

Chapter 13

Cyanide Geochemistry and Detoxification Regulations

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13.1 INTRODUCTION

Cyanide is a generic term indicating the presence of the cyanide ion (CN^-). Cyanide is a very common, naturally occurring compound produced by many biochemical reactions. Many plant species synthesize organic compounds which contain cyanide in the form of cyanogenic glycosides (Knowles, 1976). For example, trace amounts of cyanide are present in the seeds and leaves of many members of the Rosaceae (rose) family (Kingsbury, 1964).

Many common items such as lettuce, maize, sweet potatoes, kidney beans, (Oke, 1969) almonds, and cigarette smoke contain cyanide. As examples, a recent chemical analysis of chocolate-covered almonds measured a total cyanide content of about two ppm (Steffen Robertson and Kirsten, 1987); and the U.S. Surgeon General (U.S. Department of Health, 1964) has shown that cigarette smoke contains up to 1,600 ppm total cyanide.

The chemistry of cyanide solutions is complicated because the cyanide ion forms compounds and complexes with many elements. Some cyanide species are highly toxic whereas others are relatively inert and harmless. Molecular hydrogen cyanide (HCN) is the most toxic form of cyanide. Under most conditions, HCN exists as a gas which readily dissipates or reacts with the environment to form less toxic or nontoxic forms of cyanide. Thus HCN is an ephemeral toxin, and many naturally occurring geochemical processes reduce the HCN concentration of a heap system with time.

As discussed below, free cyanide includes the two species, ionic cyanide (CN^-) and molecular hydrogen cyanide. Free-cyanide toxicity in man, mammals, and aquatic species is well documented (Doudoroff, 1976; Ecological Analysts, 1979; Towill et al., 1978). The lethal doses reported for human adults vary with the type of exposure as follows:

- One to three mg/kg body weight if ingested;
- One hundred to 300 ppm if inhaled; and
- One hundred mg/kg of body weight if absorbed.

Acute toxicity of free cyanide to freshwater invertebrates ranges from 0.028 to 2.295 mg/l, depending on species and test conditions. Generally, free-cyanide concentrations greater than 0.1 mg/l are expected to kill sensitive species in freshwater or marine environments (Doudoroff, 1976;

Cardwell et al., 1976). Concentrations of HCN as low as 0.05 mg/l can be lethal to fish (Scott and Ingles, 1981). Several site specific variables including the solution pH and temperature, oxygen content of the water, ionic strength, species acclimation, and body size can affect the degree of free-cyanide toxicity.

13.2 CYANIDE TERMINOLOGY AND ANALYTICAL METHODS

One of the difficulties in discussing cyanide and the environment and establishing cyanide regulatory standards is that the terminology used to describe cyanide species is confusing. To add to the confusion, there are a variety of analytical methods used to test for the various cyanide species, and some of these methods are prone to analytical interference problems. Thus comparing analytical data from one laboratory to another may not be valid (Conn, 1981). The following discussion will attempt to clarify cyanide terminology and review the most commonly used analytical methods.

13.2.1 Free Cyanide

The term "free cyanide" means the two species, ionic cyanide (CN^-) and molecular hydrogen cyanide or hydrocyanic acid (HCN). In acidic and weakly-alkaline solutions, the dominant free cyanide species is molecular hydrogen cyanide.

Most analytical techniques for measuring free cyanide involve solvent extraction or sparging the HCN from solution and measuring the HCN (Conn, 1981). Free cyanide can also be analyzed using a specific ion electrode by comparing the potential readings of the electrode against a cyanide standard calibration curve. The specific ion electrode technique is one of the easiest and most economical methods for determining free cyanide in a field laboratory.

However, there is a significant body of data which indicate interference problems with free cyanide analyses. These data include many examples where the apparent free cyanide levels were higher than the total cyanide measured in the same sample due to the interference of thiocyanate (CNS^-) or other ions in solution. The specific ion electrode method, for example, is particularly sensitive to the presence of S^{2-} , Cl^- , and Hg^+ . Thus, free cyanide analyses may be questionable depending upon the chemical composition of the solution being analyzed.

Even though HCN is the species that is measured and is the dominant toxic species of concern, free cyanide is generally expressed in the literature as "CN⁻". To add to the confusion, free cyanide is sometimes written as "CN" (U.S. Environmental Protection Agency, 1980).

13.2.2 Total Cyanide

Total cyanide refers to the sum, in terms of cyanide ion (CN^-), of molecular hydrogen cyanide (HCN), cyanide ion (CN^-), and most cyanide bound as metallic complexes and compounds. Acid reflux/distillation using a catalyst to break down most metallic cyanide species is the analytical technique commonly used to measure total cyanide (ASTM, 1981). This method cannot measure completely the cyanide content of gold-, cobalt-, platinum-, and some iron-

cyanide species. The accuracy and precision of the method are also compromised by interference from thiocyanates (CNS^-). The thiocyanate interference problem, coupled with variations in analytical procedures, has led to great difficulties in comparing total cyanide data produced by the mining industry (Conn, 1981).

Because total cyanide is expressed in terms of (CN^-), total cyanide data can be difficult to distinguish from free cyanide data, also labeled (CN^-). The use of the words "free" and "total" can prevent this confusion.

Some cyanide regulations are expressed in terms of total cyanide rather than free cyanide. Most biologists and environmental scientists would prefer regulations expressed as free cyanide, because total cyanide is toxicologically meaningless (Conn, 1981). However, as mentioned above, there are significant analytical problems with the analysis of free cyanide.

13.2.3 Other Methods for Determining Cyanide

There are various methods for measuring free cyanide plus the cyanide evolved from certain metal cyanide complexes under specified conditions. Some cyanide regulations are based upon these determinations which measure less than total cyanide. The cyanide amenable to chlorination method is based upon the difference between total cyanide determinations on a sample before and after alkaline chlorination. The alkaline chlorination process oxidizes all cyanides except the iron complexes and thiocyanate. The difference between the two total cyanide values is reported as cyanide amenable to chlorination. This method is subject to the same drawbacks and thiocyanate interference problems as the total cyanide method (Gannon, 1981).

The weak acid dissociable method (WAD), otherwise known as Method "C" from the ASTM designation, involves a procedure similar to the total cyanide technique except that it uses different reagents. This method recovers all the cyanide from zinc- and nickel-cyanide complexes, but only recovers about 70 percent from copper- and 30 percent from cadmium-cyanide complexes. It does not recover any cyanide from ferro-, ferri-, and cobalt-cyanide complexes. There is no thiocyanate interference problem with this method (Gannon, 1981). This method is currently favored by some engineers and geochemists because it obviates the problems associated with free cyanide analyses and it is not subject to thiocyanate interference.

13.3 THE GEOCHEMISTRY OF CYANIDE IN AN ABANDONED HEAP

One approach to understanding cyanide behavior in a decommissioned heap leach operation is to identify the cyanide reactions likely to take place, and the cyanide species likely to be present in the various geochemical environments within the heap, the pad, and the underlying sediments and bedrock. Figure 13.1 is a schematic diagram of an abandoned heap system showing the major components of the system and the prevailing geochemical conditions within the heap environment. These conditions vary for different parts of the system. The upper portions of the system, including the heap itself, the pad, and the underlying weathered bedrock are likely to be oxidized, and relatively dry or at least unsaturated. The underlying unweathered bedrock is more likely to be a reduced and saturated environment.

TYPICAL CYANIDE REACTIONS EQUATION No. (SEE TEXT)
No. 1-7, 10, 11 ±8 IF SULFIDE PRESENT
No. 2-7, 10, 11 IF OXIDIZED
No. 9, 10, 12, 13 IF REDUCED
No. 1, 4-6, 8, 10, 11

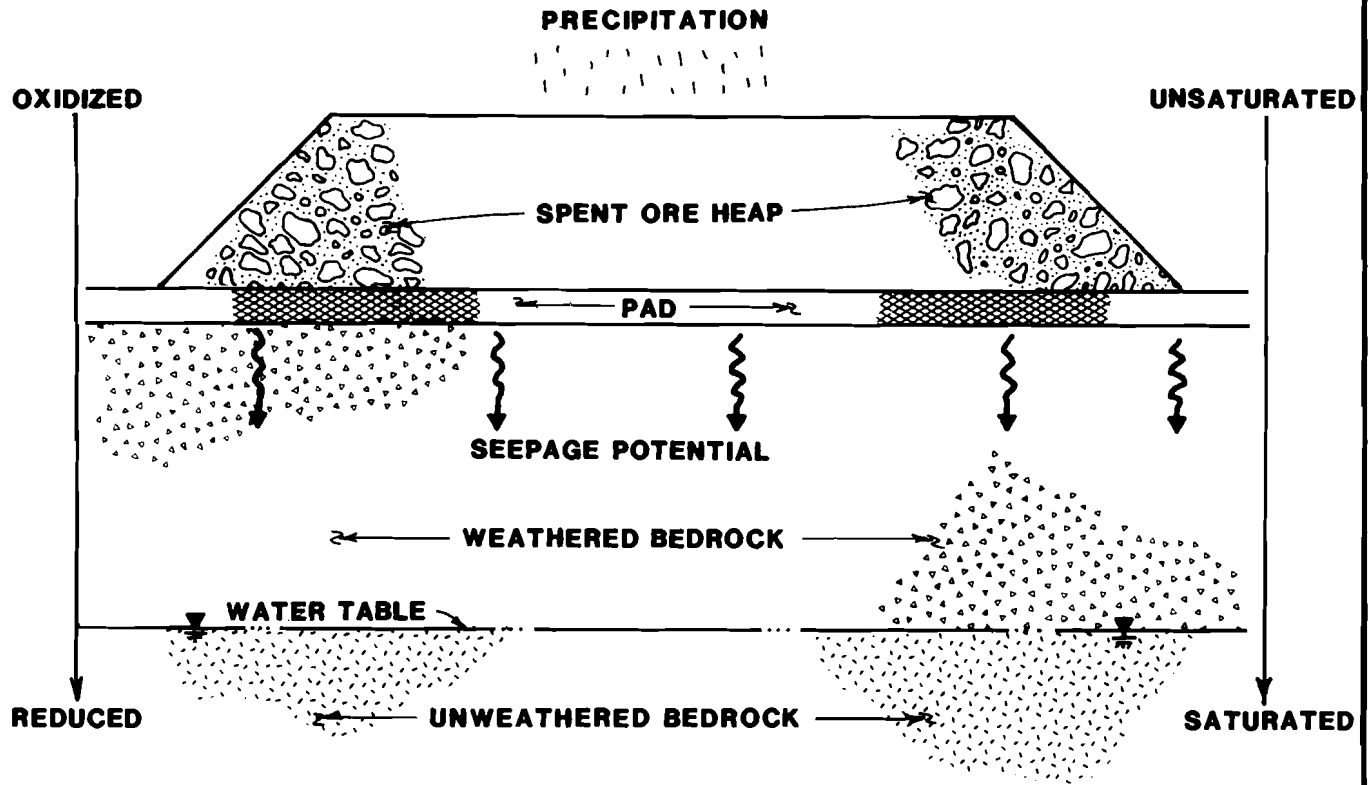


FIGURE 13.1

PREVAILING GEOCHEMICAL CONDITIONS AND TYPICAL CYANIDE REACTIONS IN THE ABANDONED HEAP ENVIRONMENT

Obviously the specific geochemical conditions within a heap leach system will be strongly influenced by site conditions such as the position of the water table, amount of precipitation falling on the heap, the mineralogy of the spent ore and of the underlying bedrock, and the fracture density and permeability of the bedrock. For purposes of this discussion, however, we will assume that the geochemical conditions shown on Figure 13.1 are the most common scenario.

The following discussion identifies the cyanide species most likely to be present within various components of the abandoned heap environment. The behavior of these cyanide species is discussed in terms of their relative toxicity and their potential effect upon the environment.

13.3.1 Hydrolysis and Volatilization

Reaction between water and the cyanide ion (hydrolysis) results in the formation of molecular hydrogen cyanide (HCN) as shown in Equation (1) and Figure 13.2.



This reaction is strongly dependent on pH. At a pH of 9.36, the pK_a of the hydrolysis reaction, the concentrations of CN^- and HCN are equal (Figure 13.2). At all lower pH values, hydrogen cyanide is the dominant species; at pH 7, 99 percent of the cyanide exists in this form (Huiatt et al., 1982). Most heaps have an operational pH of about 10.5. Following decommissioning and abandonment, there will be a gradual decrease in pH with time due to neutralization of the alkaline environment during rinsing procedures, infiltration of rain water, and carbon dioxide uptake. Thus, HCN will be produced by most newly abandoned heaps.

Molecular hydrogen cyanide (HCN) has a high vapor pressure and rapidly volatilizes into a gas. This volatilization process is moderately temperature sensitive. The HCN produced by hydrolysis of CN^- is thus readily volatilized into a gas and is continuously evolved from the heap environment through dissipation or destroyed by oxidation as discussed below. The net result is thus a loss of cyanide from the system.

As shown on Figure 13.1, hydrolysis of ionic cyanide is most likely to occur within the upper portions of the heap, under oxidized and unsaturated conditions. However, this reaction is not Eh dependent and can also occur in the reduced and saturated portions of the heap environment.

It should be noted that if the heap contains agglomerated ore, the lime agglomerating medium may buffer the hydrolysis reaction by keeping the pH above 9.36. This will temporarily prevent hydrolysis and the production of HCN. With time, infiltration of water and carbon dioxide into the heap will neutralize the cement agglomerating agents. The heap is then no longer buffered at an elevated pH, and the hydrolysis of CN^- to HCN will take place.

13.3.2 Oxidation of HCN and CN^-

The oxidation of either HCN or CN^- is generally restricted to the upper, oxidized portions of the heap environment as shown on Figure 13.1. The

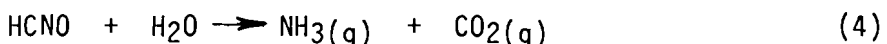
oxidation of HCN produces hydrogen cyanate (HCNO) as shown in Equation 2 (Owenback, 1978).



The direct oxidation of CN^- (Equation 3) requires a mineralogical, bacteriological, or photochemical (sunlight) catalyst, and produces cyanate ions (CNO^-).



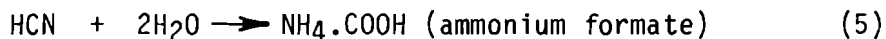
Hydrogen cyanate and cyanate ions are much less toxic than HCN. Within the heap environment, HCNO and CNO^- readily hydrolyze to form ammonia and carbon dioxide which are evolved from the system as gases as illustrated by Equation 4.



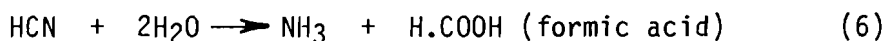
The ammonia generated in Equation 4 can either form ammonium compounds or be oxidized to form nitrates depending upon the pH (Hendrickson and Daignault, 1973). In this manner, oxidation of HCN or CN^- lowers the overall cyanide content of the system.

13.3.3 Hydrolysis/Saponification of HCN

As the system pH falls, HCN can be hydrolyzed by a different route to form formate, either formic acid or ammonium formate by:



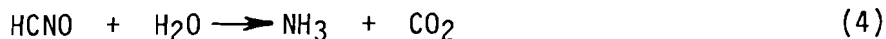
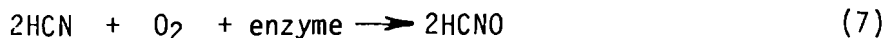
or



The system pH will determine the extent of formation of each compound, a lower pH favoring formic acid formation. This form of hydrolysis has been referred to as "saponification" by some workers, although this term normally refers to the formation of soapy compounds or fatty soaps (stearates, etc.).

13.3.4 Aerobic Biodegradation of HCN

Under aerobic conditions within the upper, oxidized portions of the heap, biological processes may consume hydrogen cyanide and generate hydrogen cyanate as shown in Equation 7 (Towill et al., 1978). The hydrogen cyanate is in turn hydrolyzed into ammonia and carbon dioxide (Equation 4).



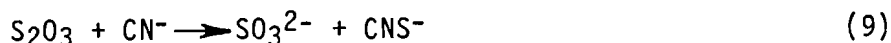
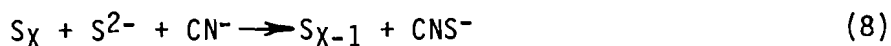
As indicated in Equation 7, this process requires an enzyme, but is otherwise identical to the oxidation reaction shown in Equation 3.

13.3.5 Formation of Thiocyanates

Thiocyanate ions (CNS^-) can be formed by the reaction between cyanide and any sulfur species such as sulfide, hydrogen sulfide, or thiosulfate.

Thiocyanate will be a common cyanide species in a heap containing sulfide ore, or in heaps placed upon sulfide-rich bedrock.

As such, thiocyanate formation depends more upon mineralogic conditions than on pH and Eh, and can occur anywhere in a heap environment with available sulfur species. Examples of thiocyanate forming reactions include the following equations:



In oxidized portions of the heap environment, the SO_3^{2-} formed in Equation 9 will react with oxygen to form sulfate (SO_4^{2-}).

Thiocyanate is a relatively stable and less toxic form of cyanide, and thiocyanate formation is an effective way of removing cyanide from the heap environment. However, in heaps with elevated sulfide concentrations, acidic conditions can form which in turn can influence the cyanide geochemistry. As described above, acidic conditions will favor the hydrolysis of CN^- to HCN. Acidic conditions may also cause the dissociation of heavy metal-cyanide complexes and compounds, resulting in the increased mobility of some heavy metals and creating potential heavy metal contamination problems.

13.3.6 Simple Cyanide Compounds

Cyanide forms simple compounds (i.e., simple salts) with single ions of certain metals. In solution, these simple cyanide compounds ionize and produce free metal cations and cyanide. An example of this type of reaction is shown in Equation 10.



Some of the metal cyanide compounds commonly found in a heap environment are listed in Table 13.1. Obviously the presence and relative abundance of any of these compounds depends upon the composition and mineralogy of the ore in the heap and the underlying bedrock.

As indicated on Table 13.1, the solubility of simple cyanide compounds ranges from readily soluble to fairly insoluble. Generally speaking, all simple cyanide compounds are relatively non-toxic, and the formation of simple cyanide compounds is another naturally occurring geochemical process that removes toxic cyanide species from the heap environment. However, the soluble simple cyanide compounds such as NaCN, KCN, $Ca(CN)_2$ and $Hg(CN)_2$ dissociate readily in solution and produce cyanide ions (Equation 10). At pH values lower than 9.36, this ionic cyanide will hydrolyze and produce toxic hydrogen cyanide (Equation 1).

13.3.7 Metal-Cyanide Complex Ions

Cyanide can also react with metals to form metal-cyanide complexes. Metal-cyanide complex ions form as the products of the reaction between the insoluble cyanide compounds and excess cyanide ions. Equation 11 is an example of this type of reaction.

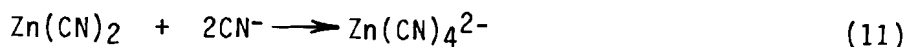


TABLE 13.1
RELATIVE STABILITY OF METAL CYANIDE COMPOUNDS AND COMPLEXES IN WATER
(LISTED IN APPROXIMATE ORDER OF INCREASING STABILITY)

CYANIDE SPECIES	EXAMPLES PRESENT IN THE HEAP ENVIRONMENT
1. Free Cyanide	CN ⁻ , HCN
2. Simple Cyanide Compounds	
a) Readily soluble	NaCN, KCN, Ca(CN) ₂ , Hg(CN) ₂
b) Relatively insoluble	Zn(CN) ₂ , CuCN, Ni(CN) ₂ , AgCN
3. Weak Metal-Cyanide Complexes	Zn(CN) ₄ ²⁻ , Cd(CN) ₃ ⁻ , Cd(CN) ₄ ²⁻
4. Moderately Strong Metal-Cyanide Complexes	Cu(CN) ₂ ⁻ , Cu(CN) ₃ ²⁻ , Ni(CN) ₄ ²⁻ , Ag(CN) ₂ ⁻
5. Strong Metal-Cyanide Complexes	Fe(CN) ₆ ³⁻ , Fe(CN) ₆ ⁴⁻ , Co(CN) ₆ ⁴⁻ , Au(CN) ₂ ⁻ , Hg(CN) ₄ ²⁻

Modified after Huiatt et al., 1982; and Brickell, 1981.

As shown on Table 13.1, some of these metal-cyanide complexes are relatively to exceptionally stable (i.e., insoluble), whereas others ionize readily and form CN⁻, which in turn hydrolyzes to form HCN (Equation 1).

As with the simple cyanide compounds, the toxicity of metal cyanide complexes is due to production of HCN as a dissociation and hydrolysis product. However, copper- and silver-cyanide complexes in their undissociated forms appear to be toxic to fish (Gannon, 1981). Although the iron-cyanide complexes are quite insoluble, they may be destroyed through photolysis (reaction with ultraviolet radiation) thereby releasing ionic cyanide (CN⁻). The rate of photolysis is highly variable depending upon site conditions. Photodecomposition of iron-cyanide complexes may be negligible in deep, turbid, or shaded waters, or within the interior of a heap.

Data developed recently, however, indicate that the "traditional" explanation of weak and strong metal complexes, while theoretically correct, may not be totally applicable in nature. Work by Ridgeway Mining Company (Smith, 1987) indicates that the stability of copper and cobalt cyanides appears to be a function of the concentration of cyanide in solution, as suggested by the data on Table 13.2.

The original, high pH solution has copper and cobalt as cyanide complexes, both ions being insoluble compared to their observed levels of occurrence in such alkaline conditions. As the cyanide levels decrease due to degradation, the copper and cobalt values drop dramatically as the solubility control changes from cyanide complexation to solution pH. These changes cannot be explained by dilution alone. The copper and cobalt complexes appear not to be stable under these conditions.

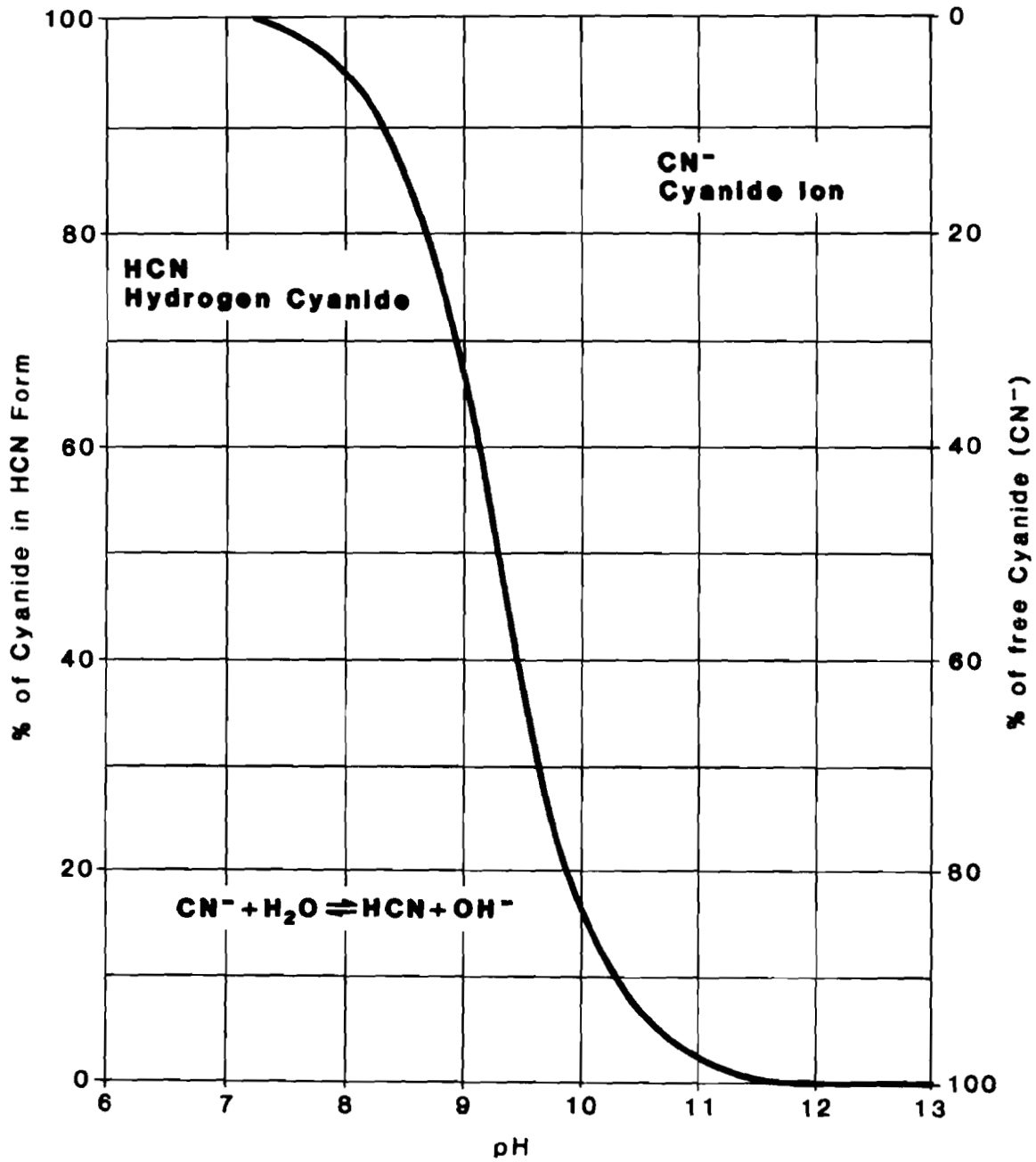


FIGURE 13.2

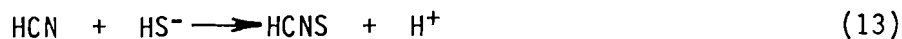
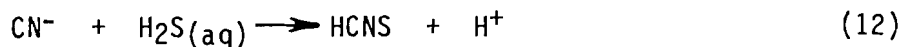
THE RELATIONSHIP BETWEEN HCN AND CN WITH PH

TABLE 13.2
 TIME/CYANIDE CONCENTRATION DEPENDENCY OF COPPER AND COBALT CYANIDE
 IN THE TAILINGS SUPERNATANT SOLUTION

PARAMETER	ORIGINAL TAILINGS SUPERNATANT	RINSED SAMPLE TIME 1	RINSED SAMPLE TIME 2
Total cyanide	170	2.66	0.90
	408	1.9	0.09
Free cyanide	170	0.92	0.04
	408	1.4	0.09
Cobalt	0.73	<0.1	<0.1
	2.21	0.05	0.05
Copper	1.81	0.04	<0.01
	6.34	0.04	<0.01

13.3.8 Anaerobic Biodegradation

Anaerobic biodegradation of cyanide and hydrogen cyanide is restricted to the moderately to strongly reduced portions of the heap environment (Figure 13.2), and can only occur if HS^- or $\text{H}_2\text{S}(\text{aq})$ are present. (The sulfur species present will depend on pH. At a pH value greater than 7, HS^- is the dominant species. At a lower pH, $\text{H}_2\text{S}(\text{aq})$ will be present). Equations 12 and 13 illustrate the anaerobic biodegradation of cyanide.



The HCNS will then hydrolyze to form NH_3 , H_2S and CO_2 (Schmidt et al., 1981).

13.3.9 Formation of HCN Polymers

There is a growing body of data indicating that, under natural conditions in or below heap leach operations or tailings facilities, HCN can form polymers. Although this may be based on theoretical considerations of the behavior of liquid HCN, it is known that HCN in the presence of trace amounts of ammonia can form adenine ($\text{C}_5\text{H}_5\text{N}_5$), a biochemically important molecule that occurs in DNA and RNA. This reaction is not shown on Figure 13.1. However, the environmental effect of cyanide polymerization would be to remove cyanide from solution by forming insoluble polymers.

13.4 SUMMARY OF THE ENVIRONMENTAL EFFECTS OF CYANIDE IN AN ABANDONED HEAP

As discussed in the preceding sections and as shown on Figure 13.1, numerous cyanide species exist within an abandoned heap environment. Many of the cyanide species present are not highly toxic and are relatively stable complexes or compounds under most conditions. Some cyanide species, however, are not stable and react with the environment to produce HCN, the toxic form of cyanide.

As described above, there are a number of potential naturally occurring geochemical reactions within the heap environment which degrade HCN into less toxic or nontoxic compounds. Thus with time, the heap environment tends to be self-neutralizing, and the HCN concentration will decrease.

Englehardt (1985) documented that in an active heap containing silver-lead ore tailings, the molecular hydrogen cyanide (HCN) content in the solutions entrained in the heap decreases rapidly due to natural degradation. Based upon data collected at regular intervals for one and one-half years, roughly 85 percent of the original cyanide content dissipated or degraded by natural processes within 18 months. Cyanide destruction in this heap occurred as a result of first order chemical reactions proportional to the concentration of the residual cyanide in the heap. Extrapolation of these data suggest that the cyanide in this heap would be totally destroyed in less than four years following closure.

More recently, Chatwin et al. (1987) on behalf of Dupont, has produced a Phase 1 report of a study on the attenuation of cyanide. Their interim conclusions suggest the major mechanisms for cyanide reduction in the vadoze (unsaturated) zone will be volatilization, chemical reaction or adsorption with soils/rocks in this zone and, possibly, biodegradation. In addition, those materials which attenuated cyanide in their tests continued to be effective at the 50 pore volume stage when the tests were halted.

13.4.1 Cyanide Neutralization Requirements for Spent Heaps

Regulatory officials from 14 states were questioned about their state's regulations concerning maximum residual cyanide concentrations in spent heaps. Table 13.3 lists the states and the regulatory agencies contacted and Table 13.4 summarizes the results of the survey.

A wide diversity of responses was received in this survey. No two states have identical regulations. However, some generalizations about the survey data can be made. Most states took one of the following approaches:

- Strict adherence to a universally applicable cyanide detoxification standard (generally the EPA drinking water guideline of 0.2 mg/l total cyanide); and
- Establish permit conditions on a case-by-case basis depending on site-specific conditions.

In most states, cyanide neutralization criteria are specified in the "zero-discharge" water quality permit required to build and operate a heap leach facility. In addition to neutralization requirements, these permits also specify design, construction, operational, and monitoring criteria.

PRECIOUS METAL HEAP LEACHING PROJECTS

TABLE 13.3
STATE AGENCIES CONTACTED FOR THIS SURVEY

STATE	ORGANIZATION
Alaska	Dept. of Environmental Conservation (907/425-1714)
Arizona	State Mine Inspector's Office (602/255-5971)
California	Southern Lahontan Region Water Quality Control Board (619/245-6583) Northern Lahontan Region Water Quality Control Board (916/544-3481) Colorado River Basin Region Water Quality Control Board (619/346-7491)
Colorado	Dept. of Natural Resources/Mined Land Reclamation Div. (303/866-3567)
Idaho	Dept. of Health and Welfare Division of Environment (208/334-4784)
Montana	Dept. of State Lands (406/444-2074)
Nevada	Dept. of Conservation and Natural Resources/Division of Environmental Protection (702/885-4670)
New Mexico	Groundwater Section New Mexico Environmental Improvement Division
North Dakota	Health Dept. - Water Supply and Pollution Control (701/224-2354)
Oregon	Dept. of Environmental Quality - Water Quality Division (503/229-5325)
South Carolina	South Carolina Land Resources Commission Division of Mining and Environment (803/758-2823)
South Dakota	Department of Water and Natural Resources (605/773-3151)
Utah	Div. of Environmental Health/Water Pollution Control (801/533-6146)
Washington	Div. of Geology and Earth Resources/Dept. of Natural Resources (206/459-6372)
Wyoming	Water Quality Division (307/777-7756)

TABLE 13.4
SUMMARY OF STATE CYANIDE REGULATIONS SURVEY

STATE	CYANIDE REGULATIONS	COMMENTS
Alaska	No specified standards	No experience with cyanide heap leach mining.
Arizona	0.2 mg/l free CN ⁻	State health standards only. Assume zero discharge. Discourage hypochlorite neutralization.
California Northern Lahontan Region	0.4 mg/l total CN ⁻ 0.2 mg/l free CN ⁻	Standards apply to remaining liquid in ponds, heaps, etc. Also have solids extraction test of less than 4.0 mg total CN ⁻ /kg spent ore and less than 1.6 mg/kg free CN ⁻ /kg spent ore.
Southern Lahontan Region	0.2 mg/l free CN ⁻	Standard applies to region remaining liquids in ponds, heaps, etc. Also have solids extraction standard of 10 mg total CN ⁻ /kg tailings.
Colorado River Basin Region	No specified standard (precedent of 10 mg/l free CN ⁻ for Mesquite)	Statistical approach: 90 percent of at least 10 samples must contain less than 10 mg/l free CN ⁻ ; no sample can contain more than 20 mg/l free CN ⁻ . Testing and sample procedures specified for 5:1 extraction performed on a 100 g sample of leached ore.
Colorado	No set standards (will be redrafting regulations)	Evaluate each site for quality of receiving surface and groundwater. Emphasize zero-discharge design controls to ensure containment.
Idaho	New regulations recently adopted. Neutralization requirement based upon site characteristics expressed in terms of pH range or free and/or WAD cyanide	Regulations do not specify one, universal CN ⁻ standard. Will evaluate each site-proximity to surface water, quality of receiving water, etc. New regulations include a bonding requirement.

PRECIOUS METAL HEAP LEACHING PROJECTS

TABLE 13.4 (con't)
SUMMARY OF STATE CYANIDE REGULATIONS SURVEY

STATE	CYANIDE REGULATIONS	COMMENTS
Montana	No set standards (nondegradation rule)	Determined by quality of receiving water. Nondegradation implies a drinking water standard (0.2 mg/l free CN^-) if high-quality receiving waters. Permits could be more lenient for lined facilities with caps and diversions to prevent drainage into streams.
New Mexico	0.2 mg/l total CN^-	Not an effluent standard per se. Will take into consideration attenuation and dilution (i.e., can have more than 0.2 mg/l total CN^- in effluent). Ortiz rinse test: 100 lb sample rinsed with one gallon fresh water; filtrate must be less than 100 ppm free CN^- . Might accept this for other lined facilities.
Nevada	No set standards 0.2 mg/l free CN^- is a "target" concentration (most operators can't meet)	Evaluate each site for proximity to valuable surface water and modify "target" concentration accordingly. Risking and testing procedures differ for agglomerated vs. nonagglomerated ore. Discourage hypochlorite and/or peroxide.
North Dakota	No set standards	No heap leach mines. Would probably impose surface water quality standards.
Oregon		In the process of drafting.
South Carolina	No set standards (Haile precedent of 10 mg/l free CN^-)	Will evaluate each site. After closure heaps at Haile will drain into stream w/pH of 4 and elevated CN^- content.
South Dakota	State standard of 0.50 WAD cyanide	Measured in effluent coming off of heap - any method of detoxification acceptable. Mean of several samples must be less than or equal to 0.50 WAD cyanide.

TABLE 13.4 (con't)
SUMMARY OF STATE CYANIDE REGULATIONS SURVEY

STATE	CYANIDE REGULATIONS	COMMENTS
Utah	No set standards (Mercur precedent of 5 ppm free CN^-)	Would look at Mercur permit as a precedent, but not a standard. Require double-lined pads w/leak detection system. Mercur uses permanent/expandable pads (i.e., heaps wasted in situ).
Washington	No set standards (in process of drafting regulations)	Will probably evaluate each site, no measurable CN^- allowed in effluent from reclaimed facilities.
Wyoming	.02 mg/l free CN^-	Based on quality of receiving water, effluent can't exceed ambient water quality. Would be more lenient for zero-discharge facilities (i.e., if no surface or groundwater impacts).

Generally speaking, most of the states adopting a drinking water guideline as their cyanide neutralization criterion do not have many active cyanide heap leach operations and thus do not have much direct experience with heap leach technology. In contrast, the states with several active cyanide heap leach projects have opted for the more site specific approach, giving some flexibility in determining permit conditions.

Those states which do consider site specificity in setting neutralization requirements and other permit conditions generally try to select reclamation procedures and neutralization and abandonment requirements appropriate for the project site. When site conditions are taken into consideration, it becomes apparent in many cases that it is impractical and unnecessary to impose drinking water guidelines on the rinsate from a detoxified heap. The environmental sensitivity of the project site may not warrant such stringent requirements. Furthermore, it may be costly, if not impossible, to neutralize to a drinking water guideline.

In evaluating a project and determining permit conditions, most of the states with experience in heap leach operations were more concerned with cyanide containment than with specific cyanide concentrations remaining in the heap. These states emphasize engineering parameters such as liner specifications and hydrologic (flood control) design criteria. Some of the more experienced states also specify detailed procedures for heap rinsing, rinsate sampling and analytical testing.

There is also no consensus among the states surveyed concerning the cyanide species specified in the regulations or permit conditions. Some of the states express their cyanide requirements in terms of free cyanide, whereas others have standards defined in terms of total cyanide. At least one state (Idaho) includes weak acid dissociable cyanide in its regulations. Some states also express neutralization requirements as a range of pH values in lieu of a specified cyanide level.

As shown on Table 13.4, some states are in the process of establishing or redrafting cyanide neutralization requirements for spent cyanided heaps. In most cases, this action has been prompted by the increasing number of permit applications for precious metal cyanide heap leach operations. The changing regulatory atmosphere is in direct response to the increasing use of heap leach techniques.

Coupled with the regulations in several states is a bonding authority governing heap leach projects. Heap leach operators in these states are required to obtain a bond to cover the cost of rinsing and detoxifying the heaps, and release of this bond is tied to neutralizing the spent heaps to a specified standard.

An understanding of cyanide geochemistry is a prerequisite to establishing realistic cyanide detoxification standards for abandoned heap leach projects. Environmental regulations should consider the self-neutralization potential of an inactive heap, the ephemeral nature of molecular hydrogen cyanide, and the environmental sensitivity of a given project. More stringent requirements should be reserved for projects with nearby, downgradient fishable streams or potable surface and groundwater supplies.

Application of a cyanide drinking water guideline on the rinsate from a neutralized heap is neither realistically achievable nor necessary in order to protect surface and groundwater resources in nearly all situations in our experience. Based upon a consideration of site conditions including the attenuating properties of site subsoils and bedrock, the distance to the nearest potential surface demonstrated that water guidelines are maintained for these receiving waters when higher residual cyanide levels are allowed in the detoxified heaps.

As more heap leach mining permit applications are reviewed and processed by regulatory agencies, more changes in the regulatory environment affecting precious metal heap leach projects can be expected. With increased experience in heap leach operations, and a broadening awareness of the short- and long-term effects of cyanide and the behavior of cyanide in the heap leach environment, more states hopefully will adopt the site-by-site approach to establishing cyanide neutralization requirements.

13.5 REFERENCES

- ASTM (1981). Proposed revision of standard methods of test for cyanide in water. Standard D-2036-81, American Society for Testing and Materials.
- Brickell, R.H. (1981). Chemistry of cyanide solutions, Proceedings from Cyanide and the Gold Mining Industry Seminar: Environment Canada, Ottawa, Ontario, Jan. 22-23.
- Cardwell, R.D., D.G. Foreman, T.R. Payne, and D.J. Wilber (1976). Acute toxicity of selected toxicants to six species of fish. U.S. Environmental Protection Agency, Duluth, MN, EPA 600/3-76-008, 116 pp.
- Chatwin, T.D., J. Trepanowski, and M.E. Wadsworth (1987). Attenuation of cyanide in soils, Phase 1 Report, Resource Recovery and Conservation Consultants, Salt Lake City, 113 pp.
- Conn, K. (1981). Cyanide analysis in mine effluents, Proceedings from Cyanide and the Gold Mining Industry Seminar: Environment Canada, Ottawa, Ontario, Jan. 22-23.
- Doudoroff, P. (1976). Toxicity to fish of cyanides and related compounds, A Review: U.S. Environmental Protection Agency Report No. EPA-600/3-76-038.
- Ecological Analysts, Inc. (1979). Cyanide, an overview and analysis of the literature on chemistry, fate, toxicity, and detection in surface waters, Prepared for the Inter-Industry Cyanide Group.
- Engelhardt P.R. (1985). Long-term degradation of cyanide in an inactive leach heap, Cyanide and the Environment, Dirk van Zyl (Ed), Geotech. Eng. Program, Civ. Eng. Dept., Colorado State University, Fort Collins, Colorado, Vol. 2, pp. 539-547.
- Gannon, D.J. (1981). Toxicity of cyanide solutions, Proceedings from Cyanide and the Gold Mining Industry Seminar: Environment Canada, Ottawa, Ontario, Jan. 22-23.

- Hendrickson, T.M. and L.W. Daignault (1973). Treatment of complex cyanide compounds for re-use or disposal: U.S. Environmental Protection Agency, Report No. EPA-R2-73-269, 151 pp.
- Huiatt, J.L., J.E. Kerrigan, F.A. Olson, and G.L. Potter, eds. (1982). Cyanide from mineral processing workshop, Salt Lake City, Utah, Feb. 2-3. U.S. Bureau Mines and Utah Mining and Mineral Resources Research Institute.
- Kingsbury, J.M. (1964). Poisonous plants of the United States and Canada, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, p. 626.
- Knowles, C.J. (1976). Microorganisms and cyanide, *Bacterial Rev.* 40: 652-680.
- Oke, O.L. (1969). The role of hydrocyanic acid in nutrition, *World Rev. Nutr. Diet.*, 11:170-198.
- Owenback, D. (1978). The instability of free cyanide in photographic process effluents, *J. App. Pht. Eng.*, Vol. 4, pp. 72-76.
- Schmidt, J.W., L. Simovic, and E. Shannon (1981). Natural degradation of cyanides in gold milling effluents, *Proc. Sem. Cyanide and Gold Mining Industry Seminar: Environment Canada, Ottawa, Ontario, Jan. 22-23.*
- Scott, J.S. and J.C. Ingles (1981). Removal of cyanide from gold mill effluents, *Cyanide and the Gold Mining Industry Seminar: Environment Canada, Ottawa, Ontario, Jan. 22-23.*
- Smith, A. (1987). Testimony to Department of Health and Environmental Control, South Carolina Permit No. SC 0041378 Appeal Hearing, Columbia, SC, December 1987.
- Smith, Jr., L.L., S.J. Broderius, D.M. Oseid, G.L. Kimball, W.M. Koenst, and D.T. Lind (1979). Acute and chronic toxicity of HCN to fish and invertebrates, U.S. Environmental Protection Agency Report No. EPA-600/3-79-009.
- Steffen Robertson and Kirsten (1987). Internal report on cyanide in natural materials, Denver, Colorado.
- Towill, L.E., J.S. Drury, B.L. Whitfield, E.B. Lewis, E.L. Galyan, and A.S. Hammons (1978). Review of the environmental effects of pollutants: Section V - cyanide. Interagency Report, Oak Ridge National Laboratory, U.S. Environmental Protection Agency Report No. EPA-600/1-78-027.
- United States Department of Health, Education & Welfare (1964). Smoking and Health Report of the Advisory Committee to the Surgeon's General of the Public Health Service, Public Health Service Report No. 1103, U.S. Government Printing Office, Washington, D.C.
- United States Environmental Protection Agency (1980). Ambient water quality criteria for cyanides. EPA 440/5-80-037, NTISEPAOWP, PBB1 117483.