CYANIDE IN MINING: SOME OBSERVATIONS ON THE CHEMISTRY, TOXICITY AND ANALYSIS OF MINING-RELATED WATERS

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Abstract. The use of cyanide compounds in mining is frequently a controversial issue. Environmental groups often focus on the acutely toxic properties of many cyanide compounds to humans. The mining industry has argued that the dilute cyanide concentrations employed, the methods of use, and the rapid decomposition of these compounds make cyanide extraction a very safe alternative. Clearly the spill of almost two tons of sodium cyanide while being transported to the Kumtor mine, and the associated medical complaints and deaths have caused the public, especially in Kyrgyzstan, to reexamine these claims. While it is reasonable to be concerned about the acute poisoning of humans and other organisms from mining-related accidents, the more common environmental problems are likely to result from the chronic contamination of surface and ground waters by lower concentrations of cyanides and related breakdown compounds. Such chronic releases are much more difficult to notice and evaluate than are acute, high concentration spills that are often associated with rapid, observable deaths of aquatic organisms. Also, because mining-related waste waters are usually complex mixes of cyanides, metals, organic reagents and other anions, it is difficult to determine which chemical constituents are causing the toxicity problems.

   Contrary to much of the literature published in mining and regulatory documents, not all of the cyanide used in mineral processing breaks down quickly into largely harmless substances. Many of the breakdown compounds, while generally less toxic than the original cyanide, are known to be toxic to aquatic organisms, and may persist in the environment for significant periods of time. Some of these toxic breakdown forms include the free cyanides, metal-cyanide complexes, organic-cyanide compounds, cyanogen chloride, cyanates, thiocyanates, chloramines, and ammonia. Unfortunately, many of these chemical species are not detected in the routine laboratory analyses normally performed on mining-related waters. Thus, it is often assumed that they do not exist. For many reasons, national and international regulatory (and lending) agencies do not require monitoring for many of these chemical species.

   Adequate sampling and analysis of waters for cyanide and related breakdown compounds is complex and subject to considerable uncertainty. Because of these technical and regulatory limitations, a great deal is not known about the actual presence, persistence, and toxicity of these compounds in natural waters. As a result, it is likely that the negative impacts to aquatic organisms, especially sensitive fish populations, from releases of cyanide and related breakdown compounds at mineral processing sites is underestimated and undetected—in both developed and less developed countries.

   NOTE: The following paper discusses only selected aspects of the chemistry and toxicity of cyanide (CN) in waters associated with hardrock mining and is not intended to be a comprehensive review. It was written for a general audience with limited knowledge of chemistry. In this paper, mining-related waters refers to water associated with mining wastes-- such as heap leach process solutions, tailings, heap leach piles, waste rock---and water such wastes may impact. The latter may include rivers, lakes, ground water, pit lakes, oceans.

Introduction. The use of cyanide (CN) compounds by the mining industry raises many conflicting and confusing issues. Mining and regulatory documents often state that cyanide in water rapidly breaks down, in the presence of sunlight, into largely harmless substances such as carbon dioxide and nitrate. A recent report sponsored by the mining and cyanide manufacturing industries (Logsdon, M.J., *et. al.*, 1999) states: " Since cyanide oxidizes when exposed to air or other oxidants, it decomposes and does not persist. While it is a deadly poison when ingested in a sufficiently high dose, it does not give rise to chronic health or environmental problems when present in low concentrations." However, cyanide also tends to react readily with many other chemical elements and molecules to form, as a minimum, hundreds of different compounds (Flynn and Haslem, 1995). Many of these breakdown compounds, while generally less toxic than the original cyanide, are known to be toxic to aquatic organisms, and persist in the environment for significant periods of time. In addition, there is evidence that some forms of these compounds can be accumulated in plant tissues (Eisler, 1991) and may be chronically toxic to fishes (Heming, 1989; and

numerous other studies discussed later in this paper). Nevertheless, regulatory agencies do not require mine operators to monitor for these toxic cyanide-related compounds. Therefore, while much of the cyanide used at mineral processing sites does break down fairly readily, either as a result of natural degradation or the various treatment processes *sometimes* employed, significant amounts of the original cyanide form other potentially toxic compounds that may persist for long periods of time, and remain unaccounted for in the monitoring.

Background. Cyanide compounds are widely used in mineral processing to assist in the extraction of both precious and non-precious metals from rock. In gold extraction, a dilute cyanide solution is sprayed on crushed ore that is placed in piles, commonly called heaps, or mixed with ore in enclosed vats. The cyanide attaches to minute particles of gold to form a water-soluble, gold-cyanide compound from which the gold can later be recovered. Cyanide is used in a similar manner to extract silver from ores. In the extraction of non-precious metals such as copper, nickel, cobalt, molybdenum, etc., cyanide is used in the milling and concentration processes to separate the desirable metals from the wastes. In both precious and non-precious metal processing, cyanide and related compounds are, therefore, often contained in discarded wastes.

The general term "cyanide" refers to numerous compounds, both natural and man-made, having the chemical group CN, that is, one atom of carbon and one atom of nitrogen. About 80 percent of the commercially produced cyanides are used in the manufacture of organic chemicals such as nitriles, nylon, and acrylic plastics (Logsdon, *et.al.*, 1999). Several plants, some soil bacteria, and several species of invertebrate organisms produce natural cyanide and related compounds. G. Dixon (personal communic.,1999) reports that some blue-green algae naturally produce free cyanide at concentrations of less than 5 micrograms per liter. Selected edible plants contain potentially toxic concentrations of various cyanide-like compounds, for example: cassava, bamboo, lima beans, almonds, sorghum (Eisler,1991). **Nevertheless, cyanide compounds are seldom present in uncontaminated waters in environmentally-significant concentrations.**

Cyanide readily combines with most major and trace metals—a property that makes it useful in extracting metals from ores. Cyanide also tends to react readily with most other chemical elements, producing a wide variety of toxic, cyanide-related compounds. And because cyanide is carbon based—an organic compound—it reacts readily with other carbon-based matter, including living organisms.

Despite this complexity, there are only three categories of cyanide that mine operators must normally be concerned with: free cyanide, weak-acid-dissociable (WAD) cyanide, or total cyanide. Often, regulators require monitoring for only one of these categories. Furthermore, the analytical procedures used to determine these categories of cyanide fail to indicate the presence of many of the other toxic breakdown products of cyanide (see later discussion). One would assume that a procedure called **total** cyanide would determine all of the various forms of cyanide, but not so. For example, routine cyanide analyses fail to identify cyanates and thiocyanates, two significant cyanide breakdown products found at mine sites. Water samples from sites where cyanide is used as a process chemical may have WAD and or total CN concentrations that are quite low or undetected, yet when the same samples are also analyzed specifically for cyanates and thiocyanates, they may show tens of milligrams per liter (mg/L) or more of these compounds.

Numerous research and regulatory documents describe these categories of cyanide-related compounds as somewhat toxic, but generally do not state at what concentrations, and regard their potential presence as unimportant. Since routine analyses do not report these other compounds, it is often impossible to know if they are present in site waters, and at what concentration.

Cyanide is used by the mining industry in tremendous quantities, with most being handled without obvious negative impacts. Nevertheless, several accidental releases of cyanide-bearing mine process wastes have recently been reported in the news media. More than 860 million gallons of cyanide-laden tailings were released into a major river in Guyana when a dam collapsed at the Omai gold mine in 1995. Failure of a leach pad structure at the Gold Quarry mine in Nevada released about 245,000 gallons of cyanide-laden wastes into two creeks in 1997. On May 29, 1998 six to seven tons of cyanide-laden tailings spilled into Whitewood Creek in the Back Hills of South Dakota, from the Homestake Mine, resulting in a substantial fish kill. A dam at the Los Frailes zinc mine in southern Spain ruptured in April 1998 releasing an estimated 1.3 billion gallons of acid, metal-laden tailings into a major river and adjacent farm lands. While the news reports of the associated massive fish kill do not mention cyanide or related compounds in the wastes, their presence seems likely given the nature of the metals extracted at this site. Finally, on May 20,1998, a truck transporting cyanide to the Kumtor mine in Kyrgyzstan plunged off a bridge spilling

almost two tons, about 1762 kilograms, of sodium cyanide into local surface waters (Hynes, *et. al.*, 1998; Moran, R. E., 1998).

The Kyrgyzstan spill and its impacts present an excellent example for examining the limitations of cyanide regulation and monitoring, and the numerous uncertainties about cyanide chemistry and toxicity to sensitive aquatic organisms. These issues are discussed at the end of this paper.

Basic Cyanide Chemistry

Much of this section is based on the following references: Smith and Mudder,(1993); Colorado Dept. of Natural Resources,(1999); Ingles and Scott,(1987); Flynn and Haslem,(1995); Scott and Ingles,(1981);Stanton,and others,(1986); Environment Australia,(1998). This and the other sections benefited from telephone discussions with Dr. Owen Mathre, consulting chemist, formerly research chemist for more than 35 years with E.I. DuPont, one of the main manufacturers of commercial cyanide.

Free Cyanide

Most commonly, cyanide used at mining sites is in the form of sodium cyanide, NaCN. This white solid dissolves readily in water, yielding sodium ion, Na^+, and cyanide ion, CN^-. Some of the CN^- then converts into HCN, hydrogen cyanide or hydrocyanic acid. The cyanide ion, CN^-, and hydrogen cyanide, HCN, are often collectively called free cyanide, and the relative amounts present are largely controlled by the water pH.

Cyanide ion, CN^-, is the predominant stable form of free cyanide above a pH of about 9.0 to 9.5, depending upon the dissolved solids concentration of the water. As the pH drops, increasing amounts of CN^- convert to hydrogen cyanide, HCN. The percentage of HCN continues to increase as the pH drops further, until at a pH of 7.0, about 99.5% of the cyanide exists as HCN. At pHs below 7.0, essentially all dissolved cyanide is present as HCN. Thus, most free cyanide in natural waters is present as HCN since the "natural" pH range is between about 6.0 and 8.5.

HCN readily forms a gas, some of which is released into the air. (This is the same gas used in execution chambers.) Mining industry literature often gives the impression that such volatilization is a major factor in reducing the concentration of cyanide compounds in mineral processing wastes. It is likely true that significant amounts of HCN gas are released into the air from process solutions (or other cyanide-water solutions), but studies by the U.S. Geological Survey (Johnson, *et. al., 1999*) indicate that this may be a minor cyanide loss pathway within some process wastes. These studies indicated that the majority of the mass of free cyanide was converted to other forms, and retained within the heap leach piles by adsorption or precipitation.

Most mining process solutions, such as tailings solutions or leach solutions, are kept at alkaline pH levels, usually above about 10.0, because metal extraction is more efficient at these pHs. This is accomplished by adding alkaline compounds such as lime or sodium hydroxide to cyanide-containing mining solutions. The elevated solution pH also prevents the formation of the HCN gas, and accidental poisoning of mine workers via inhalation. All free cyanide forms are highly toxic to humans and aquatic life if ingested, even where the solution pH is high.

Free cyanide forms readily react within a few hours to a few days with almost any other chemicals they contact, producing a wide variety of new compounds. Such compounds are often put in the following groups: simple cyanide compounds; cyanide complexes; and cyanide-related compounds.

*When technical papers mention **cyanide**, they normally mean the solid sodium cyanide, or equivalent forms, and free cyanide forms only. Thus, when it is stated that cyanide does not persist in the environment, it is technically correct, but fails to mention the numerous, other forms of toxic cyanide compounds that do persist. And, many of these compounds can later release free cyanide under favorable conditions.*

Simple Cyanide Compounds

Compounds such as sodium cyanide, NaCN, potassium cyanide, KCN, and calcium cyanide, $Ca\,(CN)_2$ are all readily soluble, and are called simple cyanide compounds. Some simple cyanide compounds are insoluble, such as $Zn(CN)_2$, CuCN, $Ni(CN)_2$, and AgCN.

Metal-Cyanide Complexes

Cyanide binds with numerous other organic and inorganic molecules to form compounds called cyanide complexes. Only the metal-cyanide complexes will be mentioned here.

A low-grade gold ore suitable for cyanide leaching might contain only 0.5 to 1 gram of gold per ton (0.5 to 1.0 parts per million gold). In contrast, this same ore may also contain other metals such as copper, zinc, and nickel in concentrations ranging from tens to thousands of parts per million. Thus, the cyanide leach solutions would contain numerous metal-cyanide complexes. These complexes are generally much less soluble than are free cyanide (Environment Australia, 1998), and frequently will form solids that drop out of solution. Once these complexes are formed and then released into the near-surface environment, they begin to decompose at varying rates, some quickly, others quite slowly. The decomposition of metal-cyanide complexes releases cyanide into the soil or water. Those complexes that most readily decompose are referred to as weak complexes, those most resistant to decomposition are called strong complexes. The weak and moderately-strong complexes will decompose in weak to moderately-strong acids, releasing environmentally significant concentrations of free cyanide. Examples of each category are:

Weak Complexes--- $Zn(CN)_4^{-2}$, $Cd(CN)_3^{-1}$.

Moderately Strong Complexes--- $Cu(CN)_2^{-1}$, $Ni(CN)_4^{-2}$, $Ag(CN)_2^{-1}$.

Strong Complexes--- $Fe(CN)_6^{-4}$, $Co(CN)_6^{-4}$, $Au(CN)_2^{-1}$.

Some of the strong complexes do not break down in the presence of strong acids, but will decompose when exposed to various wavelengths of light, releasing free cyanide. This is especially true of the iron cyanides, which are often the most common forms in mining wastes. Flynn and Haslem (1995) states that iron, cobalt, and chromium-cyanide complexes normally are not decomposed by acids or bases, but can absorb visible or ultraviolet light and decompose into free cyanide. Clearly this statement is not absolutely true since there are numerous references to such complexes being dissolved in very strong acids.

The decomposition rates of these complexes are also affected by the water temperature, pH, total dissolved solids, and complex concentration. Some complexes degrade more rapidly when exposed to sunlight, atmospheric CO_2 and air. Also, some complexes degrade more rapidly when they percolate through soils, are agitated and mixed by wind or streams, or are metabolized by bacteria.

Cyanide complexes that are stable in alkaline settings will usually decompose more rapidly in neutral or low pH environments, but some complexes may be stable for decades. The author has encountered cyanide-contaminated sediments at a cobalt-nickel mine in Missouri (USA) that contained many milligrams per kilogram of total CN more than 25 years after all processing had ceased, indicating the persistence of some complexes---probably iron cyanide and cobalt cyanide complexes. Samples of bricks, concrete, plaster and mortar from buildings at the Auschwitz-Birkenau concentration camps collected about 45 years after all use of cyanide ceased still showed detectable concentrations of cyanide, presumably as iron cyanides (Markiewicz, *et.al.*, 1994).

Cyanide-Related Compounds

Cyanide in mining solutions can undergo several types of reactions to form various toxic cyanide- related compounds. The following cyanide-related compounds are considered to be toxic to aquatic organisms (see following section), although generally at concentrations much higher than for free cyanide.

Cyanate, NCO^-, is formed when alkaline solutions of cyanide react with oxidants such as chlorine, hypochlorite, ozone, sulfur dioxide/ oxygen and hydrogen peroxide. In fact, the mining industry often uses several of these oxidants to decompose cyanide in wastes. When hypochlorite is used to destroy cyanide in alkaline solutions (the process is referred to as alkaline chlorination), an intermediate toxic compound is formed, **cyanogen chloride,** ClCN, which is then converted to cyanate. Since cyanogen chloride is more volatile than HCN, it may be less persistent, and decomposes within minutes to cyanate at pH 10 to 11. There seems to be considerable uncertainty about the chemical behavior of cyanogen chloride at lower pHs. Hynes, *et. al.*(1998) state that cyanogen chloride is a soluble gas that remains in solution above pH 8. Various strains of microorganisms will also convert cyanide into cyanate, and then to carbon dioxide. Alkaline chlorination may also result in the formation of **chloramine**, NH_2Cl, or similar chlorinated ammonia compounds. Chloramine is less toxic than CN^-, but is likely to be present in much higher concentrations, and may persist for significant periods of time.

Free cyanide also reacts with forms of sulfur in mining effluents, such as sulfur, thiosulfates, or sulfide ions, to produce **thiocyanates**, SCN^-. Thiocyanate also combines with metals to form metal-thiocyanate complexes. Plumlee and others, (1995) report that relatively high concentrations of thiocyanate may persist in the presence of acidic solutions. Once formed, thiocyanate may also convert to free cyanide and sulfate, especially at cyanide destruction facilities where insufficient oxidant has been used. Thiocyanate concentrations in the range of tens of milligrams per liter have also been reported in copper tailings waters with pHs above 10.0. The INCO cyanide destruction process converts many cyanide compounds to cyanate

and thiocyanate. Thiocyanate concentrations of 168 to 680 mg/L have been detected in effluents following such treatment (Lanno and Dixon, 1994).

Free cyanide will also form **cyanogen**, NC-CN, under acid conditions if an oxidant such as oxidized copper minerals is present. The formation of cyanogen would not be expected where mining solutions remain strongly alkaline, but might develop if acid mine drainage were to form, or if acidic solutions were to contact cyanide –bearing solutions. Cyanogen is a gas at room temperatures that was used in poison gas warfare. It is unclear whether cyanogen is stable in mildly alkaline or circum-neutral pH waters.

The chemical breakdown of many of the above-mentioned cyanide and cyanide-related compounds often results in the formation of high concentrations of **nitrate** and, or **ammonia**. The latter may also reach concentrations toxic to aquatic organisms. While many cyanide forms begin to degrade readily when exposed to air, water, and sunlight, these same compounds may persist in the environment if released during winter when lakes or streams may have snow and ice cover, and temperatures are reduced. Areas with high rainfall and persistent cloud cover also have restricted rates of natural cyanide destruction. (Environment Australia, 1998). This phenomenon indicates that similar restrictions can be expected at sites in the tropics.

In general, most cyanide research relevant to mineral processing has been done under alkaline conditions. As a result, much less is known about the stability, persistence, and fate of many cyanides and related compounds in mildly-alkaline and acidic environments.

Toxicity of Cyanide Compounds
(The following is based largely on Ingles and Scott,1987; Eisler,1991; Heming,1989; and Palmes,1991 Lanno and Dixon, 1996; Kevan, and Dixon, 1991,1996; Brown., et.al., 1995; Lanno and Dixon, 1994; Ruby,et.al.,1979; Dixon and Leduc, 1981; Dixon and Sprague, 1981).; and on conversations with D.G. Dixon, Professor of Biology, U. of Waterloo,Canada).

Given the limitations of routine analytical techniques for measuring cyanide, and the presence of cyanide breakdown forms in mining waste waters, it follows that considerable uncertainty exists regarding the actual toxicity of various cyanide forms to living organisms. Much of the uncertainty exists because mining-related waters generally contain complex mixtures of potentially-toxic metals and non-metals, along with the cyanide and related compounds. Determining which chemical constituents are actually causing a toxic response can be very difficult.

Mineral industry literature seldom reports specific toxicity data on cyanide compounds. Instead, it is more common to read statements like the following: " Hydrogen cyanate and cyanate ions are significantly less toxic than HCN." And, " Thiocyanate is relatively non-toxic, when compared with cyanide"(Smith and Mudder, 1993). In this setting, the toxic role of cyanide breakdown compounds is generally neglected.

Cyanide is present in mining-related waters in many forms, most of which have no established water quality criteria. The current U.S. Environmental Protection Agency water quality criterion for cyanide is 5.2 micrograms per liter (µg/L) for freshwater aquatic life, and 1.0µg/L for marine aquatic life and wildlife (EPA,1986). Yet no criteria exist for other toxic cyanide-related compounds, including cyanate, thiocyanate, cyanogen chloride and the metal-cyanide complexes.

Toxicity to Fish

Table 1 summarizes some of the toxicity data for cyanide and related compounds that can be found at mineral processing sites. Discussions on toxicity for each of these compounds focus on fish, since they are the most sensitive species, and are impacted by relatively low cyanide concentrations. For example, fish are killed by cyanide concentrations in the *microgram per liter* range, whereas bird and mammal deaths generally result from cyanide concentrations in the *milligram per liter* range.

Acute toxicity is described as those concentrations of cyanides that lead to the death of more than 50 percent of the test population within 96 hours (Ingles and Scott, 1987). Chronic exposure may be described as exposure to less-than-lethal concentrations of cyanides. Some chronic effects may last for 10 days after an individual spill. In addition, chronic cyanide exposure may affect reproduction, physiology, and levels of activity of many fish species, and may render the fishery resource non-viable. Whether the toxic effects of HCN are cumulative is apparently not known.

Table 2 lists several other factors that affect cyanide toxicity to freshwater fish.

Modern cyanide leach processes use *dilute* solutions of sodium cyanide, yet such solutions may initially contain from 100 to 500 mg/L free cyanide. After use in leaching processes, barren solutions may contain from 50 to 2000 mg/L total cyanide (Logsdon, *et.al.,*1999). Lanno and Dixon (1994) report thiocyanate concentrations to range between 168 and 680 mg/L in effluents from gold ore concentrators using the INCO cyanide destruction process. Unfortunately, concentration data for cyanide breakdown compounds are not routinely collected or reported.

George Dixon of the University of Waterloo, Canada (personal communications, 1999) argues that there are great gaps in our understanding of cyanide toxicity to aquatic organisms. Thus, the information in Table 1 provides only a rudimentary picture of the toxicity complexities. For example, very little is known about the biological and chemical transformations that solid metal-cyanide complexes go through when they are consumed by organisms. Little is known about the potential toxicity of such complexes to fish and invertebrates, or the rates at which such complexes decompose yielding free cyanide. Mineral process sites that use the INCO cyanide degradation procedure often generate effluents that contain cyanate, thiocyanate, and free cyanide at the same time. Theoretically, such mixtures should produce synergistic toxic responses, but such details are not understood. Few details are known about the chronic toxicity of cyanate. The toxicity of cyanate and thiocyanate may be underestimated because experiments are often performed using fish eggs that are not permeable to these constituents. Eggs are permeable for approximately 20 minutes after being laid; after this time the membranes harden.

While most regulated process effluents comply with their chemical discharge standards (in Canada), they are often still toxic to organisms in bioassay tests. Thus, the complex mixtures produce toxicity effects we don't understand, or there are toxic constituents in these waters that are not being detected or regulated. Dr. Dixon considers waters with greater than 0.20 milligrams per liter WAD cyanide acutely toxic to all fish.

Toxicity to Humans

The topic of cyanide toxicity to humans comes loaded with a lot of psychological baggage. While it is correct that cyanide compounds are widely used in modern society, and that they are only one type of many potential poisons we use daily (i.e. lime, gasoline, household cleaning supplies), cyanides are different. Part of this difference results from the extremely complex chemical interactions cyanides can undergo. More compelling, however, is its use in human executions. HCN was the active ingredient in Zyklon B, the chemical used by the Germans to execute inmates in the concentration camps of Auschwitz, Birkenau and Majdanek (Pressac, 1989). Yes, the general public may overreact whenever cyanides are the topic of discussion---but there are understandable historic roots to such responses.

Stanton and others (1986) states that HCN ingested orally is fatal to humans in doses ranging from 50 to 200mg, about the size of a grain of rice. Dr. Gerry Henningsen, a toxicologist with the U.S. Environmental Protection Agency reports that HCN concentrations above 40 to 200 mg/L are likely to be toxic to mammals, including humans (oral communication, Sept. 1998). If exposed to a sufficiently-high dose, humans may die within a few minutes.

According to numerous industry documents, sodium cyanide has been used for decades in mining, and no recorded accidental fatalities have been associated with its use. One of the most recent industry-sponsored reports (Logsdon, *et. al.*, 1999) states that a search of industrial accident records in Australia, Canada, New Zealand and the United States revealed that cyanide was implicated in only three accidental deaths at gold mine sites in the past 100 years. In May 1998, four deaths were reported by government officials in Kyrgyzstan to be due to, or at least aggravated by contact with cyanide that spilled while being transported to a mine. A report sponsored by CANMET (Hynes, *et.al.*, 1998) argues that none of these reported deaths were directly attributable to the cyanide spill (see Kyrgyzstan Case Study, pg. 7).

Monitoring and Analysis of Cyanide at Mine Sites
(Much of the following is taken from Amer. Public Health Assoc.,1995, section 4500-CN.; Smith and Mudder,1993.)

"Despite its critical importance, the analysis for cyanide in mining-related solutions remains a source of concern and confusion to both operators and regulators alike." Smith and Mudder, (1993).

The great reactivity of cyanide and related compounds makes sample analysis difficult and the resulting data often subject to significant errors. Also, natural water samples often contain chemicals that act as

interferences to the analysis of cyanide forms.   Nevertheless, water samples from mining sites are most commonly analyzed for only three forms of cyanide: free cyanide; weak acid dissociable (WAD) cyanide; and total cyanide.

Cyanide Analytical Methods

The free CN analytical method reports the sum of both forms of free cyanide—the cyanide ion and hydrogen cyanide. The "WAD cyanide" method measures the free cyanides plus the cyanide complexes that break down in a hot, mildly acid solution--about pH 4.5. The "total cyanide" analysis measures the free and WAD cyanide forms, plus those metal complexes that break down in a hot, concentrated acid solution (pH <1.0). The total analysis includes **most** metal –cyanide complexes, including most strong complexes, but may not detect many of the organic –cyanide compounds. (Although organic-cyanide compounds are not reported found in significant concentrations at mineral process sites, it is unclear whether samples have been analyzed adequately to determine the presence of these compounds.)

Both the WAD and the total CN methods fail to detect many forms of cyanide or cyanide-related compounds that are likely to be present at mining sites**. The WAD method, for example, fails to detect: cyanates, thiocyanates, most cyanogen, cyanogen chloride, chloramines, most organo-cyanide compounds, and most gold, platinum, and cobalt complexes, and most importantly, iron cyanide complexes. The total cyanide method fails to detect: cyanates, thiocyanates, chloramines, most organic-cyanide compounds, and most cobalt and platinum cyanide complexes.** Thus, neither the total or WAD methods measure the total concentration of cyanide and related forms. If one wishes to determine, for example, the concentration of cyanates and, or thiocyanates, analyses specific for these parameters must be requested from the laboratory.

Many regulatory agencies require monitoring for free or WAD cyanide, especially during closure. The other cyanide-related forms discussed in this report are generally neglected. Given the variable stabilities of the metal-cyanide complexes, **total** cyanide would provide a more realistic measure of potential toxicity. This is especially relevant since fish and mammal guts are strongly acid, pH 0.9-1.8, and total analyses would better represent the free cyanide likely to be released under such conditions.

Because of the previously-mentioned complexities and uncertainties involved in cyanide analysis, it is usually not reasonable to interpret routine cyanide analytical data more precisely than ± 0.005 mg/L, or even ± 0.01mg/L in many cases. Concentrations reported below these levels are often not meaningful, except under research conditions.

Case Study:Cyanide Spill in Kyrgyzstan

On May 20, 1998, a truck transporting cyanide to the Kumtor gold mine in Kyrgyzstan plunged off a bridge, spilling about 1762 kilograms (kg) of sodium cyanide into a river upstream of several villages. While the material spilled was a concentrated form of cyanide and not tailings or heap leach waters, the incident illustrates many of the environmental and regulatory problems discussed in this paper. What transpired in the few days after the spill has been the subject of considerable speculation and disagreement. Within days after the spill, hundreds and possibly thousands of local residents sought treatment at local medical clinics. According to a report by the Russian Federation Ministry of Defense, at least one death was related to the cyanide spill. The mining company and some officials of the Kyrgyz government, which holds a majority ownership in the mine, argued that few if any significant impacts occurred to any living organisms or the overall environment, as a result of the spill. This general conclusion was also presented in an assessment by scientists from Canada and Russia, overseen by CANMET. (Hynes, *et.al.,* August,1998).

Some of the major conclusions of the CANMET-sponsored study were (wording is quoted):

1. All the cyanide concentrations in air were well below safe industrial hygiene/ occupational guidelines.
2. There was no possible exposure to cyanogen chloride as it could not have been generated in significant quantities. The potential for cyanogen chloride generation did exist due to the operating pH (pH 8.5). However, the sodium or calcium hypochlorite was added to areas with low cyanide concentrations so insignificant concentrations of cyanogen chloride were formed.
3. The cyanide concentration in Barskaun River water was potentially high enough to cause serious health effects at least several hours after the spill to anyone who drank a sufficient quantity of the water. River modelling indicates the travel time from the accident site to the lake was 4 hours. The total time required for the cyanide to clear from the Barskaun river would have been approximately 10 hours.

4. In the days following the spill, fish habitats had been repopulated indicative of low cyanide levels in the Barskaun River and the Issyk-Kul lake following the spill. This observation provides evidence to confirm the river/ lake environment is safe for public use.
5. There was no reasonable cyanide exposure route to people eating fish.
6. There has been no damage to Lake Issyk-Kul either in the short or long term.
7. Cyanide concentrations in the ditches of the villages of Barskaun and Tamga do not support cases of cyanide exposure causing human health effects. Nor is there any possible cyanide exposure route for the villages of Tosor, Chon-Dzargylchak and Al-Terek.
8. Up to 16 cases of cyanide exposure could have occurred; however, these cases have not been confirmed. No medical evidence has yet been supplied to support these cases as being cyanide related. Thus this committee is not able on a scientific basis to confirm that these people suffered adverse health effects as a direct result of the cyanide spill.
9. None of the 16 potential cases are likely to experience long-term health effects in the future. Nor would cyanide exposure normally have required hospitalization for more than a few days.
10. There were no reported deaths within the first 72 hours; deaths after this time cannot be directly attributed to cyanide exposure in this situation.
11. Widespread use of the cyanide antidotes was inappropriate, and may have itself caused harmful health effects to the patients.
   Some of the report recommendations were:
1. The use of sodium hypochlorite should be discouraged as a response to the treatment of cyanide spills in the environment due to the potential formation of cyanogen chloride.
2. A reassessment of the four fatalities should be completed to determine the exact cause of death.
   The authors further state that:
   - Some river fish were killed by the spill.
   - At present we have been informed of approximately 2600 cases of cyanide exposure from the Barskaun spill, with four resulting fatalities. We have attempted to verify the diagnosis of this large number of people by requesting copies of their medical information from the Kyrgyz Ministry of Health, through the Canadian Embassy and later through Kumtor Operating Co. To date, we have not been given access to these records, so we are unable to assess the diagnosis made in individual cases.

These findings suggest some comments. Water samples collected about 20 meters from the spill site (presumably downstream) within hours of the accident contained up to 79.5 mg/L of **free cyanide, which was the only cyanide form reported**. Since standard cyanide analytical techniques fail to detect several forms of cyanide and cyanide-related compounds, the reported concentrations would not include cyanide from many of the stronger metal-cyanide complexes, nor would they include cyanates, thiocyanates, cyanogen, cyanogen chloride, or indications of ammonia or chloramine concentrations. All of these compounds could have formed following the spill, and all are toxic to aquatic organisms. Furthermore, it is unclear that any of the early samples were collected prior to the application of the sodium hypochlorite. Thus, available data give an incomplete picture of the toxic forms of cyanide potentially present at the spill site.

According to Dr. Owen Mathre, a former research chemist for E.I. DuPont, the dissolution of approximately 1800kg (about two tons) of solid sodium cyanide under these conditions would probably require several hours to complete. Since the pre-spill pH of the river was likely less than 9.0, most of the dissolved cyanide would have formed HCN, a toxic gas that would have escaped into the air. Within a few hours of the accident, sodium hypochlorite was applied to areas near the spill site to break down the cyanide. Application of this chemical, however, would likely result in the formation of cyanate and cyanogen chloride, cyanide-related compounds that are toxic to aquatic organisms. Cyanogen chloride is a heavy gas that could have traveled significant distances from the spill, and has been known to cause throat and eye irritation in mine workers. Therefore, this compound, together with the presence of gaseous ammonia, may have contributed to some of the medical complaints of the citizens.

The CANMET authors were certain that insignificant amounts of cyanogen chloride were generated because the hypochlorite was added to areas with low cyanide concentrations. If the areas had been doused with hypochlorite, the investigators would have been unable to determine the early cyanide concentrations. Also, their certainty about the predictions of the exact maximum cyanogen chloride concentration (0.0117 mg/m^3) is impressive given the general uncertainty of the literature on cyanogen chloride formation outside the laboratory. Such information is especially uncertain below pH 10 to11. Such a spill is not a controlled

event as in a laboratory; it is much more complicated. Flynn and Haslem (1995) state that cyanide can be oxidized to cyanogen, but only in acid solutions. Could this process have occurred at circum-neutral pH, before the addition of hypochlorite? Apparently no field measurements (temperature, specific conductance, or pH) were made and no "complete" water quality samples were collected and analyzed during the days immediately following the spill.

The main report makes no mention of detailed evaluations of fish or benthic invertebrate population studies after the spill, either in the river or at the lake. (The report appendices were not available to the author). The fact that fish have returned to an area says little about the extent of either the acute or chronic impacts from the event. It is reasonable to assume that metal-cyanide complexes formed in the river sediments and lake sediments near the river mouth.

Given the lack of complete, reliable data from the first two days after the spill, it is unlikely that the details of the cyanide chemical interactions can be determined, except very generally. A review of the medical records by unbiased observers would aid the interpretation of the human toxicity questions greatly.

Conclusions

While much of the cyanide present in mining-related waters breaks down into largely harmless compounds, significant concentrations of other potentially toxic cyanide breakdown compounds may persist. These compounds present the most risk to sensitive freshwater fish species. Such compounds include many metal-cyanide complexes, cyanates, thiocyanates, cyanogen, cyanogen chloride, chloramines, together with ammonia, and nitrate. No regulatory standards exist for most of these potentially toxic constituents, with the exception of ammonia and nitrate. Most state and federal agencies require mining-related water samples to be analyzed using either the free or WAD cyanide methods only. Neither method detects the majority of the cyanide-related compounds. A tailings or heap leach pad water sample can easily have a WAD cyanide concentration of less than 0.05 mg/L and still contain concentrations of cyanate, thiocyanate, or metal-cyanide complexes, for example, that are potentially toxic to fish.

Not only are there gaps in U.S. water quality regulations pertaining to cyanide and related compounds, but substantial problems exist in developing regions such as Latin America, Africa, and Asia. In many developing countries oversight and enforcement of mining regulations are often quite lax, and mining operations are often owned, at least partly, by the government, creating regulatory conflicts of interest. Thus, reasonable enforcement of cyanide-related regulations becomes even more difficult.

Table 1. **Toxicity of Cyanides and Cyanide-Breakdown Compounds to Freshwater Fish**
Free cyanides: free cyanides (the cyanide ion and hydrogen cyanide) are well known to be the cyanide forms most toxic to mammals and aquatic life. Acute toxicity to various fish species ranges from about 20 – 640 micrograms per liter (Ingles and Scott, 1987).
 The more sensitive rainbow and brown trout generally exhibit acute toxicity in the range of 20 – 80micrograms per liter. Chronic toxic effects are reported in fish in the range of 5-20 micrograms per liter.

Metal-cyanide complexes: Such complexes are generally thought to be less toxic than free cyanide. However, they are less well understood. Metal-cyanide complexes break up to yield HCN, which is the usual cause of toxicity. Some complexes, including silver, copper and nickel cyanides may themselves be toxic. The iron cyanide complexes are not particularly toxic, but release free cyanide on exposure to sunlight. Ingles and Scott (1987) report the following acute toxicity ranges for selected cyanide complexes (for selected freshwater fish species): sodium and potassium cyanides 0.02 - 0.3 mg/L; zinc cyanide 0.02-0.3 mg/L (Environment Australia, 1998, reports 0.18 mg/L); cadmium cyanide 0.02 – 0.3 mg/L; copper cyanides 0.4 – 4.0 mg/L; nickel cyanide 0.4 mg/L (pH 6.5) – 730 mg/L (pH 8.0); and iron cyanides 300 mg/L in darkness and less than 0.2 mg/L in light (Environment Australia,1998, reports 860mg/L – 1210 mg/L in darkness, and 35 mg/L in light for both the ferrocyanide and ferricyanide complexes). Ingles and Scott (1987) state that the ferrocyanide complex is the more toxic of the two since it contains about five times as much free cyanide. Doudoroff, (1976) stated that the chronic toxicity of metal-cyanide complexes needed to be investigated. This conclusion is still relevant.

Organic-cyanide compounds: These compounds vary greatly in their toxicity; minimal data has been published relative to fish. Doudoroff, (1976) states that malano nitrile, which has been used to extract gold from ores, is cumulatively toxic at concentrations similar to those of free cyanide.

Cyanogen chloride: Cyanogen Chloride is an intermediate toxic compound that is formed when hypochlorite or chlorine is combined with cyanide or thiocyanate in alkaline solutions. This compound may be more toxic to fish than free cyanide (Doudoroff,1976). Ingles and Scott,(1987) state that it has about the same toxicity as cyanide.

Cyanates: Cyanate is the main form of cyanide resulting from most cyanide decomposition processes employed at mineral process sites. Cyanate may persist in water for significant, but undefined periods of time. Ingles and Scott, (1987) report cyanates to be toxic to trout at concentrations ranging from 13 to 82 mg/L cyanate.

Thiocyanates: . Ingles and Scott,(1987) report thiocyanate toxicity for fish to range between 90 and 200milligrams per liter. Heming and Thurston, (1985), and Heming and others,(1985) report toxicity to be between 24 to 70 mg/L thiocyanate, SCN^-, for brook trout. Heming and Blumhagen(1989) report that thiocyanates cause "sudden death syndrome" in trout, partly as a response to stress, and because thiocyanate is accumulated ---contrary to much previously published literature. Lanno and Dixon (1994), report that juvenile fathead minnows showed numerous negative effects after chronic (124 days) exposure to thiocyanate: thyroid tissue changes started as low as 1.1 mg/L; reproduction effects were noted at 7.3 mg/L and above; overt goiter was noted as low as 7.3 mg/L. Many of these effects are believed to be controlled by the antithyroid activity of thiocyanate.

Chloramines: Chloramines are chlorinated ammonia compounds that are less toxic than free cyanide, but are likely to be present in much higher concentrations. Chloramines can be formed as a result of alkaline chlorination. The presence of chloramines is normally determined via analysis for total residual chlorine. EPA (1986) states that freshwater aquatic organisms should not be exposed to total residual chlorine concentrations exceeding 11 to 19 micrograms per liter.

Ammonia: Ammonia is a routinely encountered breakdown product wherever cyanide mineral processing occurs. It is the only cyanide-related compound discussed in this report that is regulated by state or federal agencies. It is considered to be about as toxic to fish as cyanide. U.S. EPA (1986) reports ammonia to be toxic to fish at concentrations between 0.083 and 4.6 mg/L. Some data indicate that the combined effect of ammonia and cyanide is greater than would be assumed on the basis of their individual toxicities. As mentioned above, ammonia may be present indirectly as chlorinated ammonia compounds such as chloramines.

Table 2. Factors Affecting Cyanide Toxicity to Freshwater Fish

Cyanide concentration: Toxicity increases with higher concentrations of cyanides.

Oxygen concentration: Cyanide toxicity increases with any reduction in dissolved oxygen below 100%.

Temperature: Toxicity increases 3-fold with a 12 degree C decrease in temperature.

pH: Slight decrease in toxicity at pH above about 8.5 due to conversion to CN^-.

Chloride: Greater than about 8.8 parts per thousand of chloride decreases survival time.

Other dissolved constituents: The presence of zinc and ammonia results in a greater-than-additive increase in toxicity.

Other Factors: Toxicity will also depend on the age and health of the fish, the amounts of water ingested, and the stress level on the animal.

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