MERG Report 2001-2

Cyanide – The Facts

By Laberge Environmental Services

2001

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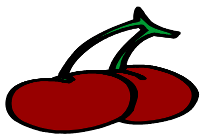
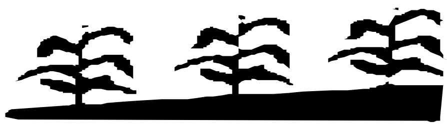
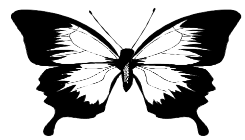
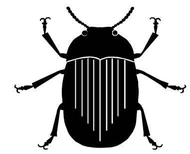
CYANIDE : THE FACTS

Cyanide is probably one of the most universally recognized poisons. Because cyanide has been widely used in the Yukon mining industry, a fact sheet on this chemical is timely. Cyanide contains a carbon atom connected to a nitrogen atom, hence the chemical formula CN. However, the term cyanide is used to refer to a wide array of cyanide containing chemicals. Cyanides can be manufactured but they also occur in nature. In the natural environment, cyanide containing chemicals are produced by a wide range of organisms and plants as part of their normal metabolism. Bacteria and fungi are known producers of cyanide. A few species of centipedes, millipedes, insects, beetles, moths and butterflies secrete cyanide for defensive purposes in repelling predators such as toads and birds. Some of the common plants that contain cyanide are cassava, sweet potatoes, corn, lima beans, almonds, radishes, cabbage, kale, brussel sprouts, cauliflower, broccoli, turnips, lettuce, kidney beans, and it can be found in the pits or seeds of cherries, plums, apricots, pears and apples.









The small amounts of cyanide entering our bodies from our daily intake of the above foods, is removed by the liver to prevent harmful levels building up in our systems.

Cyanide is manufactured from ammonia and natural gas, or is a by-product of the manufacture of acrylic fibres and plastics.

What are the forms of Cyanide?

Cyanide can occur in many forms. It can exist as a free ion or can combine with many different elements. Below is a general description of the various categories.

Term	Description	Example
Cyanide ion	the free cyanide ion	CN^-
Molecular HCN	hydrogen cyanide or hydrocyanic acid	HCN
Free Cyanide	includes the cyanide ion and hydrogen cyanide	CN^- + HCN
Simple cyanide	a salt which dissociates to form a cyanide ion	NaCN
Complex cyanide	dissociates to form another cyanide compound	$Au(CN)_2$
WAD cyanide	weak acid dissociable, cyanide that is readily released from cyanide containing compounds when the pH is lowered	$Cd(CN)_2$
SAD cyanide	strong acid dissociable, cyanide that is released from cyanide containing compounds under highly acidic conditions	$Co(CN)_6^{4-}$
Total cyanide	the sum of all of the different forms of cyanide present in a system	

The form of cyanide in water is dependent primarily on pH but is also influenced by temperature, dissolved oxygen, sunlight and the presence of other ions. It has been observed that there are 28 elements which can react with cyanide capable of producing 72 different complexes.

The form usually used in mining is sodium cyanide (NaCN), which is stable in solid form.

A Yukon mill where cyanide was used to recover gold.

When mixed with water the pH must be kept above 11 or the poisonous hydrogen cyanide (HCN) gas is formed. There are strict safety procedures to be followed when transporting, storing and handling cyanide products.

The toxicity of cyanide depends on the form of cyanide present, ranging from the highly toxic 'free cyanide' to the non or less toxic stable strong complexes.

What is Cyanide used for?

Cyanide compounds have many useful purposes. The word cyanide comes from the Greek word Cyanine which means blue. Cyanide has been used in synthetic dyes since the 1850s and it is what makes your blue jeans blue.

Due to its toxic nature, it has been used as a fumigant and poison since early time. It has been known for 2000 years that consuming sufficient quantities of bitter almonds, cherry laurel leaves and cassava are poisonous. On its more notorious side, cyanide has been used to kill people in judicial executions, genocide, and mass suicide, and has been used as a chemical warfare agent.

Cyanide is also used in the manufacture of nylon, plastic glass, perfume, soaps, fertilizers, paints, animal food supplements, and pharmaceuticals, including heart medication and medical test kits. Cyanide compounds are used in surgical dressings that promote healing and reduce scarring, in anti-cancer preparations, and in drugs to reduce high-blood pressure.

Cyanide is used in electroplating where it 'plates' one type of metal onto another. Examples are silver and gold plated dinnerware and jewellery, and brass plated bathroom fixtures

However, its most familiar use in the Yukon is in the mining industry. Over 90% of the gold mined in Canada, is extracted using a cyanidation process. Cyanide forms a very stable complex with several metals and has been used since 1887 to extract gold, silver, copper, zinc and molybdenum from ores. Cyanide plays an important role in the mining industry because it allows for the economical recovery of microscopic metals from low grade ore. It is used in the milling process where it dissolves the precious metals. Cyanide has been used in mills at the mines at Faro, Elsa, Mt. Nansen, Mt. Skukum, near Ross River at Ketza, near Carcross at Venus and Arctic Gold and Silver, and near Watson Lake at Sä Dena Hes. Heap leaching with cyanide is a newer technology which is currently being utilized at Viceroy Minerals Corporation's Brewery Creek gold mining property near Dawson, and is proposed to be used at the Dublin Gulch property near Mayo.

How does heap leaching work?

In a heap leach operation, a very dilute cyanide leaching solution is sprayed or dripped onto ore stacked on an impermeable pad. As the solution percolates through the heap, precious metals are complexed with the cyanide ion and dissolved. Depending on the height of the pad and grain size of the ore, it can take anywhere from thirty days to several months for the solution to make its way by gravity through the heap. The pregnant solution is recovered, and the precious metals are concentrated with activated carbon. After stripping and electroplating processes, the resultant sludge is filtered, dried and smelted into gold/silver bars. The barren solution (the solution that does not contain the precious metals) is recirculated, with cyanide being replenished continuously. The concentration of cyanide necessary to extract gold from the heap is dictated by characteristics of the ore. After a certain period of leaching, it is no longer economical to continue leaching residual gold from a heap, and the heap is closed. Residual cyanide remains in the heap either in solution, or sorbed (attached) to the ore surface. As a result, the leachate from a spent heap generally contains levels of cyanide above the regulatory limit and will require rinsing and detoxifying prior to abandonment.

A weak cyanide solution sprayed onto a heap.

What is done with the waste Cyanide in tailings ponds and abandoned heap leach pads?

There are several methods to destroy, degrade and detoxify cyanide which involve physical, biological and chemical processes.

Natural Degradation or Attenuation

Natural degradation or attenuation are general terms for all the processes that may reduce cyanide concentrations of a waste without human intervention. These processes that remove cyanide include volatilization, oxidation, bio-degradation, photodecomposition and adsorption (attachment) onto the surfaces of solids. Each mechanism is governed by variables such as pH (a measure of acidity), temperature and water chemistry. The pH of barren water entering tailings or leach ponds is initially high in order to keep cyanide available to complex with gold. As the pH naturally decreases below 9, more of the free cyanide is in the form of HCN which has a high vapour pressure and readily evaporates (volatilizes). Oxidation occurs when cyanide reacts with air and water to produce ammonia and bicarbonate. Several species of bacteria degrade cyanide, and this process is known as biodegradation. Photodecomposition occurs when ultraviolet radiation (sunlight) breaks down cyanide complexes. Iron cyanide compounds are susceptible to this process.

To enhance natural degradation, shallow ponds with large surface areas are used. This provides greater contact with atmospheric carbon dioxide which lowers the pH. This in turn increases the rate of conversion to HCN and hence volatilization.

Before the mid 1970s, natural degradation was the only treatment method used by the Canadian mining industry for degrading cyanide in tailings ponds. Very little natural degradation appears to take place in the winter under ice cover. Natural degradation and attenuation pathways will account for much of the destruction of free cyanide. However, strongly complexed cyanides are extremely unlikely to release free cyanide at a rate fast enough to be significant, therefore other methods are employed.

Chemical Degradation

Due to the introduction of environmental regulations in the late 1970s, mining operations were required to design and construct additional treatment systems for wastes containing cyanide. Some of the more common processes used to degrade cyanide are the hydrogen peroxide process, alkaline chlorination, and sulphur dioxide-air oxidation. These methods generally oxidize the weaker cyanide complexes and precipitate the stronger stable ones.

Microbial Process

Chemical oxidation of cyanide is expensive regardless of the technique used. An alternate procedure uses cyanide-oxidizing bacteria. Microbial action transforms cyanide to ammonia. Further microbial action will convert ammonia to nitrate. The object of biological treatment is to increase the rate of these natural transformations.

Research has been done into biological degradation as early as 1913. A wide variety of bacteria and fungi can degrade cyanide compounds and may be useful in the treatment of cyanide wastes. The dried mycelia (tissue) of several species of fungi can degrade cyanide and it is sold commercially to detoxify cyanide in industrial wastes. The use of cyanide destroying bacteria is not suitable for all cyanide destruction applications, especially as an on-going treatment method in the mining industry. It has however, proven successful as treatment of spent leach heaps in Canada, the United States and Australia.

In the Yukon, investigations were conducted at the Brewery Creek Mine near Dawson in 1999, to determine the potential of using cyanide-degrading bacteria as a treatment method in the heaps at abandonment. Cyanide-degrading bacteria were found to be widespread in the local area and were cultured. The bacteria were placed in columns containing cyanide treated ore, representative of spent ore that would remain on the heap leach pads at closure.

Column tests of cyanide degrading bacteria using various concentrations and growth conditions at the Brewery Creek Mine.

To check against other methods, water rinsing and peroxide treatment was applied to two other columns of ore. This research produced encouraging results. Under experimental conditions, microbial destruction was more successful at removing cyanide than the other two treatments. A further benefit to using the biological method was the additional treatment of ammonia by nitrifying bacteria which were also present. Ammonia is also produced in the peroxide treatment but may require the added expense of further treatment.

What about spills?

Bulk cyanide is transported in special lined and sealed containers and trucked to the minesite.

A container of sodium cyanide in solid "briquette" form.

Spills can occur in a transportation accident or by the accidental release at the minesite. The objective of cleaning up a spill is to immobilize and contain the cyanide and/or convert it to less toxic compounds. The form and amount of cyanide, the area and type of environment affected, the response time and accessibility to the spill, will determine how to respond to the problem. Spills on the ground of solid cyanide, such as sodium cyanide, pose little danger if kept dry and quickly removed. The soil may need to be decontaminated using household bleach or the contaminated layer may need to be removed.

Liquid spills on land, if noticed promptly, may be treated with appropriate oxidizing agents by trained personnel and effectively cleaned up. Some land spills may result in local or widespread contamination of groundwater.

Spills into surface waters on the other hand are very difficult to treat due to rapid dispersal of the cyanide and the addition of oxidizing agents may further damage the water body. Usually little can be done except to dilute and disperse the spill and encourage natural degradation. Although rapid detoxification of cyanide can occur in the environment, massive kills of freshwater fish by accidental discharges of cyanide wastes have been documented at various sites throughout the world.

To prevent spills and leakage to surface and groundwater, ponds and pads must be lined with impervious material and all pipelines and storage areas must have secondary containment systems.

What are the detrimental human health effects of Cyanide?

Cyanide is a very fast acting poison capable of killing a person within minutes if they are exposed to a lethal dose without prompt first aid treatment. Poisoning occurs through inhalation, skin absorption or swallowing. Personnel involved in the transport and handling of cyanide are fully trained in all safety aspects including the proper first aid treatments.

Cyanide is toxic to humans and mammals because it binds to key iron-containing enzymes required for cells to use oxygen. The tissues are then unable to take up oxygen from the blood and the end result, much like drowning, is suffocation. People exposed to non-fatal doses normally recover in a short time, and there has been no evidence to suggest that it causes cancer or affects the reproduction system.

As mentioned earlier, cyanide is found naturally in many foods. Cassava, also known as manioc, tapioca, yuca or guacamate, is one of the most important food crops which contain cyanide toxicity problems. Cassava is the major food source for people and livestock in many parts of the world and has been under cultivation in tropical America for around 5000 years. The root is usually dried in the sun before consumption which removes most of the cyanide. However, during periods of drought and famine, cassava is not always prepared properly and poisoning can occur if sufficient quantities are consumed.

Cyanide is also contained in cigarette smoke. The US Department of Health has shown that smoke can contain up to 1,600 ppm (parts per million) of cyanide.

What are the environmental impacts of Cyanide?

Cyanide has low persistence in the environment and is not accumulated or stored in any mammals that have been studied. Cyanide biomagnification in food webs has not been reported possibly due to rapid detoxification at sublethal doses, and death at higher doses. Low levels of cyanide may be harmless under seasonal or other variations that allow organisms to recover and detoxify.

Cyanide is seldom persistent in surface waters and soils due to complexion or sedimentation, microbial metabolism and loss from volatilization, but may persist in groundwater for extended periods of time. More research is required regarding the fate of cyanide in groundwater.

Long term adverse effects associated with mining sites are related primarily to metals rather than cyanide. Cyanide can naturally degrade rapidly in the environment by volatilizing to hydrogen cyanide gas (HCN). This gas is very dangerous when in a closed system such as a warehouse, but the aim is to encourage the gradual release of cyanide to the air in the out-of-doors environment. Cyanide can mix with air and water to produce ammonia and bicarbonate. Ammonia can be toxic in the aquatic system, but is an important component of the nitrogen cycle, vital for plant growth. Consequently, low concentrations of ammonia are rapidly assimilated.

Cyanide is toxic to most species in varying amounts. Aquatic organisms are very sensitive to cyanide. Fish have been shown to be the most sensitive aquatic organism, followed by invertebrates. Algae and aquatic plants have been shown to be comparatively tolerant to cyanide. Low concentrations can sometimes enhance germination and growth. Elevated concentrations inhibit respiration and can lead to death.

Birds seem to have varying sensitivity to cyanide. Migratory birds have suffered from cyanide poisoning associated with heap leaching facilities and tailings ponds. They may absorb cyanide through their skin when wading or swimming, or ingest it through drinking. Small mammals, such as rodents, foxes, rabbits, bats, etc. have been found dead near cyanide containing tailings ponds, which they have used as a drinking water source. The prevention of bird and mammal deaths is accomplished by fencing the area, screening or netting the ponds, or decreasing the concentration of cyanide in the ponds. Ponds that are too large to be netted can have floating balls distributed throughout to scare wildlife. The heap leaching operation at Brewery Creek is well fenced and the ponds are covered with nets.

Criteria for Cyanide

The toxicity of cyanide is very dependent on its form. Mine effluents, tailings and leach pond water can contain cyanide in many forms ranging from the cyanide ion to strong metal cyanide complexes. Different metal complexes have varying degrees of stability. The toxicity of cyanide compounds depends on the compound's ability to release the cyanide. Some can dissociate easily to form HCN, others break down under the effects of sunlight. These factors and more create problems when developing criteria on cyanide discharge limits.

Biologists object to the analysis of total cyanide as being meaningless since it overestimates the actual cyanide toxicity. Free cyanide is the most toxic form and when testing for toxicological purposes, analysis of free cyanide should be performed. Testing for weak acid dissociable (WAD) cyanide is also considered a good measure for assessing human and animal toxicity as it measures free cyanide as well as cyanide that is readily released from cyanide-containing complexes when the pH is lowered. When determining the fate of cyanide in the receiving environment, all forms of cyanide and its degradation products should ultimately be analyzed, which obviously, can become very expensive.

Each mine in the Yukon must abide by a Water License issued by the Yukon Territory Water Board. The license has standards of cyanide concentration that must be met in the effluent before it is discharged to the receiving environment. In general, the discharge limits are 0.5 mg/L of **total cyanide** and 0.2 mg/L of **WAD cyanide**.

Guidelines for acceptable concentrations of **free cyanide** have been published by the US Department of Fish and Wildlife Service and the Canadian Council of Ministers of the Environment.

A Final Word

All of us are in daily contact with cyanide through the foods we eat and the products we use. Although cyanide is extremely toxic, it is definitely beneficial to our lives. With the proper transportation, handling, care and disposal methods, cyanide will not harm ourselves or the environment.

Funded by Mining Environmental Research Group **Prepared by Laberge Environmental Services** **Layout Design by Nancy Lewis-de Graff**