.

Doudoroff (1976) discussed the role of acclimation in cyanide tolerance. Malacea (1968; cited in Doudoroff 1976) showed increased resistance to cyanide (.5 mg/l as CN) with prior exposure to .1 mg/l for a period of two days.

Neil (1957; cited in Doudoroff 1976), however, found that the concentrations to which brook trout were acclimated had an effect on whether a degree of protection was conferred. Fish acclimated to .01 mg/l were more resistant than unacclimated controls when subjected to lethal cyanide concentrations. Fish acclimated to .03 or .05 mg/l wre less tolerant than controls when exposed to .30 mg/l, but more resistant when exposed to .40 or .50 mg/l. Finally, Brockway (1963; cited in Doudoroff 1976) found acclimation to .02, .06, and .10 mg/l as CN to increase tolerance of cichlids (*Cichlasoma bimaculatum*) to low cyanide concentrations but not to rapidly lethal levels.

The studies by Malacea and Neil suggest that prior exposure to low, sublethal levels of cyanide may confer a degree of resistance to lethal concentrations. Prior exposure to higher sublethal levels, however, may result in injury and a lower tolerance (Doudoroff 1976). The study by Brockway contradicts this interpretation.

Studies examining the effect of body size on sensitivity to cyanide have produced contradictory results. Work by Herbert and Merkens (1952; cited in Doudoroff 1976) and Herbert and Downing (1955; cited in Doudoroff 1976) found resistance to cyanide to decline with increasing body length. Anderson and Weber (1975) examined the response to KCN as a function of body mass in mature male guppies. The following empirical relationship was found:

$$LC50 = 0.147W^{0.72}$$

where LC50 is the 96 h median lethal concentration (mg/l CN) and W is the mass of a group of ten fish of a given size class (or the mass of an individual fish of average size multiplied by 10) in g.

From this function, it is evident that, on a mass-specific basis, cyanide toxicity is greater for smaller organisms. The exact nature of the relationship will depend on a number of parameters, including the entry route of dosage administration, and life stage and sex of the organism (Anderson and Weber 1975).

Contradicting these findings, Sumner and Doudoroff (1948; cited in Doudoroff 1976) observed no significant difference in resistance to KCN between small and large longjaw gobies (Gillichthys mirabilis). Wells (1916; cited in Doudoroff 1976) showed survival of rock bass (Ambloplites rupestris), exposed to 1.0 mg/l as CN, was inversely proportional to body mass. Survival periods of fish weighing 80 to 200 g were 2.3 times less than those seen for fish weighing 1.0 to 1.5 g.

5.3.2 Chronic Toxicity

Exposure to cyanide may result in a variety of sublethal effects, including changes in egg viability and hatchability, growth and development, and swimming ability, among others. Results of studies on these aspects are discussed below.

5.3.2.1 Reproduction. Leduc (1978) studied the effects of cyanide exposures, ranging from 0.01 to 0.10 mg/l (as HCN), on early life stages of the Atlantic salmon (Salmo salar). Length of incubation periods in experimental fish exceeded that seen in controls by 6 to 9 d at cyanide exposures of 0.08 and 0.10 mg/l HCN. Hatching success declined with increasing cyanide concentration. Hatching failures of 20 to 46% were seen from exposed fish, compared to 10% failure noted for controls. Those eggs that did hatch resulted in a large number of fry with gross, readily observable defects.

Koenst et al. (1977) reported on the effects of cyanide toxicity on reproduction in brook trout. Egg production was significantly ($p < .05$) less at cyanide concentrations above 5.7 ug/l, ranging from 56 to 100% less than control fish at concentrations of 11.2 to 75.3 ug/l. Viability of eggs was not statistically different than that seen in control fish for exposures from 5.7 to 53.9 ug/l. No fertile eggs were found at 64.9 and 75.3 ug/l.

Egg production in fathead minnows was significantly reduced upon exposure to HCN concentrations of 19.6 ug/l or more (Lind et al. 1977). The mean percentage hatch was significantly less at concentrations of 44.2 and 72.8 ug/l. The authors estimated that, based on egg production, the highest no-effect level of HCN for the test fish lies between 12.9 and 19.6 ug/l.

Experiments by Kimball et al. (1978) suggest an inhibition of spawning in bluegill at HCN concentrations of 5.2 ug/l or below, although a single female did spawn at 80.0 ug/l. Egg production of this lone female was four to nine times less than that seen for control groups. The no adverse effect level, based on reproductive aspects, was estimated at less than 5.2 ug/l.

5.3.2.2 Growth. Fathead minnows exposed as embryos to HCN concentrations ranging from 5.9 to 98.1 ug/l exhibited a range in body masses, from 130 to 65% of control fish masses at 56 d post-hatching (Lind et al. 1977). A trend of declining mean body mass with increasing HCN concentration was evident. By 84 d post-hatching, body masses were 128 to 86% of control mean body masses and no trend with HCN concentration was seen.

Lind et al. (1977) carried the analysis of growth response into the F1 generation. At 28 d post-hatching, those fish exposed to HCN concentrations of 34.8 ug/l or more were significantly shorter than controls. Fish exposed to 26.3 ug/l HCN were longer than control fish. By 56 d post-hatching, mean lengths and masses of fish exposed to 61.6, 70.5, 95.9, and 105.8 ug/l HCN were less than those of controls. All other exposure groups were indistinguishable from control fish.

Leduc (1978) found no noticeable differences in the length of Atlantic salmon fry at hatching, at HCN concentrations of 10 to 20 ug/l. Eggs exposed to 40 to 100 ug/l HCN resulted in fry approximately 10% shorter than unexposed fish. A similar trend was seen for mean dry weights of fry at hatching; those fish exposed to the greatest concentrations of HCN exhibiting masses about 40% less than controls. The differences in body length and mass were largely absent by 58 d post-hatching, presumably due to acceleration of growth in the experimental fish relative to controls.

Kovacs and Leduc (1982) noted reduced mean specific growth rates in rainbow trout during a 20 d exposure to HCN ranging in concentration from 0.005 to 0.045 mg/l. Depression of growth was prominent over the first 10 d, but was less pronounced thereafter due to an acceleration of growth rates in exposed fish. The change in growth rates at lower concentrations of HCN was attributed to a return to greater energy-releasing aerobic metabolism, following an initial stimulation of glycolysis upon exposure to HCN.

Brook trout fry, at the time of hatching, failed to exhibit differences in body length or mass, relative to controls, at HCN concentrations of 5.5 to 77.5 ug/l (Koenst et al. 1977). Juvenile body length was reduced at all exposures greater than 11 ug/l HCN. Body length was greater than that of controls at 5.6 ug/l HCN, while no difference was noted at 11 ug/l HCN. Reduced growth rates were maintained at concentrations of 33 ug/l HCN or more throughout a 90 d experiment. Adult trout did not show reduced growth relative to controls.

5.3.2.3 Swimming Ability. The effects of cyanide on swimming ability of fish is immediate and apparently long-lasting. Neil (1957) and Broderius (1970; both cited in Leduc et al. 1982) showed that maximum inhibition was reached within 24 hrs of exposure and that full recovery of chronically exposed salmonids was not complete 15 to 20 days after removal from cyanide-containing water.

In one study, rainbow trout previously exposed for 21 d to a free cyanide level of 0.02 mg/l showed a 75% reduction in duration of swimming against a current of 47 cm/sec, compared to controls (Speyer 1975; cited in Doudoroff 1980). Doudoroff (1976) showed similar results at even lower concentrations (0.01 mg/l) of cyanide.

Kovacs (1979; cited in Doudoroff 1980) showed the effect on swimming ability increased markedly with decreasing temperature (over a range from 18° to 6°C). At low temperatures a pronounced adverse effect on swimming ability was demonstrated at HCN levels as low as 0.005 mg/l.

5.3.3 Interaction of Cyanides with Metals and Other Toxins

In most polluted systems, effluents are typically comprised of a number of toxic substances. The potential interactions of these substances must be understood to accurately project detrimental effects on the system of interest.

Anderson and D'Apollonia (1978) have described the mechanisms of interaction between toxins. Simplistically, two toxins whose combined toxicity is merely the sum of their individual toxicities may be termed additive. The substances are said to act synergistically or supra-additively if the combined toxicity exceeds that predicted due to simple addition of individual effects. Finally, toxins which combine to produce an effect less than that seen due to simple addition are labeled antagonistic.

5.3.3.1 Cyanides and Non-metal Toxins. Broderius and Smith (1979) studied the interaction between HCN and ammonia and the consequent toxicity to the fathead minnow and rainbow trout. The compounds were found to interact synergistically, yielding a toxic effect 1.2 times that predicted based on addition of individual toxicities.

5.3.3.2 Toxicity of Complex Cyanides. A number of studies have examined the relative toxicity of free cyanides and metal-cyanide complexes. Broderius and Smith (1979) compared the toxicities of chromium cyanide (HCN-CrIV) and zinc cyanide (HCN-Zn) mixtures with the toxicities predicted through summation of individual component toxicities. HCN-Zn mixtures were found to be 1.4 times more toxic to fathead minnows than predicted. In contrast to this supra-additive effect, free cyanide and chromium acted antagonistically when combined. The HCN-Cr mixture was 76% as toxic as predicted.

Doudoroff (1956) looked at the relative toxicities of NaCN, and cyanide complexes of zinc, cadmium, nickel, copper, and iron, using the fathead minnow as a test organism. The toxicities of solutions of NaCN and zinc sulfate, and NaCN and cadmium sulfate were both more toxic to fish than a simple NaCN solution. Zinc-cyanide complexes resulted in 24 h, 48 h, and 96 h LC50s ranging from 78 to 80% of the corresponding values for uncomplexed cyanide. The LC50 values for cadmium-cyanide complexes were 74 to 92% of those for NaCN alone. The increase in toxicity of either complex could not be attributed solely to the presence of the heavy metal (Doudoroff 1956).

Free cyanide combined readily with nickel ions over a wide range of concentrations of the two substances. The result was a formation of fairly stable complexes, having the effect of reducing the toxicity of the cyanide and nickel alike. This reduction in toxicity, achieved under alkaline conditions, failed to persist at lower pH. Dissociation of nickelocyanide ions rose dramatically as pH declined from 8.0 to 6.5, such that 1.0 ppm cyanide (as CN-), combined with nickel at pH 6.5, was more toxic than 1,000 ppm cyanide (as CN-) at pH 8.0. The toxicity of nickel-cyanide complexes at pH 6.5, well within the range of pH for natural, unpolluted waters, was similar to that of free cyanide alone.

Complexation of cyanide with copper sulfate resulted in a drastic reduction in toxicity of free ionic copper. In ordinary soft experimental water, copper sulfate equivalent to 0.1 ppm copper killed all fish within 24 h whereas 0.8 ppm copper, combined with 1.0 ppm cyanide (as CN-) resulted in no deaths over a 96 h period. This antagonism was absent in extremely soft, aerated water and the solution was toxic. This change in toxicity was considered to be due to release of copper ions (Doudoroff 1956).

Mixtures of NaCN and iron sulfate proved fatal to fish at all concentrations, whereas the addition of pure potassium ferrocyanide, equivalent to 10 ppm cyanide (as CN-), to experimental water killed no fish in 48 h. These seemingly spurious results were considered the outcome of little, if any, combination of cyanide and ferrous ions in the original mixture (Doudoroff 1956).

Doudoroff (1956) also briefly examined the toxicities of mixtures of NaCN and paired heavy-metal sulfates. In one experiment, nickel sulfate was added to a mixture of NaCN and zinc sulfate for total concentrations of 1.0 ppm cyanide (as CN-), 0.6 ppm zinc and 0.13 nickel. The solution killed all fish within 16 h in each of two tests. In a similar experiment, nickel sulfate was added to a NaCN-$CuSO_4$ mixture, again failing to reduce the latter solution's toxicity.

In contrast, the addition of NaCN to experimental waters containing zinc and copper sulfates effected a dramatic reduction in metal toxicity. Solutions containing 0.025 ppm copper and 1.0 ppm zinc killed all fish within 14 h. Addition of 0.05 ppm cyanide (as CN-) permitted survival of all fish for 96 h. Similar results were found with solution concentrations of 1.0 ppm zinc, 0.25 ppm copper and 0.33 ppm cyanide (as CN-).

Doudoroff et al. (1966) found evidence of heavy-metal poisoning in bluegill exposed to silver-cyanide complexes. Fish placed in a silver containing solution of pH 7.5, in which HCN concentration was barely measurable, did not live appreciably longer than fish exposed to a solution (pH 6.5) with an HCN concentration of about 0.12 mg/l. It was postulated that the silver complex ion, Ag(CN), may have caused or contributed to the toxicity of one or both solutions.

Burdick and Lipschuetz (1950) conducted a number of experiments on the toxicity of ferro- and ferricyanide solutions to emerald shiners (*Notropis atherinoides*), blacknose dace (*Rhinichthys atratulus*), creek chub (*Semotilus atromaculatus*) and a minnow (*Hybognathus regius*). The initial complex concentrations, the consequent cyanide ion concentrations, and the toxic effects are listed in Table 4-1 for the low complex concentrations tested.

5.4 Toxicity to Higher Vertebrates

Towill et al. (1978) reviewed the literature on toxicology of cyanide to higher vertebrates. Most studies have been of the effects on livestock of feeding on varous wild vegetation containing cyanogenic glycosides. Chronic effects include induced sulfur deficiency and thyroid disfunction. The latter has also been noted in certain human populations eating similar vegetation.

Acute toxicity in humans has been associated primarily with inhalation. Inhalation of 270 ppm HCN vapor brings death immediately, while 135 ppm is fatal after 30 minutes (Fassett 1963; cited in Towill et al. 1978). Inhalation exposure to cyanogen (CN_3) is likely because it is a gas at room temperature. However, the lethal dose of CN_3 to rats is greater than for HCN. Cyanogen is also an irritant causing eye and nasal inflammation at concentrations as low as 16 ppm.

Halogenated cyanogens such as cyanogen chloride or cyanogen bromide are comparable in toxicity to HCN when inhaled, causing marked irritation of the respiratory system with hemmorrage and pulmanary edema (Fassett, 1963 and Prentiss, 1937; cited in Towill et al. 1978).

TABLE 4-1. TOXICITY OF FERRO- AND FERRICYANIDE SOLUTIONS (table reproduced from Burdick and Lipscheutz 1950)

Salt and concentration	Species	CN- (p.p.m.)	Preliminary exposure	Results
Ferrocyanide (1 p.p.m.)	R.[1] atratulus S.[2] atromaculatus	.05-.16	Variable	No effect to 5 hours
Ferrocyanide (2 p.p.m.)	R. atratulus S. atromaculatus H.[3] regius	.365-.48	½ to 1½ hrs	Dead, from 1 to 1½ hours
Ferrocyanide (3 p.p.m.)	S. atromaculatus	.72	½ hour	Dead, 25 minutes
Ferrocyanide (5 p.p.m.)	R. atratulus S. atromaculatus H. regius	.5-.84	None to 3 hours	All fish died--Time variable
Ferricyanide (1 p.p.m.)	R. atratulus S. atromaculatus	?-.205	Variable	Lethal only once. CN- not determined.
Ferricyanide (2 p.p.m.)	S. atromaculatus N.[4] atherinoides	.36-.48	½ to 1½ hrs	Dead, from 13-38 minutes
Ferricyanide (3 p.p.m.)	S. atromaculatus	.64	½ hour	Dead, 2½ hours
Ferricyanide (5 p.p.m.)	R. atratulus	1.0	3 hours	Dead, 47 minutes

[1] Rhinichthys
[2] Semotilus
[3] Hybognathus
[4] Notropis

HCN in either liquid or vapor form is absorbed through the skin. Absorption is probably increased if the skin is cut, abraided, or moist. Potter (1950; cited in Towill et al. 1978) described the case of a worker whose hand was exposed to liquid HCN. The worker was wearing a respirator. He collapsed into deep unconsciousness within 5 min., suggesting significant percutaneous absorption.

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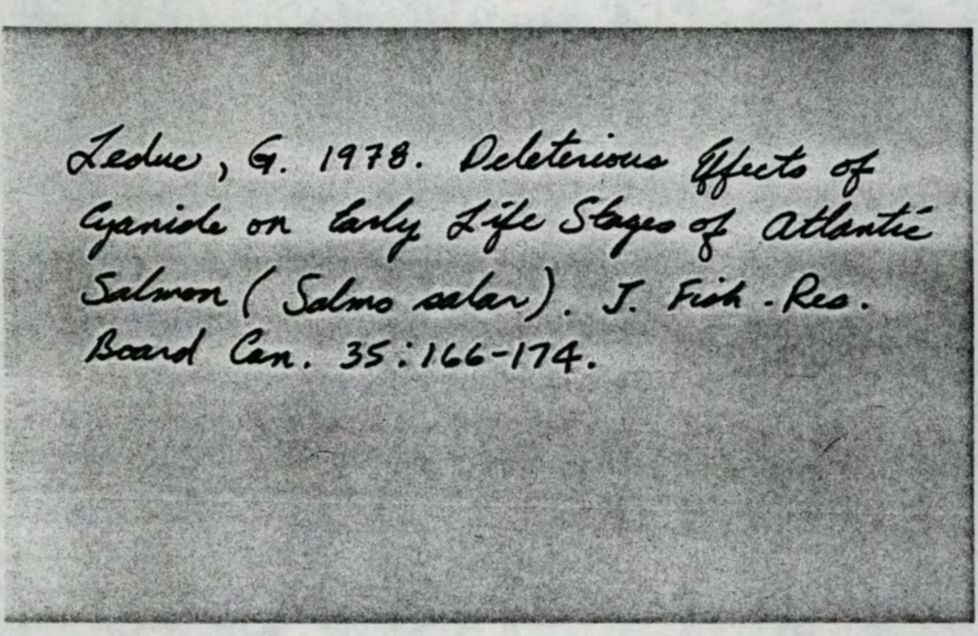

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