Cyanide Uncertainties

Observations on the Chemistry, Toxicity, and Analysis of Cyanide in Mining-Related Waters

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FOREWORD

The hardrock mining industry has derived big profits from cyanide. This toxic chemical has made it possible for mining companies to mine low-grade ore bodies for microscopic flecks of gold and silver, and still turn a profit.

The use of cyanide in mining, however, is becoming more and more controversial. Mining such low-grade ore creates vast open pits, and produces huge quantities of waste rock. In addition, cyanide is a toxic chemical—one teaspoon of two percent cyanide solution can cause death in humans. And in recent years, a string of cyanide-related mine accidents has added to community fears and concerns. (See box on page 5.)

The most dramatic mine-related cyanide spill occurred this year in Kyrgyzstan. On May 20, 1998, a truck transporting cyanide to the Kumtor gold mine plunged off a bridge, spilling almost two tons of sodium cyanide into a local river. In the aftermath, hundreds were treated at local hospitals, and a Kyrgyz government report documented at least one human fatality. The mining company, Cameco Corporation, disputes this report.

Nevertheless, the mining industry maintains that cyanide breaks down quickly in the environment, and that mining companies safely handle large quantities of this chemical.

The Rest of the Story

As this report demonstrates, however, there is much that is unknown and uncertain about the toxicity of cyanide. The mining industry and regulators claim that cyanide rapidly breaks down in water into harmless compounds, but this is only part of the cyanide story. The rest of the story is that cyanide also breaks down into compounds that are potentially toxic to fish and other aquatic organisms. Many of these compounds are generally less toxic than the original cyanide, but may persist for long periods of time. And there is evidence that some of these compounds are stored, or bioaccumulate, in plant and fish tissue.

In addition, when mine operators test for cyanide, they are not required to test for these breakdown compounds. In essence, these compounds go unregulated despite the potential environmental impacts.

There are many legitimate questions about environmental and human health impacts related to the use of cyanide at mining operations that mine operators, regulators, and health officials are simply unable to answer at this time. Mineral Policy Center has produced Cyanide Uncertainties to help industry, government regulators, and local citizens begin the process of assessing these very real, and very serious uncertainties related to cyanide.

Stephen D'Esposito
President
Mineral Policy Center

MPC'S RECOMMENDED STEPS TOWARD ASSESSMENT OF CYANIDE UNCERTAINTIES

Voluntary industry monitoring of all cyanide-related compounds at mines, with public release of the information.

Immediate U.S. Environmental Protection Agency investigation to determine standards for these potentially toxic cyanide-related compounds.

Adoption of stricter environmental standards for all mining operations that use cyanide and are funded by public institutions. Such projects should be subject to greater public disclosure.

Appointment of citizen oversight boards at all mines that use cyanide to ensure public access to information.

Independent environmental audits of all U.S. and international mining operations that use cyanide.

INTRODUCTION

The use of cyanide compounds by the mining industry, coupled with limitations in current analysis and monitoring of these compounds, raises serious concerns regarding public safety and environmental protection at mine sites using cyanide processing.

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 or ammonia. However, cyanide also tends to react readily with many other chemical elements, and is known to form, at 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. In addition, they may persist in the environment for long periods of time, and there is evidence that some forms of these compounds can be accumulated in plant (Eisler, 1991) and fish tissues. (Heming, 1989)

Despite the risks posed by these cyanide-related breakdown compounds, regulatory agencies do not require mine operators to monitor this group of chemicals in mining-related waters. Therefore, while much of the cyanide used at mining 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 potentially toxic compounds that remain unaccounted for in the monitoring of mining operations.

Mining with Cyanide

Cyanide compounds are widely used by the mining industry to assist in the extraction of both precious and non-precious metals from rock. In gold mining, 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, and molybdenum, cyanide is used in the milling and concentration processes to separate the desirable metals from the wastes. Consequently, cyanide and related compounds often are contained in discarded mine wastes.

While most of the cyanide used by the industry is handled without obvious negative impact, the unique chemical behavior and toxic nature of these compounds, combined with the risk of serious mine waste spills, suggest that this topic merits a closer look.

Complex Chemical Behavior

The general term "cyanide" refers to various compounds having the chemical group CN, that is, one single atom of carbon (C) and one single atom of nitrogen (N). Several plants, some soil bacteria, and several species of invertebrate organisms produce natural cyanide and related compounds. Nevertheless, cyanide compounds are seldom present in uncontaminated waters in measurable 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 many 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, regulators generally require that mine operators monitor for only three categories of cyanide: free cyanide, weak-acid-dissociable (WAD) cyanide, and total cyanide. 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 page 12 for discussion on analytical procedures.)

For example, routine analyses of cyanide fail to identify cyanates and thiocyanates, two significant cyanide breakdown products found at mine sites. Water samples from mining sites where cyanide is used as a process chemical may have WAD and/or total cyanide concentrations that are quite low or undetected, yet when the same samples are 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 at a mine site, and at what concentration.

Mine Waste Spills
In recent years, a number of cyanide-related leaks, discharges, and accidents at U.S. and international mine sites have been reported in the news media. (See box on page 5.) These accidents raise questions about the current operating practices, monitoring, and enforcement at cyanide-related mine sites worldwide.

EXAMPLES OF RECENT
CYANIDE-RELATED MINE ACCIDENTS

Colorado, U.S.A.: In Colorado, spills of cyanide and other contaminants from the Summitville gold mine, owned by Galactic Resources Ltd, contributed to severe environmental problems on a 17-mile stretch of the Alamosa River. The mine was opened in 1986, and abandoned in 1992. It is now a federal Superfund site.

Montana, U.S.A.: Pegasus Corporation recently closed the Zortman-Landusky gold mine in Montana. Opened in 1979, it was the first large-scale cyanide heap leach mine in the United States. The mine experienced repeated leaks and discharges of cyanide solution throughout its operating life, resulting in wildlife deaths and severe contamination of streams and groundwater.

Nevada, U.S.A.: Following the failure of a leach pad structure in 1997, the Gold Quarry mine in Nevada released about 245,000 gallons of cyanide-laden waste into two local creeks. In 1989 and 1990, a series of eight cyanide leaks occurred at Echo Bay Company's McCoy/Cove gold mine in Nevada, releasing a total of almost 900 pounds of cyanide into the environment.

South Dakota, U.S.A.: On May 29, 1998, six to seven tons of cyanide-laced tailings spilled from the Homestake Mine into Whitewood Creek in the Black Hills of South Dakota, resulting in a substantial fish kill. It is likely to be years before the stream fully recovers.

Kyrgyzstan: On May 20,1998, a truck transporting cyanide to the Kumtor mine in Kyrgyzstan plunged off a bridge, spilling almost two tons of sodium cyanide (1,762 kilograms) into local surface waters.

Guyana: In 1995, more than 860 million gallons of cyanide-laden tailings were released into a major river in Guyana when a dam collapsed at Cambior mining company's Omai gold mine.

Spain: 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 over adjacent farm lands. While news reports of the associated massive fish kill did not mention cyanide or related compounds in the wastes, their presence seems likely given the nature of the metals extracted at this site.

BASIC CHEMISTRY AND TOXICITY OF CYANIDE COMPOUNDS

Most commonly, cyanide used at mining sites is in the form of sodium cyanide, NaCN. This white solid dissolves readily in water, yielding a sodium ion (Na+) and a cyanide ion (CN-). Some of the cyanide ion then converts into hydrogen cyanide (HCN) or hydrocyanic acid.

Free Cyanide and Water pH

The cyanide ion (CN-) and hydrogen cyanide (HCN) are often referred to as free cyanide. Both free cyanide forms are highly toxic to humans and aquatic life if ingested. The relative amounts of both forms of free cyanide are largely controlled by water pH—a scale designed to measure the acidity or alkalinity of materials. Most cyanide in natural waters, which have a pH ranging between 6.0 and 8.5, is present as HCN. (Streams and groundwater contaminated with acid mine drainage often have a pH of 4.5 or lower.)

The cyanide ion (CN-) is the predominant stable form of free cyanide above a pH of about 9.2. 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 percent of the cyanide exists as HCN. At a pH below 7.0, essentially all dissolved cyanide is present as HCN. HCN readily forms a gas—the same gas used in execution chambers—which is released into the air.

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 levels. 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. (Such high pH mine solutions would be extremely toxic if ingested.)

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 categorized as simple cyanide compounds, cyanide complexes, and cyanide-related compounds. The following sections focus on cyanide breakdown compounds most commonly found at mine sites.

Simple Cyanide Compounds

Simple cyanide compounds consist of only a single metal ion in combination with CN. Simple cyanide compounds include sodium cyanide, potassium cyanide, and calcium cyanide—all of which are readily soluble. Some simple cyanide compounds are insoluble.

Metal-Cyanide Complexes

Cyanide complexes are compounds of cyanide bound together with numerous other organic and inorganic compounds. Only the metal-cyanide complexes, which are commonly formed in mining effluents, will be discussed in this section.

When metal-cyanide complexes are formed and released into the near-surface environment, they begin to decompose at varying rates, some quickly, others quite slowly. This breakdown releases cyanide into the soil or water, generally at relatively low concentrations. Those complexes that most readily decompose are referred to as weak complexes, those most resistant to decomposition are called strong complexes. Examples of weak cyanide complexes include zinc and cadmium cyanides. Moderately strong complexes include copper, nickel, and silver cyanides. And strong complexes include iron, cobalt, and gold cyanides. 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 cyanide ions. This is especially true of the iron cyanides, which are often the most common forms of these complexes found in mining wastes.

The decomposition rates of these complexes also are affected by the water temperature, pH, total dissolved solids, and complex concentration. Some metal-cyanide complexes degrade more rapidly when exposed to sunlight, atmospheric carbon dioxide, and air. And 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 degrade more rapidly in neutral or low pH environments, but some may be stable for decades. The author has encountered cyanide-contaminated sediments at a cobalt-nickel mine that contained many milligrams per kilogram of total CN more than 25 years after all processing had ceased, indicating the persistence of these complexes—probably iron cyanide and cobalt cyanide complexes.

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, although generally at concentrations much higher than for the free cyanide forms.

Cyanate (NCO-) is a cyanide-related compound that is formed when alkaline solutions of cyanide react with oxidants such as chlorine, hypochlorite, ozone, and hydrogen peroxide. In fact, the mining industry often uses several of these oxidants to decompose cyanide in wastes. When hypochlorite is combined with 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. 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** (NH2Cl), or similar chlorinated ammonia compounds. Chloramine is less toxic than CN-, but is likely to be present in much higher concentrations. Free cyanide also reacts with forms of sulfur in mining effluents, including thiosulfates, or sulfide ions, to produce **thiocyanates** (SCN-). Relatively high concentrations of thiocyanate may persist in the presence of acidic solutions. (Plumlee and others, 1995) Thiocyanate concentrations in the range of tens of milligrams per liter have also been reported in copper tailings waters with a pH above 10. 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 alkaline, but might develop if acid mine drainage were to form, or if acidic solutions were to contact cyanide-bearing solutions.

Nitrate and Ammonia
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 reach concentrations toxic to aquatic organisms.

While most 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.

Toxicity of Cyanide Compounds

Given the limitations of routine analytical techniques for measuring cyanide, and the presence of breakdown cyanide 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 along with the cyanide and related compounds. And determining which chemical constituents are actually causing a toxic response can be very difficult. Instead of specific toxicity data on cyanide compounds, it is more common to read general 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.

There are no established water quality criteria for most forms of cyanide derivatives found in mining-related waters. The current U.S. Environmental Protection Agency water quality criterion for cyanide is 5.2 micrograms per liter for freshwater aquatic life, and 1.0 microgram per liter for marine aquatic life and wildlife. (EPA, 1986) Yet no criteria exist for cyanide-related compounds, including cyanate, thiocyanate, cyanogen chloride and the metal-cyanide complexes.

Toxicity to Fish

The box on pages 10 and 11 highlights the toxicity of cyanide-related breakdown compounds that can be found at mine sites. Discussions on toxicity for each of these compounds focuses 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 cyanide 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 cyanide. 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.

Toxicity to Humans

Stanton and others (1986) states that HCN ingested orally is fatal to humans in doses ranging from 50 to 200 milligrams, 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 milligrams per liter are likely to be toxic to mammals, including humans.

According to numerous industry documents, sodium cyanide has been used for decades in mining, and no accidental fatality has been recorded associated with its use. However, in May 1998, at least one death was reported by government officials in Kyrgyzstan to be due to, or aggravated by, contact with cyanide that spilled while being transported to a mine in Kyrgyzstan. (See case study analysis on page 14.)

Much of this section is based on the following references: Smith and Mudder, 1993; Colorado Dept. of Natural Resources, Nov. 1997; Ingles and Scott, 1987; Flynn and Haslem, 1995; Scott and Ingles, 1981; and Stanton and others, 1986. This and other sections benefited from telephone discussions with Dr. Owen Mathre, consulting chemist and former research chemist for more than 35 years with E.I. DuPont, one of the main manufacturers of commercial cyanide. Sections on toxicity are based largely on Ingles and Scott, 1987; Eisler, 1991; Heming, 1989; and Palmes, 1991.

FACTORS AFFECTING CYANIDE TOXICITY
TO FRESHWATER FISH

Cyanide concentration: Toxicity increases with higher concentrations of cyanide.

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

Temperature: Toxicity increases three-fold with a 12 degree celsius 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.

Toxicity of Cyanide and Cyanide-Breakdown Compounds to Freshwater Fish

Free cyanides: Free cyanides (the cyanide ion and hydrogen cyanide) are well known to be the forms of cyanide derivatives 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 20-80 micrograms per liter of free cyanide. Chronic toxic effects are reported in fish in the range of 5-20 micrograms per liter.

Metal-cyanide complexes: Metal-cyanide complexes are generally thought to be less toxic than free cyanide. However, they are less well understood. These complexes break up to yield hydrogen cyanide, which is the usual cause of toxicity. Some metal cyanide 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 toxicity ranges of selected metal-cyanide complexes: sodium and potassium cyanides 0.02-0.3 mg/L; zinc cyanide 0.02-0.3 mg/L; cadmium cyanide 0.02-0.3 mg/L; copper cyanides 0.4-4.0 mg/L; nickel cyanide 0.4 mg/L (6.5 pH) and 730 mg/L (8.0 pH); and iron cyanides 300 mg/L in darkness and less than 0.2 mg/L in light. Doudoroff (1976) states that the chronic toxicity of metal-cyanide complexes needs to be investigated.

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 is combined with cyanide 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. It is unclear whether cyanogen chloride persists in alkaline mining wastes.

Cyanates: Cyanate is the main form of cyanide resulting from most cyanide decomposition processes employed at mine 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 - 82 milligrams per liter cyanate.

Thiocyanates: Ingles and Scott (1987) report thiocyanate toxicity for fish to range between 90 and 200 milligrams per liter. Heming and Thurston (1985) and Heming and others (1985) report toxicity to be between 24 and 70 milligrams per liter thiocyanate for brook trout. Heming and Blumhagen (1989) report that thiocyanates cause "sudden death syndrome" in trout, partly as a response to stress, and because they accumulate—which is contrary to much previously published literature.

Chloramines: Chloramines are chlorinated ammonia compounds that are less toxic than CN-, 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. The U.S. EPA criteria document for freshwater aquatic organisms states that the total residual chlorine concentration should not exceed 11-19 micrograms per liter. (EPA, 1986)

Ammonia: Ammonia is a routinely encountered breakdown product wherever cyanide 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. Environmental Protection Agency (1986) reports ammonia to be toxic to fish at concentrations between 0.083 and 4.6 milligrams per liter. Some data indicate that the combined effect of ammonia and cyanide is greater than would be assumed on the basis of their individual toxicities.

MONITORING AND ANALYSIS OF CYANIDE AT MINE SITES

"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. In addition, 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 cyanide" analytical method reports the sum of both forms of free cyanide—the cyanide ion (CN-) and hydrogen cyanide (HCN), plus cyanide from the breakdown of many of the weak complexes (which does not include complexes of nickel, iron, cobalt, gold, platinum, and palladium).

The "WAD cyanide" method measures the free cyanides plus many of the weak 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 less than 1.0). This includes most metal cyanide complexes, including most strong complexes. But this method may not detect many of the organic cyanide compounds. (Although organic-cyanide compounds are not reported to be found in significant concentrations at mining sites, it is unclear whether mining samples have been analyzed adequately to determine the presence of these compounds.)

Both the WAD and the total cyanide 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, cyanogen chloride, chloramines, most cyanogen, and most organo-cyanide compounds, 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.

Most mining regulatory agencies require that water samples be analyzed for WAD and/or total cyanide forms, especially during mine closure. The other cyanide-related forms discussed in this report, however, are generally neglected.

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.

Much of this section has been taken from American Public Health Assoc., 1995, section 4500-CN.; and Smith and Mudder, 1993.

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 1,762 kilograms (kg) of sodium cyanide into a river upstream of several villages. (The material that spilled was a concentrated form of cyanide and not cyanide-bearing tailings or heap leach waters. This incident illustrates many of the environmental and regulatory problems discussed in this paper.) Within days after the spill, hundreds of local residents sought treatment at medical clinics. According to a report by the Russian Federation Ministry of Defense, at least one human 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, have argued that few if any significant impacts have occurred to any living organisms or the overall environment, as a result of the spill.

According to Dr. Owen Mathre, a former research chemist for E.I.DuPont, the dissolution of approximately 1,800 kg (about 2 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 local citizens.

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. However, since standard cyanide analytical techniques fail to detect several forms of cyanide and cyanide-related compounds, the concentrations reported would not include cyanide from many of the stronger metal-cyanide complexes, nor would they include the toxic cyanide breakdown products in cyanates, thiocyanates, cyanogen, and 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 from the cyanide spill in Kyrgyzstan provides an incomplete picture of the toxic forms of cyanide potentially present at the spill site.

CONCLUSION

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 fresh water fish species. Such compounds include many metal-cyanide complexes, cyanates, thiocyanates, cyanogen, cyanogen chloride, chloramines, ammonia, and nitrate.

Gaps in Standards and Analysis

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 WAD or total cyanide methods only. Neither method detects the majority of the cyanide-related compounds likely to be present at a mine site. 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 or thiocyanate that are potentially toxic to fish.

Risks in Developing Countries

Not only are there gaps in U.S. water quality regulations pertaining to cyanide and related compounds, but even more substantial problems exist in developing countries in Africa, Asia, and Latin America. Here, mine contaminated rivers may be used as a source of drinking water. 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.

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ACKNOWLEDGEMENTS

Mineral Policy Center and Dr. Moran would like to thank the following individuals who reviewed various drafts of this report: Glenn Miller, Ph.D., University of Nevada at Reno, Reno, Nevada; David Chambers, Ph.D., Executive Director of Center for Science in Public Participation, Bozeman, Montana; Tom Hemming, Ph.D., Associate Professor, Marine Biomedical Institute, Galveston, Texas; and Carolyn Harper, Ph.D., Agency for Toxic Substances and Disease Registry, Atlanta, Georgia.

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