
CHAPTER 39

SODIUM CYANIDE: PROPERTIES, TOXICITY, USES AND ENVIRONMENTAL IMPACTS

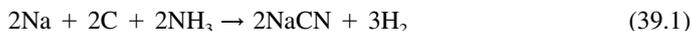
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39.1 PROPERTIES

Sodium cyanide (CAS No. 143-33-9) was first produced in 1834 by F. and E. Rogers, who heated Prussian blue (highly colored mixed oxidation state $\text{Fe}^{\text{II/III}}$ derivatives) and sodium carbonate together (King, 1994). The mixture was cooled and sodium cyanide was extracted with alcohol. The compound had no intended purpose until J. S. MacArthur and the Forrest brothers patented a process for extracting gold and silver from ores in 1887 (*Kirk-Othmer*, 1979a).

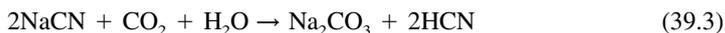
By 1899, half the cyanide manufactured in Europe was produced by the Beilby process. From 1900 to 1961, another process, called the Castner process, was used to make sodium cyanide. The Castner process is shown below:



Today, a process based on the neutralization of sodium hydroxide (aqueous) and hydrogen cyanide (gas) is the preferred method, as shown below (*Kirk-Othmer*, 1993):

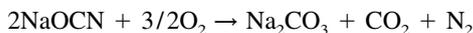
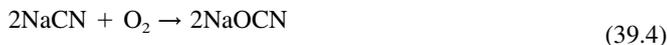


A few chemical reactions that occur with sodium cyanide should be mentioned. In moist air, carbon dioxide (CO_2) slowly decomposes sodium cyanide to hydrogen cyanide according to this reaction:

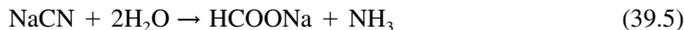


The carbonate salt produced becomes a brownish color due to the formation of polymerization products of HCN (*Ullmann's*, 1987).

At elevated temperatures, oxygen reacts with sodium cyanide to yield nitrogen, carbonate, and carbon dioxide according to the two-step reaction (*Ullmann's*, 1987):



When sodium cyanide is either stored for a long time or heated, there is a slow hydrolysis of the C≡N bond as per the equation (*Ullmann's*, 1987):



Some basic physical properties of sodium cyanide are shown in Table 39.1. It should be noted that sodium cyanide has only a faint odor and is not detectable at concentrations that would provide a margin of safety. Sodium cyanide also sinks and is quite soluble in water—480,000 ppm at a temperature of 10°C. There are two different hydrates of sodium cyanide: the more common NaCN·2H₂O (below 35°C) and NaCN·½ H₂O (>35°C) (*Environment Canada*, 1984; *Ullmann's*, 1987).

39.2 TOXICITY

It is estimated that the average lethal dose (LD₅₀) of sodium cyanide for humans is 2.86 mg/kg (Corn, 1993). Cyanide, originating by disassociation of sodium cyanide, complexes with the ferric iron ion (3+) in metalloenzymes, resulting in anoxia through inhibition of cytochrome oxidase, which inhibits cellular oxygenation. The enzyme becomes unable to catalyze the reactions in which electrons would be transferred from reduced cytochrome to oxygen. Thus, cellular oxygen utilization is impaired. The inhibition of oxygen causes oxygen hunger to rise in peripheral tissues. Thus, oxyhemoglobin is carried in the venous blood (TPF, 1997). This causes the pink or red discoloration of the skin that is seen in cyanide poisoning, which is the oxyhemoglobin entering the skin to provide the necessary oxygen.

Not all the cyanide that is absorbed by the body undergoes oxygen inhibition. It is known that 80% of the absorbed cyanide is detoxified in the liver by the enzyme mitochondrial rhodanase. The enzyme catalyzes the transfer of a sulfur atom to combine with the cyanide to form the less toxic thiocyanate, which is excreted in the urine. In high exposures to cyanide, the sulfur donors are rapidly depleted and cyanide metabolism is slowed (Pope and Rall, 1995). The half-life for the conversion of cyanide to thiocyanate from a nonlethal dose in humans is between 20 and 60 minutes (CHEM-BANK, 1999).

Other pathways to elimination of cyanide are possible. About 1 to 2% of cyanide is lost through the lungs by exhalation. Another 15% is released by conversion to 2-aminothiazaline-4-carboxylic acid, incorporation into the one-carbon metabolic pool, or the combination with hydroxycobalamin (vitamin B_{12a}) to form cyanocobalamin (Pope and Rall, 1995).

In normal, healthy human organs, cyanide is present at concentrations ranging up to 0.5 mg/kg (CHEM-BANK, 1999) and the relative proportion of thiocyanate to cyanide in body fluids is about 1,000:1. Normal plasma thiocyanate levels are 0.01 mg/mL for both smokers and non-smokers. Lethal values of thiocyanates range from 0.05 to 0.2 mg/mL (Pope and Rall, 1995). Smokers are included in the data because heavy smoking increases the urinary concentrations of thiocyanate levels and can be misleading for cyanide exposure (Corn, 1993).

Sodium cyanide is known to be very toxic to humans. Some human toxicity data are shown in Table 39.3. To put the data into perspective, for oral—human LD_{Lo} 2.857 mg/kg, a human of 70 kg (154 lbs) would only have to ingest 0.2 g (200 mg) in order to be in the range of a lethal dose. The data in Table 39.3 demonstrate that even small amounts of sodium cyanide can cause harm to the human body.

Other data from the testing of sodium cyanide on animal species also show that sodium cyanide is very toxic. For example, as shown in Table 39.4, a small dose of 0.0085 g of sodium cyanide per kilogram administered to quail has killed half of the test animals.

TABLE 39.1 Physical Properties of Sodium Cyanide

Properties	Sodium cyanide
Appearance	White, granular or crystalline solid (<i>NIOSH Pocket Guide to Chemical Hazards</i>)
Odor	Faint almond-like odor (<i>NIOSH Pocket Guide to Chemical Hazards</i>)
Odor threshold	0.2 to 5 ppm (as HCN), poor warning properties, not detectable at concentrations providing a margin of safety (MSDS Database A and B)
Reaction with water	Sinks and mixes with water (CHRIS Database)
Molecular weight	49.015
Melting point	561.7°C (98 wt%), 562°C (<i>Kirk-Othmer</i> , 1993), 560°C (CHEMtox, 1999)
Boiling point	1500 ± 10°C, 1530°C (<i>Kirk-Othmer</i> , 1993), 1499.9°C (CHEMtox Database, 1999)
Density of solid	1.620 g/cm ³ (6°C, rhombic)
Density of solid	1.595 g/cm ³ (20°C, cubic), 1.60 (<i>Kirk-Othmer</i> , 1993)
Density of solid	1.19 g/cm ³ (850°C, fused)
Density of 10% (w/v) aqueous solution	1.047 g/mL (25°C) (<i>Kirk-Othmer</i> , 1993)
Density of 20% (w/v) aqueous solution	1.098 g/mL (25°C) (<i>Kirk-Othmer</i> , 1993)
Density of 30% (w/v) aqueous solution	1.150 g/mL (25°C) (<i>Kirk-Othmer</i> , 1993)
Viscosity	4 cP (30°C) (26% aqueous solution)
Biological oxygen demand (BOD)	(theoretical) 6%, 7 days (CHRIS Database)
Bioaccumulation and tainting	No evidence to support any rating (CHRIS Database)
Specific heat capacity (Cp)	1.667 kJ/kg · K (0.1°C)
Specific heat capacity (Cp)	31.630 kJ/kg · K (15.5°C)
Specific heat capacity (Cp)	1.402 kJ/kg · K (25.6°C)
Enthalpy at 25°C (H)	-89.9 kJ/mol
Heat of fusion	314 kJ/kg
Heat of formation	-89.9 kJ/mol (<i>Kirk-Othmer</i> , 1993)
Heat of vaporization (ΔH_v)	3185 kJ/kg, 3041 kJ/kg (<i>Kirk-Othmer</i> , 1979b), 3190 kJ/kg (Hazardous Substances Data Bank)
Heat of solution (ΔH_{soln})	-1.548 kJ/mol (<i>Kirk-Othmer</i> , 1993), 1.51 kJ/mol (Hazardous Substances Data Bank)
Hydrolysis constant, K_h at 25°C	0.0000251 (<i>Kirk-Othmer</i> , 1993)
Vapor pressure (P_v) at 800°C	0.1 kPa, 0.1013 kPa (<i>Kirk-Othmer</i> , 1993)
Vapor pressure (P_v) at 1,000°C	1.65 kPa
Vapor pressure (P_v) at 1,200°C	11.98 kPa
Vapor pressure (P_v) at 1,350°C	39.10 kPa
Vapor pressure (P_v) at 1,360°C	41.8 kPa (<i>Kirk-Othmer</i> , 1993)
Index of refraction	1.452
Solubility (10°C)	480,000 ppm
Solubility (35°C)	820,000 ppm
Solubility of NaCN · 2H ₂ O per 100 g of saturated solution	26.01 (-15°C) (<i>Kirk-Othmer</i> , 1993)
Solubility of NaCN · 2H ₂ O per 100 g of saturated solution	32.8 (10°C) (<i>Kirk-Othmer</i> , 1993)
Solubility of NaCN · 2H ₂ O per 100 g of saturated solution	34.2 (15°C) (<i>Kirk-Othmer</i> , 1993)
Solubility of NaCN · 2H ₂ O per 100 g of saturated solution	45 (34.7°C) (<i>Kirk-Othmer</i> , 1993)
Solubility in 100 g of ethanol (100%)	1.235 g (25°C)
Solubility in 100 g of ethanol (95%)	2.445 g (25°C)
Solubility in 100 g of anhydrous methanol	6.44 g (15°C)
Solubility in 100 g of anhydrous methanol	4.58 g (25°C)
Solubility in 100 g of anhydrous methanol	4.10 g (67.4°C)
Solubility in 100 g of NH ₃ , liquid	58 g (-31°C)

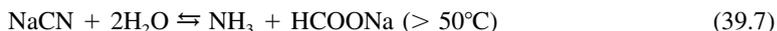
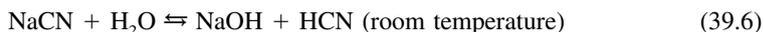
Source: *Kirk-Othmer*, 1979a; *Ullmann's*, 1987; CHEM-BANK, 1999.

TABLE 39.2 Blood Cyanide Effects

Whole blood cyanide level concentrations (mg/mL)	Effect on body
Less than 0.0002	No symptoms of toxicity
0.0004 (in smokers)	No symptoms of toxicity
0.0005 to 0.001	Untreated patients may be conscious, flushed, and tachycardic
0.001 to 0.0025	Stupor and agitation
Greater than 0.0025	Coma and potentially fatal without treatment

Source: Pope and Rall, 1995.

When sodium cyanide mixes with water and comes in contact with aquatic species, the results are also detrimental to the health of the species. When mixed with water, sodium cyanide can undergo two possible reactions (*Kirk-Othmer*, 1993).



As in the case of most accidental spills, Eq. (39.6) would be the reaction since the water is generally not above 50°C. Thus, a spill of sodium cyanide in water would form hydrocyanic acid and sodium hydroxide.

In water, the pH is affected by how much sodium cyanide is added. The concentration of sodium cyanide added correlated to the pH of the water is shown in Table 39.5. The aqueous solutions are strongly alkaline. At pH 9.4, in an aqueous solution of sodium cyanide, half of the total cyanide is present as hydrogen cyanide as in Eq. (39.6) (*Ullmann's*, 1987).

The toxicity of sodium cyanide on freshwater aquatic life is shown in Table 39.6. Sodium cyanide is detrimental to aquatic life because of the dual toxicity effect of an acid and a base impacting the environment. A range of tolerance is shown in the table. For example, bluegill at 96 hours TL_m is 0.15 mg/kg, whereas oligochaete at 96 hours LC₅₀ is 11 mg/L. Thus, it takes 73 times more sodium cyanide to kill half the oligochaete than it takes to kill half of the bluegill.

It should also be noted that cyanide toxicity to fish increases with any reduction in dissolved oxygen below 100%. The presence of zinc and ammonia results in a greater than additive increase in toxicity (Moran, 1998). Fish are about 1000 times more sensitive to cyanide than are humans. Even if the levels are less than lethal, there are still toxic effects, including physiological and pathological responses. For example, cyanide can reduce swimming ability, which will leave fish more vulnerable to predators, or interfere with reproductive capacity, which can lead to deformed offspring. It should be noted that cyanide toxicity in fish increases three-fold with a 12°C decrease in temperature. As well, 17 parts per thousand (ppt) of chloride ion or 8.8 ppt (Moran, 1998) is known to decrease the survival time (UNEP/OCHA, 2000).

TABLE 39.3 Human Toxicity Data

Oral—man LD _{Lo} 6.557 mg/kg (gastrointestinal, gastritis)
Oral—human LD _{Lo} 2.857 mg/kg
Unreported—human LD _{Lo} 2.206 mg/kg
Oral—man TD _{Lo} 0.714 mg/kg (hallucinations, distorted perceptions, muscle weakness)

Source: CHEMtox Database, 1999; RTECS Database.

TABLE 39.4 Animal Toxicity

Oral—rat LD ₅₀ 6.44 mg/kg
Intraperitoneal—rat LD ₅₀ 4.3 mg/kg
Oral—quail LD ₅₀ 8.5 mg/kg
Oral—wild bird species LD ₅₀ 4 mg/kg

Source: CHEMtox Database, 1999; RTECS Database.

There is some saltwater toxicity data as well, although it is not as extensive as freshwater data. This is shown in Table 39.7.

39.3 CATEGORIZATIONS AND GUIDELINES

A compilation of classifications, guidelines, and legislative limits is given in Table 39.8. The information from Transport of Dangerous Goods (TDG) states that sodium cyanide is a poison. Other references, such as the National Fire Protection Association (NFPA) and the Hazardous Materials Identification System (HMIS), identify sodium cyanide as a serious health hazard. The classifications suggest that it is not a flammability hazard and is not very reactive (stable). Also note that the drinking water standards have been set at 0.2 mg/L for safe drinking water. At a sodium cyanide level of 0.2 mg/L, not all of the fish are safe. Note that at this concentration, from Table 39.6, half of the bluegill will die after 48 hours and half of the rainbow trout after 144 hours.

39.4 INDUSTRIAL USES

During the 1950s, almost all sodium cyanide was used in case hardening and electroplating. Today, case hardening is a minor use, while electroplating or metal plating, gold and silver extraction, and chemical synthesis are major applications of sodium cyanide (*Kirk-Othmer*, 1979a).

Figure 39.1 shows a comparison of how much sodium cyanide is consumed in these processes relative to the other major uses from 1976 to 1997. It can be seen that gold cyanidation is the most prominent process. A description of the different processes will follow.

TABLE 39.5 pH of Sodium Cyanide

Concentration of sodium cyanide (mol/L)	Concentration of sodium cyanide (ppm)	pH
1	49,015	11.64
0.1	4,902	11.15
0.01	490	10.67
0.001	49	10.15
0.0001	4.9	9.6
0.00001	0.5	8.9

Source: Ullmann's, 1987.

TABLE 39.6 Freshwater Toxicity of Sodium Cyanide

Species	Concentration (mg/kg)	Exposure (hours)	Effect
Apple snail	1.6–2.9 (mg/L)	96	LC ₅₀
Fathead minnow	0.25	24	TLm
Fathead minnow	0.24	48	TLm
Fathead minnow	0.23	96	TLm
Yellow perch	0.0758–0.337 (mg/L)	96	LC ₅₀
Bluegill	5	2	Killed
Bluegill	0.1959 (mg/L)	3.36	LT ₅₀
Bluegill	0.16	48	LC ₅₀
Bluegill	0.16 (mg/L)	72	LC ₅₀
Bluegill	0.15	96	TLm
Eurasian water milfoil	22.4 (as CN)		IL ₅₀ , root weight
Eurasian water milfoil	28.6 (as CN)		IL ₅₀ , root length
Eurasian water milfoil	20 (as CN)		IL ₅₀ , stem weight
Eurasian water milfoil	27.3 (as CN)		IL ₅₀ , stem length
Archiannelid	8.9–11 (mg/L)	24	LC ₅₀
Archiannelid	7.1–9.5 (mg/L)	48	LC ₅₀
Archiannelid	6.7–8.5 (mg/L)	72	LC ₅₀
Archiannelid	5.9–7.6 (mg/L)	96	LC ₅₀
River snail	940 (mg/L)	24	LC ₅₀
River snail	760 (mg/L)	48	LC ₅₀
Water flea	<3.4		Immobilized
Water flea	0.09–0.3 (mg/L)	96	LC ₅₀
Water flea	0.02–0.05 (mg/L)	120	LOEC REP
<i>Polycelis nigra</i>	30		Threshold concentration
Trout	0.08		Nontoxic
Trout	2	1	100% mortality
Trout	0.05	124	100% mortality
Oligochaete	11 (mg/L)	96	LC ₅₀
Pond snail	3.3 (mg/L)	24	LC ₅₀
Pond snail	3.3 (mg/L)	48	LC ₅₀
Pond snail	2.4–2.5 (mg/L)	96	LC ₅₀
Fish (<i>Labeo bata</i>)	0.4–1.9 (mg/L)	96	LC ₅₀
Rohu	0.3–1.9 (mg/L)	96	LC ₅₀
Catla	0.5–1.7 (mg/L)	96	LC ₅₀
Cyclopoid copepod	0.1–0.3 (mg/L)	96	LC ₅₀
Calanoid copepod	0.1–0.3 (mg/L)	96	LC ₅₀
Scud	0.9 (mg/L)	96	LC ₅₀
Rainbow trout	0.05–0.09 (mg/L)	96	LC ₅₀
Rainbow trout	0.098 (mg/L)	144	LC ₅₀
Minnows	0.4	1	Stopped eating
Minnows	0.33–0.35	2.5	Lethal
Minnows	0.5 to 0.7	24	25% mortality
Minnows	0.75	24	50% mortality
Minnows	0.8	24	100% mortality

TABLE 39.6 Freshwater Toxicity of Sodium Cyanide (*Continued*)

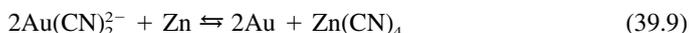
Species	Concentration (mg/kg)	Exposure (hours)	Effect
Pouch snail	2.4 (mg/L)	24	LC ₅₀
Pouch snail	135 (mg/L)	48	LC ₅₀
Stickleback	2		Lethal
Hardy carp	4.3		Paralyzed
Shiner	10	0.06	Killed
Shiner	2	0.2	Killed
Snail	2.9 (mg/L)	96	LC ₅₀
Carp, hawk fish	0.37 (mg/L)	96	LC ₅₀
Trout fingerlings	0.02		No effect
Gold and green sunfish	0.5	4 to 6	Lethal
Sea lamprey	5.0	2	Ill, but survived

Source: Sax, 1989; Aquire Database, 1994.

Cyanidation is a chemical process used to recover gold and other metals that are very finely distributed in the ore, or gold that is complexed with sulfides. The ore or tailings are added to a cyanide solution (0.2 to 0.05%), which is aerated to provide oxygen to dissolve the gold as Na[Au(CN)₂]. A typical concentration of cyanide usage is 1 to 2.5 kg NaCN per metric ton of ore (*Kirk-Othmer*, 1995b), or 0.25 to 1.0 kg (Ingles and Scott, 1987). This is known as the MacArthur process and is shown in the following equation:



The solution is then treated and clarified and the gold is precipitated by the addition of zinc dust according to the following reaction (Clayton and Clayton, 1991; CIS, 1998; *Kirk-Othmer*, 1980):



Sodium cyanide is used in the extraction of gold and silver from ores because of the very stable linear cyano complexes formed with these metals. The molecular bonding for silver cyano complexes is drawn as [:N≡C—Ag—C≡N:]⁻ and similarly for gold complexes [:N≡C—Au—C≡N:]⁻ (King, 1994).

Sodium cyanide is also used in the electroplating industry. Cadmium is usually plated from cyanide solutions from a still plating process (90 to 120 g/L NaCN), or barrel plating

TABLE 39.7 Saltwater Toxicity of Sodium Cyanide

Species	Concentration (mg/kg)	Exposure (hours)	Effect
Aquatic sowbug	1.7 (mg/L)	96	LC ₅₀
Prawn	0.25	48	LC ₅₀
Cockle	>25	48	LC ₅₀
Three-spine stickleback	0.2254 (mg/L)	3.36	LC ₅₀
Three-spine stickleback	0.1312 (mg/L)	13.68	LC ₅₀
Crab	75	48	LC ₅₀

Source: Sax, 1989; Aquire Database, 1994.

TABLE 39.8 Legislative Limits and Classifications

Topic	Limit
TDG classification	6.1, 9.2 (9.2 applies if regulated limit is exceeded) Regulated Limit (Schedule XII) S4, UN1689 Regulated Limit (Schedule XIII) 0.5 kg UN1689 (CCOHS, 2000e)
Packing group	I
Emergency response assistance planning requirements of Sections 7.16 to 7.19 of TDG	For quantities exceeding 1,000 kg or L net per consignment
Consumer commodity	Prohibited
Limited quantity	Prohibited
Passenger road/railway vehicles	Maximum net quantity per package is 5 kg
Standard industry trade classification	52381 (CHRIS Database)
Stability during transport	Stable (CHRIS Database)
RCRA hazardous waste	No. P106 (<i>Genium's</i> , 1999)
Fire diamond (NFPA hazard rating)	3 health hazard (extreme danger) 0 Flammability (will not burn) 0 Reactivity (stable and not reactive with water) (<i>Genium's</i> , 1999)
The Hazardous Materials Identification System (HMIS)	H 3 (serious health hazard) F 1 (slight flammability hazard) R 1 (slight reactivity hazard) (<i>Genium's</i> , 1999)
Wilson's Risk Scale of Material Hazards (RISK)	R 1 (reactivity: stable at room temperature; may be unstable at elevated temperatures) I 2 [inhalation: TLV 101 to 500 ppm (vapor) or 1.1 to 10 mg/m ³ (solid)] S 3 (skin contact: severe irritation; tissue corrosion within short time period) K 0 (kindling: will not burn) (<i>Genium's</i> , 1999)
Workplace Hazardous Materials Information System (WHMIS)	D1A (very toxic material) D2B (other toxic effects that are not immediate and serious) E (corrosive) (<i>Chemical Advisor</i>)
IDLH	25 mg/m ³ (as CN)
TLV-TWA (ceiling exposure limit)	4.7 ppm to 10 minutes (as CN) skin designation
NIOSH recommendations	4.7 ppm (hydrogen cyanide and cyanide salts)
Federal drinking water guidelines	0.2 mg/L (cyanide ion)

Source: CHRIS Database.

(70 to 90 g/L NaCN). Because cadmium is very harmful to the environment, the use of plating with cadmium is declining (*Kirk-Othmer*, 1979b).

Reactions that are of commercial importance in electroplating require sodium cyanide. In the reaction shown in the following equations, silver is dissolved by sodium cyanide solutions as the anode,



or in the presence of oxygen to form $\text{NaAg}(\text{CN})_2$ (*Kirk-Othmer*, 1984):

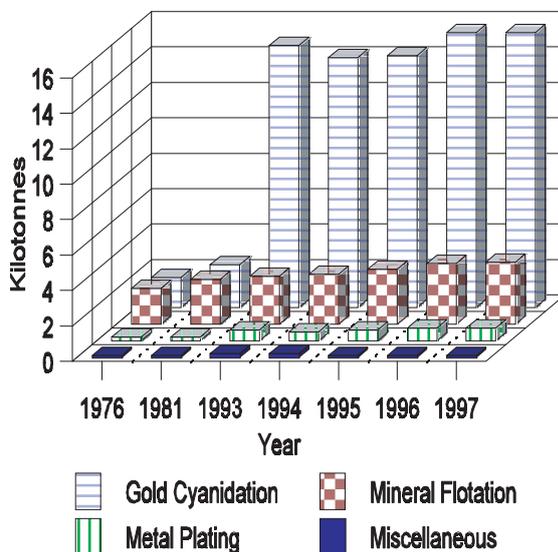


FIGURE 39.1 Uses of sodium cyanide—1976–1997. (Source: CIS, 1998.)



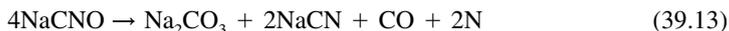
Brass is plated not only for decorative purposes but also to ensure a good adhesion of rubber to steel wire, which is used in tires. An example of such a plating bath uses a concentration of sodium cyanide at 90 g/L for a 70/30 brass plating. For white brass plating, the amount of sodium cyanide is 52 to 60 g/L (*Kirk-Othmer*, 1979b). In the late 1980s, cyanides were largely removed from plating baths due to the environmental hazards of using them. Since 1995, cyanide-containing cleaners are rare and are used only for special purposes.

Sodium cyanide is also used as a depressant in the mining industry. A depressant is a reagent that selectively prevents the reaction between a collector and a mineral. In other words, a depressant prevents the mineral from flotation. The use of sodium cyanide, in this case, is to selectively depress sphalerite (zinc sulfide) and pyrite (iron sulfide) but not galena. Sodium cyanide therefore enhances flotation of galena (*Kirk-Othmer*, 1995b).

In the process known as cyaniding, carbon and alloy steels are combined at high temperatures in a liquid bath from which they absorb both carbon and nitrogen simultaneously. The purpose of the nascent nitrogen is to increase the metal's surface hardness. The typical composition of the liquid bath is 30% sodium chloride, 40% sodium carbonate, and 30% sodium cyanide. The sodium cyanide concentration may range from 97 to 45%. The following are equations for producing nitrogen and carbon.



The sodium cyanate created breaks down to form nascent nitrogen:



The carbon monoxide (CO) produces carbon dioxide:



The carbon dioxide reacts with sodium cyanide:

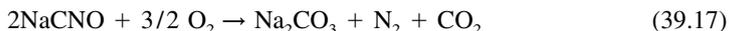


The carbon monoxide (CO) further reacts to produce more carbon (C).

The following three reactions lead to the decomposition of the sodium cyanate (NaCNO) (*Kirk-Othmer*, 1981):

1. $\text{NaCNO} + \text{C} \rightarrow \text{NaCN} + \text{CO}$
2. $4\text{NaCNO} + 4\text{CO}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + 2\text{CO} + 4\text{N} + 2\text{C}$
3. $4\text{NaCNO} + 4\text{CO}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + 6\text{CO} + 4\text{N}$

Sodium cyanide is used for case hardening of steels. Trace amounts of iron or nickel oxide are used to cause a rapid oxidation of the cyanide in air, first to the cyanate, then to carbonate, by the following reactions:



Case hardening of steel using a sodium cyanide molten bath depends on the above reactions where the active carbon and nitrogen are absorbed into the steel surface. Sodium cyanide is a good reducing agent and the oxides of tin, lead, copper, or manganese are readily reduced (*Kirk-Othmer*, 1993).

39.4.1 Chemical Synthesis Using Sodium Cyanide

For chemical synthesis of a phosphorus–carbon bond, sodium cyanide can be used as shown below (*Kirk-Othmer*, 1982a):



Ethylene cyanohydrin is obtained from ethylene chlorohydrin and sodium cyanide in this reaction (*Kirk-Othmer*, 1978a):



Sodium cyanide reacts with 1,2-dichloroethane to produce 2-chloropropionitrile in this reaction (*Kirk-Othmer*, 1979a):



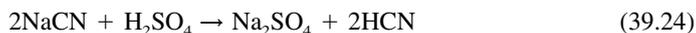
Thiocyanocarbons are prepared using sodium cyanide shown below (*Kirk-Othmer*, 1979a):



A chemical process to synthesize malonates uses sodium cyanide. In this procedure, a 25% solution of sodium cyanide in water is heated to 65 to 70°C. The reaction is shown below (*Kirk-Othmer*, 1995a):



Sulfuric acid reacts with sodium cyanide according to the reaction (*Ullmann's*, 1987):



39.4.2 Miscellaneous Uses of Sodium Cyanide

Sodium cyanide is also used as a radioactive tracer, sodium [^{14}C]-cyanide (*Kirk-Othmer*, 1996). In the United States, it is used as an active ingredient in a predator collar around a sheep's neck to poison coyotes (*Kirk-Othmer*, 1982b).

For the purpose of sterilization, sodium cyanide is used to remove fish, nuisance vegetation, and predators of fry by applying a concentration of 5 ppm to the water. Since sodium cyanide has a rapid rate of deterioration, fry can be restocked soon after the chemical has sterilized the pond (*Kirk-Othmer*, 1978b).

39.5 IMPORTS AND COSTS

Countries that imported sodium cyanide from 1976 to 1997 are shown in Fig. 39.2. It can be seen that the United States is a major user of sodium cyanide, followed by the United Kingdom.

As shown in Table 39.9, the cost ranges within each year depend on supply and demand. Also from 1993 to 1997, costs have risen 77 cents per kilogram from the extreme low to the extreme high end.

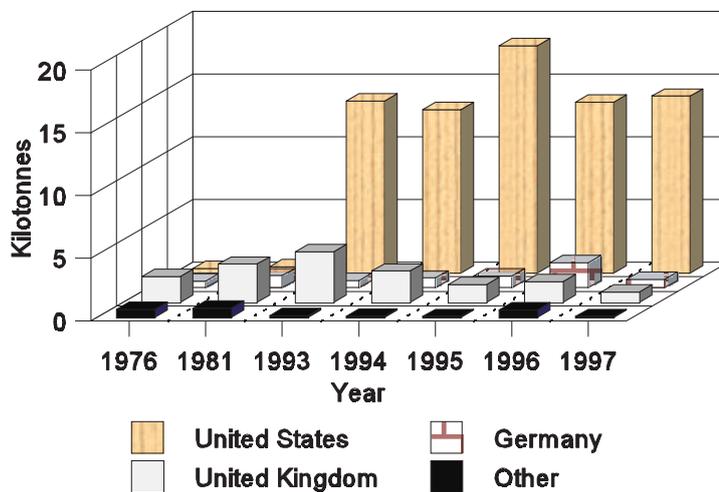


FIGURE 39.2 Imports of sodium cyanide by country. (Source: CIS, 1998.)

TABLE 39.9 Price History

Year	Bulk, tons/liter delivered to mine site: cents/kilogram	
	High	Low
1993	153	148
1994	153	153
1995	185	153
1996	225	185
1997	225	225

Source: CIS, 1998.

39.6 SPILL DATA

Cyanide spills in general were tracked using data from National Analysis of Trends in Emergencies Systems (NATES) for 1974 to 1995 (Environment Canada, 2000). This is shown in Fig. 39.3 and includes spills of cyanide leachates, sodium cyanide, cyanide not otherwise specified (nos), and cyanide/copper tailings. As can be seen in Fig. 39.4, cyanide nos is the largest of the spills and may contain any cations with cyanide or the cyanide ion itself.

The number of reported spills of sodium cyanide from 1974 to 1995 was extracted from the same NATES databank. It can be seen in Fig. 39.3 that no more than 2 spills of sodium

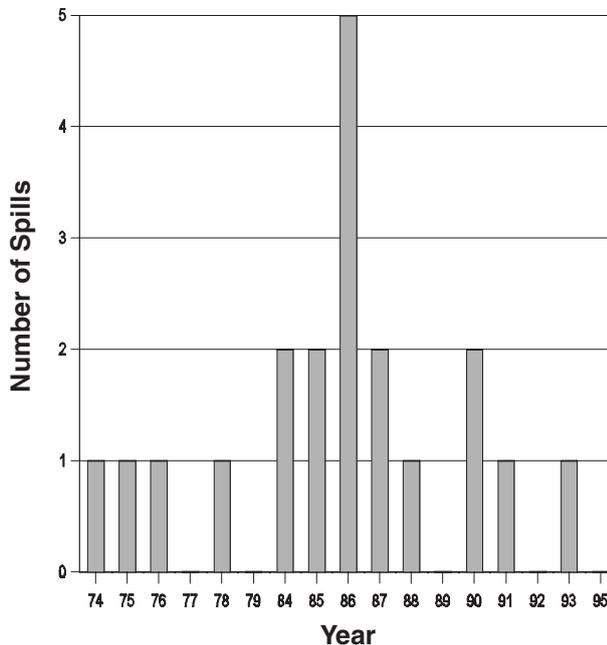


FIGURE 39.3 Number of sodium cyanide spills from 1974–1995. (Source: Environment Canada, 2000.)

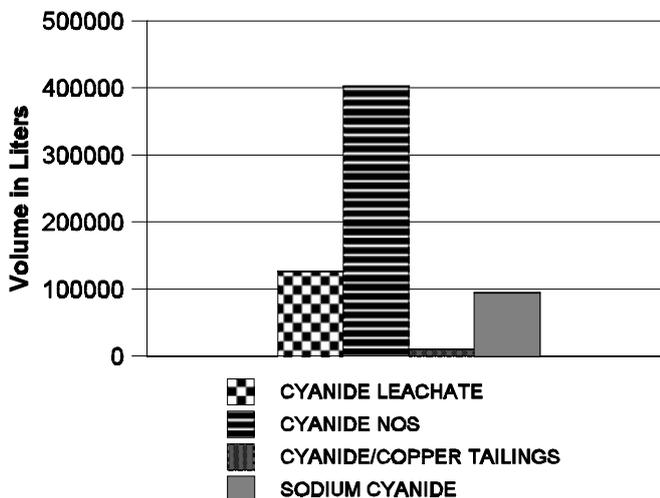


FIGURE 39.4 Cyanide spills from 1974–1995. (Source: *Environment Canada, 2000.*)

cyanide typically occur each year. However, Fig. 39.4 shows that sodium cyanide spills released just under 100,000 L into the environment from a total of 20 spills recorded in Fig. 39.3.

39.7 POTENTIAL COMPLEXES OF SODIUM CYANIDE IN A SPILL

Cyanide will form complexes of very stable, insoluble, or slightly soluble simple cyanides with heavy metals. Unidentate cyanide always bonds to the metal via its carbon atom, but the $M-C\equiv N-M$ links can be seen in many of the solid cyanides (King, 1994). There may be some settling of heavy metal cyanide complexes to the sediment. Some of the more stable complexes and their respective dissociation properties are shown in Table 39.10.

When metal cyanide complexes are formed and released into the environment, they begin to decompose at varying rates. The weak cyanide complexes, such as zinc and cadmium, will decompose faster than strong complexes such as copper, nickel, iron, cobalt, gold, and silver cyanides. Strong cyanide complexes do not break down in the presence of strong acids, such as hydrochloric acid or sulfuric acid, but will decompose when exposed to various wavelengths of light. Cyanide ions will be released when the decomposition process begins (Moran, 1998).

39.8 SPILLS OF SODIUM CYANIDE

39.8.1 Cyanide Spill at Gold Mine, Romania

On January 30, 2000, the Baia Mare gold mine in Romania reported a massive cyanide spill when the tailings dam collapsed due to pressure from snow buildup. Baia Mare is owned and operated by the Romanian company Aurul and Esmeralda Explorations Limited of Perth,

TABLE 39.10 Cyanide Dissociation Equilibria

Dissociation equilibria	pK _{dissociation}	Toxicity range for freshwater fish (mg/L)
$[\text{Pb}(\text{CN})_4]^{2-} \rightleftharpoons \text{Pb}^{2+} + 4\text{CN}^-$	10.3	
$[\text{Cd}(\text{CN})_4]^{2-} \rightleftharpoons [\text{Cd}(\text{CN})_3]^- + \text{CN}^-$	2.5	0.02–0.3
$[\text{Cd}(\text{CN})_3]^- \rightleftharpoons \text{Cd}^{2+} + 3\text{CN}^-$	14.7	0.02–0.3
$[\text{Zn}(\text{CN})_4]^{2-} \rightleftharpoons [\text{Zn}(\text{CN})_3]^- + \text{CN}^-$	1	0.02–0.3
$[\text{Zn}(\text{CN})_3]^- \rightleftharpoons \text{Zn}^{2+} + 3\text{CN}^-$	17.9	0.02–0.3
$[\text{Ag}(\text{CN})_2]^- \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$	20.9	
$[\text{Ni}(\text{CN})_4]^{2-} \rightleftharpoons \text{Ni}^{2+} + 4\text{CN}^-$	22	0.4 (pH 6.5), 730 (pH 8)
$[\text{Cu}(\text{CN})_4]^{3-} \rightleftharpoons [\text{Cu}(\text{CN})_3]^{2-} + \text{CN}^-$	1.5	0.4–4.0
$[\text{Cu}(\text{CN})_3]^{2-} \rightleftharpoons [\text{Cu}(\text{CN})_2]^- + \text{CN}^-$	5.3	0.4–4.0
$[\text{Cu}(\text{CN})_2]^- \rightleftharpoons \text{Cu}^{2+} + 2\text{CN}^-$	23.9	0.4–4.0
$[\text{Fe}(\text{CN})_6]^{3-} \rightleftharpoons \text{Fe}^{2+} + 6\text{CN}^-$	36	300 (in darkness), <0.2 (in light)
$[\text{Au}(\text{CN})_2]^- \rightleftharpoons \text{Au}^{2+} + 2\text{CN}^-$	37	
$[\text{Hg}(\text{CN})_4]^{2-} \rightleftharpoons \text{Hg}^{2+} + 4\text{CN}^-$	40.5	
$[\text{Fe}(\text{CN})_6]^{4-} \rightleftharpoons \text{Fe}^{2+} + 6\text{CN}^-$	42	
$[\text{Co}(\text{CN})_6]^{4-} \rightleftharpoons \text{Co}^{2+} + 6\text{CN}^-$	64	
$[\text{Pt}(\text{CN})_4]^{2-} \rightleftharpoons \text{Pt}^{2+} + 4\text{CN}^-$	40	
$[\text{Pd}(\text{CN})_4]^{2-} \rightleftharpoons \text{Pd}^{2+} + 4\text{CN}^-$	42	

Source: Ullmann's, 1987; Moran, 1998.

Australia. The spill was estimated to be 26 million gallons (98,410,000 L) (OSHS, 2000a) of wastewater, highly contaminated with cyanides and heavy metals (WWF, 2000a, b). The tailings flowed into the Szamos River in Hungary, then proceeded to flow down the Tisza River and into the Serbian Republic to the larger Danube upstream of Belgrade in Yugoslavia.

The wave of cyanide-contaminated tailings took several days to travel the rivers to Belgrade. As can be seen in Fig. 39.5, samples taken from the Szamos River at Csenger on February 1, 2000 were 32.6 ppm cyanide. On February 11, samples from the Tisza River at Tiszasziget showed concentrations of 1.49 ppm cyanide. These concentrations could kill some fish species. Along the way, the authorities closed water intakes and warned the public against any contact with the river water or dead fish. The city of Szolnok, which depends entirely on the Tisza for drinking water, was forced to use additional chlorine and ozone as a neutralization method. (OSHS, 2000b).

The company treated the spillage with sodium hypochlorite to neutralize the cyanide. The desired reaction is shown below (McGill and Comba, 1990):



The wave of cyanide had a negative impact on life in the Tisza River and killed an estimated 80% of the fish in the river (see Fig. 39.6).

On February 8, it was found that eight drinking wells were contaminated with cyanide (UNEP/OCHA, 2000). A week later, the water appeared to be safe to drink. On March 6, 17 scientists from seven countries finished sampling the water of the Danube River, 800 km downstream from the mine. A total of 180 tons of dead fish were removed from Hungary's Szamos and Tisza Rivers. According to Hungary's Minister of the Environment, the recovered fish represented only 15% of the total fish killed, while an estimated 15% drifted down the Tisza into Yugoslavia and another 15% were still trapped under ice.

The Australian mining company maintained that there was no scientific evidence linking extensive fish kills with the spill of tailing pond water (OSHS, 2000a, b). This comment is in stark contrast to that of György Gado, Conservation Director of the World Wildlife Fed-



FIGURE 39.5 Tracking the sodium cyanide spill from Baia Mare. (Source: MTI, 2000.)

eration in Hungary, who stated, “This spill has, in practical terms, eradicated all life from a stretch of up to 400 km of the Tisza River” (WWF, 2000c).

The chairman of the Hungarian government’s Environment Committee was very concerned that the heavy metals in the environment could pose a far greater health threat in the long term (Ottawa Citizen Online, 2000). Given the complexes that cyanide can form with heavy metals, the sediment could remain highly toxic for some time. It was found that the contamination in the sediments decreased rapidly with increased distance from the source of the spill. The concentrations of heavy metals in the Lapus River were high or extremely high (UNEP/OCHA, 2000).



FIGURE 39.6 Fishermen from the Tisza region collecting dead fish. (Source: WWF, 2000a, b, c.)

The breached tailings pond at the gold mine, which was 93 ha in area and about 20 m deep, was lined with a plastic membrane and held approximately 4.43 million tons of flotation solid wastes. Due to an imbalance between water burden, unexpected quantities of water from the addition of snow and rain, and safe storage volume, the capacity of the pond was insufficient to safely store the slimes. It was estimated that 50 to 100 tons of cyanide were released into the river (UNEP/OCHA, 2000).

Although the company was operating with a government permit, no contingency plan was in place. The emergency preparedness and response procedures were rudimentary considering the quantities of chemicals involved and the mine's proximity to human population and the river systems (UNEP/OCHA, 2000).

It was recommended that a risk assessment be carried out on the entire system, that the process water ponds be reduced to sizes that could be handled in emergencies, and that emergency water supplies be available (UNEP/OCHA, 2000).

The following are the impacts of the spill:

- 180 tons (ETK, 2000) or 1,000 tons (UNEP/OCHA, 2000) of dead fish
- Cyanide and cyanide-heavy metal contamination in riverbeds of Tisza and Szamos Rivers
- Otters are now extinct in the Tisza and Szamos Rivers
- Birds and animals died from eating contaminated fish
- Groundwater resources contaminated

It is estimated that it will take 1 to 2 years to rehabilitate the water and 10 years for the riverbed to recover (ETK, 2000).

39.8.2 Cyanide Spill at Omai Gold Mines, Guyana

An uncontrolled release of cyanide-contaminated wastewater occurred on August 19, 1995, at a gold mine in central Guyana (see Fig. 39.7). The mine was operated by Omai Gold Mines Limited (OGML), a Canadian- (Cambior Inc.) and U.S.-owned company. The failure of the dam was caused by massive loss of core integrity from internal erosion of the dam fill, a process called piping (Vick et al., 1995). On August 24, the spill was contained and diverted to an open pit mine. It was estimated that 2.6 to 2.7 million m³ of contaminated water flowed into the Essequibo River. This is the country's major river, used for drinking, bathing, and fishing (NEEC Alert, 1995).

The spill was colored red by the clay saprolite core material of the dam. The release flowed into the Omai River, which is 3 to 5 m wide, before entering the Essequibo River. It was estimated that the dilution factor would be 150:1 in the Essequibo River and that this

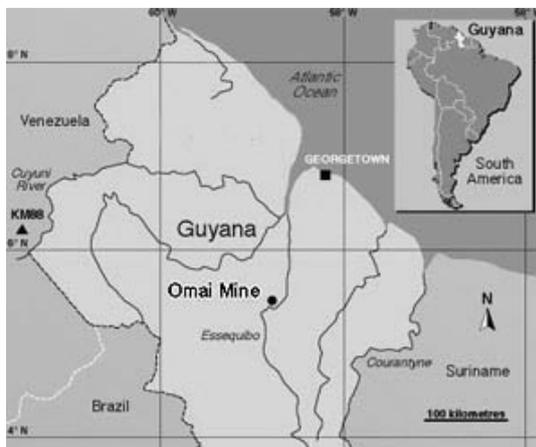


FIGURE 39.7 Omai Mine in Guyana. (Source: *Geocities.com*, 1995.)

would increase downstream as the river expanded. The initial concentration of total cyanide was 25 mg/L from the water discharging from the tailings pond. In the Essequibo River the average cyanide level was 0.12 mg/L. After the spill, 200 dead fish were sighted in the Omai River (Feasby, 1995), but there were no human casualties.

There was concern that 5 ppm of cyanide in water could be lethal to a 7-kg infant. A lethal dose for an adult weighing 60 kg would be a concentration of 34 mg/L of cyanide in the water (Feasby, 1995). On August 21, the Pan American Health Organization (PAHO) reported cyanide levels in the Omai River to be 5.42 ppm and rising. Officials informed the people not to drink the water and began distributing drinking water to affected communities. Helicopters were mobilized to inform people of the potential dangers (NEEC Alert, 1995).

According to Environment Canada, the long-term impact of the spill will be negligible since cyanide degrades rapidly. Also, the high volume of the Essequibo River diluted the cyanide levels so that there were no visible environmental impacts downstream from the entry point of the spill, where the Essequibo and Omai Rivers intersect (Trip and Blakeman, 1995).

39.8.3 Cyanide Spill in Central Asia

On May 20, 1998, in Kyrgyzstan in central Asia, a truck carrying 20 tons of sodium cyanide crashed through the railing of a narrow bridge into the Barskaun River (Fig. 39.8). This river empties into Lake Issyk-Kul. The truck was en route to the Kumtor gold mine.

Because the police were not immediately notified of the spill, five hours passed before the public was notified. Company employees were preoccupied with attempts to rescue the driver from the truck and getting the container out of the water. It was found that 1,762 kg of cyanide briquets were missing. The Ministry of Environmental Protection found cyanide levels in the river to be 1,600 times the maximum acceptable level during the spill, but a day later the concentrations fell to acceptable levels.

A water sample taken hours after the accident 20 m from the spill site showed free cyanide concentrations of 79.5 mg/L. This sample did not include cyanates, thiocyanates, cyanogen, cyanogen chloride, ammonia, chloramine, or metal cyanide complexes that are forms of cyanide-related compounds (Moran, 1998).



FIGURE 39.8 The bridge where the truck broke through and the river as seen from the bridge. (Source: CBC, 1998.)

Before the spill, the pH level of the river was probably less than 9. Most of the dissolved cyanide would therefore have formed hydrocyanic acid (HCN), a toxic gas that would have dissipated into the air. After a few hours, sodium hypochlorite was added, which would have resulted in the formation of cyanate and cyanogen chloride. Cyanogen chloride can cause throat and eye irritations and, being heavier than air, could have traveled significant distances from the spill (Moran, 1998).

Two days after the spill, villagers started showing up at hospitals, which evidently confused the responders. A representative of Cameco (owner of the mine) stated that it was “highly unlikely, if not impossible” that the villagers’ symptoms were due to the cyanide spill. The argument was that “cyanide poisoning would manifest itself almost immediately” (OSHS, 1998). A pediatrician at the children’s hospital in Kyrgyzstan reported that one patient was in serious condition and others had enlarged livers (CBC, 1998). Another report suggested that the spill led to a fish kill, but there were no confirmed reports of sick villagers and livestock (OSHS, 1998).

The comments in Table 39.11 demonstrate the confusion and conflicting reports on the spill.

39.9 NEUTRALIZATION OF CYANIDE SPILLS

A typical cyanide neutralization is shown below.

For alkaline chlorination:

1. $\text{NaCN} + 2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaCNO} + 2\text{NaCl} + \text{H}_2\text{O}$
2. $2\text{NaCNO} + 4\text{NaOH} + 3\text{Cl}_2 \rightarrow 6\text{NaCl} + \text{N}_2 + 2\text{H}_2\text{O} + 2\text{CO}_2$

This procedure uses sodium hydroxide and pH has to be maintained at above 9, preferably pH 9 to pH 11, to avoid formation of toxic nitrogen trichloride (Kirk-Othmer, 1993).

Hypochlorite neutralization is shown here (McGill and Comba, 1990):

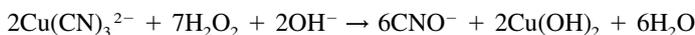
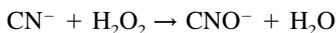
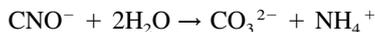


The cyanide solutions are oxidized to the less toxic cyanate (Corn, 1993). Cyanates are toxic to trout at concentrations ranging from 13 to 82 mg/L cyanate (Moran, 1998).

Cyanide spills can also be neutralized with peroxide by the Degussa method, in which the pH is maintained above 9 (between 9.0 and 10.5) to avoid formation of toxic NCl_3 , nitrogen trichloride. The Degussa method is shown below:

TABLE 39.11 Conflicting Reports on Cyanide Spill

Number of dead	Number effected
Two died.	“ . . . 2,533 poisoned, most from local village of Barskaun.” (Ling, 1998)
“No one died as a result of the spill of sodium cyanide.”	“Although there was potential for up to 16 people to become exposed as a result of cyanide . . . no medical evidence has been supplied to the commission to support these cases as being affected by cyanide.” (Cameco, 1998)
“A second person has died from cyanide poisoning.”	“444 people remain in hospital since the May 20 accident, including six who are in grave condition.” (Perreaux, 1998)
“A woman has died after a river has been contaminated with cyanides.”	“Kyrgyz officials . . . say a total of 506 local residents had been hospitalized by June 3.” (<i>Financial Post</i> , 1998)
“Doctor blames cyanide for a woman’s death.”	“Hundreds flooded to hospitals complaining of being sick.” (CTV, 1998)
“She died of sodium cyanide poisoning that aggravated a previous illness.”	“Some 600 people have sought medical treatment for poisoning. About 100 of those have been hospitalized.” (<i>Globe and Mail</i> , 1998)
“No cyanide-related deaths.”	“Maximum of 16 potential cases of direct cyanide exposure. . . .” (CNW, 1998)

1. Oxidation:**2. Precipitation:****3. Hydrolysis of cyanate:****4. Side reactions (McGill and Comba, 1990):**

When 200 L of cyanide were spilled into the River Wey in Surrey, England in May 1999, peroxide was added to the river to save the fish. The peroxide breaks down into water and oxygen and raises the pH of the polluted water, causing the cyanide to break down more rapidly. The fish were saved by the additional oxygen added. The Environment Agency’s Thames Region now includes peroxide crystals, or sodium carbonate peroxyhydrate, in their response kits for cyanide spills (OSHS, 1999).

Peroxide was used to increase the oxygen content of a small pond of fish about 0.1 ha in size. The oxygen content was at 13%, but within two hours of about 200 kg of liquid sodium peroxide being added, the oxygen content rose to 35% (OSHS, 1999).

39.10 CONCLUSIONS

Sodium cyanide is highly toxic to humans and the environment. Its usage in the mining industry has called into question the responsibility of the owners and operators to create a safe environment. As can be seen in the case studies, cyanide spillages into waterways are catastrophic. A recent comment on March 22, 2000 regarding a helicopter spillage of sodium cyanide shows the changing tide for tolerating cyanide spills. According to the Mineral Policy Institute in Sydney, Australia, "There is mounting evidence that using cyanide to extract gold is inherently dangerous. The high risk of cyanide accidents outweigh the dubious benefits of mining gold. We are being forced to question whether cyanide usage in gold mining should be limited or even banned" (Evans, 2000). These are questions that could change the future of the usage of sodium cyanide.

39.11 ACKNOWLEDGMENTS

The authors acknowledge Carol Lau from the National Environmental Emergency Centre (NEEC) of Environment Canada for providing information from the NATES database.

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