

# THE CYANIC THREAT TO POTABLE WATER

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## ABSTRACT

Cyanide is one of the most lethal and rapidly acting poisons known to man. Clinical symptoms can occur within minutes of exposure, and exposure to this toxicant can be fatal. Since terrorists have threatened and attempted to contaminate the U.S. drinking water using cyanide, water utilities should understand (1) what cyanic compounds water utilities should be concerned about, (2) what health effects would be noticeable during cyanide poisoning, (3) what water quality changes would be noticeable when cyanide contamination occurred, (4) what are the available commercial detection equipment for drinking water, and (5) how to treat water containing cyanide. This paper includes results from a literature study. Specific water utility recommendations have also been provided.

## INTRODUCTION

The cyanic threat to U.S. drinking water is real. On February 4, 2002 four Moroccans were arrested while plotting to contaminate the U.S. Embassy drinking water system in Rome, Italy (Lyman, 2002). These Moroccans were arrested before they could initiate their plan that included ten pounds of powdered potassium ferricyanide. Shortly thereafter, the U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM) branch located at Aberdeen Proving Ground, MD was asked to determine the cyanic threat to potable water as well as provide recommendations to the USACHPPM European branch on how water utilities should better monitor for and handle such an event.

Many terrorist groups and rouge individuals have chosen to use cyanic compounds to contaminate drinking water. For thousands of years, cyanide has been used as a drinking water poison. Dating as far back to the ancient Romans, power hungry leaders eliminated their opponents by providing them water spiked with cyanide (Hickman, 1999). In the mid-1980s the U.S. Federal Bureau of Investigation (FBI) uncovered a plot to poison water supplies with cyanide in major U.S. cities (Stern et al., 2000). Fortunately, this group underestimated the amount of cyanide required and the plot was uncovered and foiled before the terrorists could act. Other more recent arrests and incidents have revealed that terrorist organizations and rogue individuals have easily acquired cyanide and some have even planned to contaminate drinking water (CNN, 2002; Lyman, 2002; Katzanell, 2002; Mark, 2002; Pierre, 2002; Rice, 2002; Rubo and Gos, 2002; Sargent, 2002; Stinson, 2002).

Undoubtedly, the effect of a terrorist attack could result in multiple fatalities and some residual effects could be long-lasting and psychological in nature (North et al., 1999; Blendon et al., 2002; Schlenger et al., 2002). As a result, drinking water utilities must take all available efforts to protect the drinking water and its consumers.

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In an effort to better prepare water utilities, the U.S. Environmental Protection Agency formally allocated research funds in December 2002 to assess cyanide detection technology (AWWA, 2002). In the absence of these results and reports that specifically evaluate the cyanic threat, the USACHPPM Water Supply Management Program developed this paper. The objective of this research was to conduct a literature search to determine (1) what cyanic compounds water utilities should be concerned about, (2) what health affects would be noticeable during cyanide poisoning, (3) what water quality changes are noticeable when cyanide contamination occurs, (4) what are the available commercial detection equipment for drinking water, and (5) how to treat water containing cyanide.

## CYANIC COMPOUNDS IN SOCIETY

Cyanide (CN<sup>-</sup>) containing compounds are naturally occurring, man-made, and are widely used. Some bacteria have even been identified with the ability to synthesize hydrogen cyanide (Kremer and Souissi, 2001). Also, many cyanic compounds have been found in foods and plants (CHA, 1993; Shifrin et al., 1996; Sidell et al., 1997). For instance, some researchers in toxicology and biology have found cyanide present inside peach and apricot pits as well as apple seeds (CHA, 1993).

Cyanide has not only been found in nature, but has also been found in our body. In one study, non-cigarette smokers contained an average of 0.06 µg/mL in their blood while individuals who smoke cigarettes were found to have a 0.17-µg/mL blood-cyanide concentration (Sidell et al., 1997). Researchers have also determined that cyanide is present in the organs of healthy individuals at concentrations as high as 0.5 mg cyanide per kg of body weight (DHEW, 1976).

Several roadway de-icing salts contain cyanide, although, most cyanide in the environment comes from industrial processes (Novotny et al., 1998; Siller and Winter, 1998). In the U.S. cyanic compounds are produced at about 2-3 million tons per year (Gijzen et al., 2000). Several different cyanic compounds are used during electroplating, metal treatment, gold and silver extraction, plastics processing, and in the manufacture of fumigants (Sidell et al., 1997; DHEW, 1976; Jolley et al., 1985; HDR, 2001). Typically, accidental cyanide releases into waters can be traced back to industrial users (Bordeaux, 1998; McMahon, 2000). Some fishermen in Indonesia use cyanide illegally in order to stun the fish so that they can easily be harvested (Barber and Pratt, 1998).

Historically, hydrogen cyanide (HCN) and cyanogen chloride (CNCl) are the two most studied cyanide containing chemical warfare agents (Siddell et al., 1997; Burrows and Renner, 1999; Hickman, 1999; Karalliedde et al., 2000). These agents have primarily been tested and used in aerosol form and are considered non-persistent in air. Hydrogen cyanide (HCN) was used in World War I by France, by Germany in World War II, and by Iraq against the Kurds in the 1980s.

Cyanide contamination exists in some ground and surface waters (Watts, 1998). At one abandoned industrial site, groundwater concentrations have been reported as high as 411 µg/L (Hartman et al., 2001). In contrast, the U.S. Environmental Protection Agency (EPA) reported considerably lower aqueous concentrations in a 1970 survey of 969 water supplies. The average and maximum aqueous concentrations were 0.09 µg/L and 8 µg/L, respectively (HDR, 2001).

Cyanogen chloride (CNCl) is also another form of cyanide that has received some attention. Similar to the cyanide ion, CNCl has also been identified in drinking water but as a disinfectant byproduct. Cyanogen chloride is produced by a reaction between formaldehyde and the alternative disinfectant monochloramine (Krasner et al., 1991, Pedersen et al., 1995, Pedersen et al., 1999). Cyanogen chloride concentrations in drinking water have been identified as high as 12 µg/L (Krasner et al., 1991).

## NOTABLE COMPOUNDS

Cyanic compounds can be found in two forms, simple and complex. Generally, simple cyanic forms are more toxic than complex forms. The two most notable simple cyanide species are hydrogen cyanide, also known as AC and hydrocyanic acid, and cyanogen chloride, also referred to as CK. This paper will primarily focus on these simple cyanide species. Physical properties and sensory attributes of several cyanic compounds are provided in Table 1 (Lide, 2001).

**Table 1. Physical Properties and Attributes of Several Cyanic Compounds<sup>1</sup>**

Chemical Formula	Chemical Name	Typical Phase	Color Descriptor	Odor Descriptor	Water Soluble (Yes/No)
HCN	Hydrogen Cyanide	Gas or Liquid	Colorless, yellow or-brown	Bitter almond Marzipan <sup>a</sup> , ratafia <sup>b</sup> , peach kernels	Yes
NaCN	Sodium Cyanide	Solid	White	Almond-like	Yes
KCN	Potassium Cyanide	Solid	White	Almond-like	Yes
CNCl	Cyanogen Chloride	Gas or Liquid	Colorless	Pepperish	Yes
K <sub>3</sub> Fe (CN) <sub>6</sub>	Potassium Ferricyanide	Solid	Yellow	Odorless	Yes
K <sub>4</sub> Fe (CN) <sub>6</sub> * 3H <sub>2</sub> O	Potassium Ferrocyanide	Solid	Red or yellow	Odorless	Yes
CuCN	Copper (+1) Cyanide	Solid	White, green, or red	Odorless	No
AgCN	Silver (+1) Cyanide	Solid	White or gray	Odorless	No

1. Data taken from NIOSH (1997)

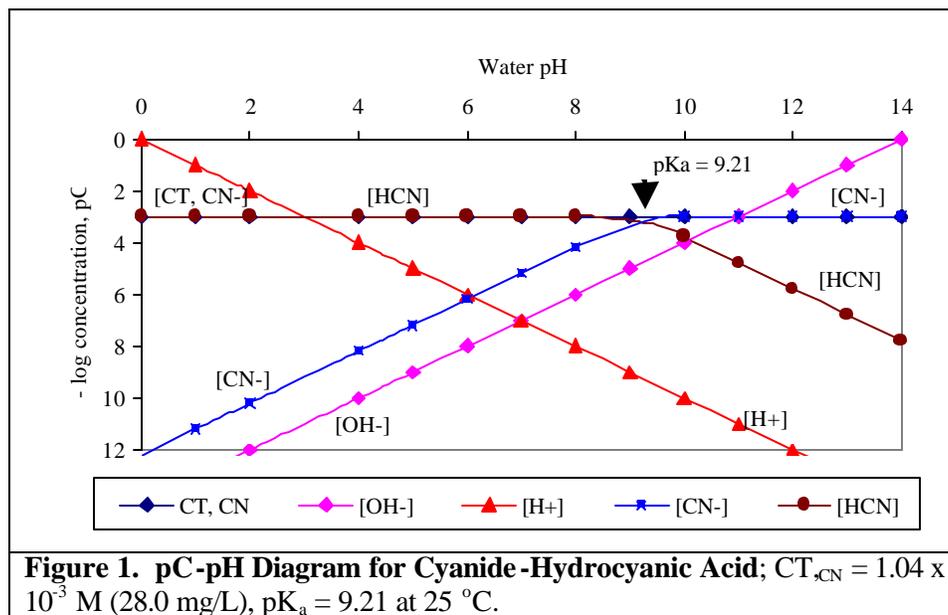
- a. A food made of almonds, egg whites, and sugar
- b. Flavored with fruit kernels or almonds

Some references suggest that HCN and CNCl are the only cyanic compounds with identified sensory attributes. The odor characteristics of HCN and CNCl have been identified as bitter almond or peach kernel odor and a pepperish odor, respectively (USACHPPM, 1996; Karalliedde et al., 2000). The odor threshold of HCN has been reported as 1 ppm, although no information was provided in the literature on the odor threshold for CNCl. Some data indicates that individuals exposed to cyanide experience metallic tastes (Karalliedde et al., 2000).

At room temperature, most cyanic compounds are present as a solid or powder; HCN and CNCl are the exceptions. HCN is a colorless or yellow-brown liquid below 26 °C (78 °F), and a gas above this temperature. CNCl is almost always present as a colorless gas, while below 12 °C (54 °F) it is a liquid. Because of the high volatility of both HCN (vapor pressure 742 mmHg at 25 °C) and CNCl (vapor pressure 1,000 mmHg at 25 °C), extreme caution must be taken when handling these chemicals.

Cyanic salts such as calcium cyanide ( $\text{Ca}(\text{CN})_2$ ), potassium cyanide ( $\text{KCN}$ ), and sodium cyanide ( $\text{NaCN}$ ) are commonly added to water to form aqueous  $\text{HCN}$ . When these simple cyanides are added to water they dissociate producing cyanide ions; for example,  $\text{Ca}(\text{CN})_2 \rightarrow \text{Ca}^{2+} + 2\text{CN}^-$ . Once dissolved in water cyanide ions then combine with hydrogen (depending upon water pH) to form hydrogen cyanide  $\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$ . In natural water, cyanide ions can also combine with metals such as iron, copper, and silver.

The amount of cyanide present in water as  $\text{CN}^-$  and  $\text{HCN}$  is highly dependant upon pH. The dissociation constant ( $\text{pK}_a$ ) for molecular  $\text{HCN}$  is approximately 9.2 (Snoeyink and Jenkins, 1980; APHA, 1998). As indicated in Figure 1, at pH values less than 9.2, most of the cyanide in water (containing only  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ , and  $\text{HCN}$ ) is present as hydrogen cyanide, whereas above 9.2, the majority of cyanide is present as free cyanide ion. Therefore, in most drinking waters (pH 7-9), cyanide will be present as  $\text{HCN}$  (Kim et al., 2001). More specifically, more than 90% of the cyanide between pH 6-8.5 will be in the form of molecular  $\text{HCN}$ . While the pC-pH diagram only considers  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{CN}^-$ , and  $\text{HCN}$ , this diagram does not account for any cyanide complexed with metals, which is likely in natural waters. These metallocomplexes result in relatively insoluble cyanic compounds as shown in Table 1. Much of the literature indicates that metallocomplexed cyanides will not dissociate in water.



## CYANIDE POISONING

### *Physiological Effects*

Cyanide poisoning occurs when the body is exposed to cyanide concentrations greater than its normal rate of detoxification and can be fatal. Once cyanide enters the body it dissolves into the blood stream and interferes with respiration on a cellular level. This chemical is absorbed through the lungs, intestinal tract, and skin and reacts with heavy metal ions, which can quickly interfere with the enzyme systems (DHEW, 1976). According to the National Institute for Occupational Safety and Health (NIOSH), cyanide affects the central nervous system, cardiovascular system, thyroid, and blood (NIOSH, 1997).

The physiological affect of cyanide poisoning is that while the cell is fully oxygenated, cyanide ions bind with the enzyme cytochrome oxidase. This binding does not allow the cell to utilize oxygen. A cherry-red appearance of the blood has been noticed of people experiencing cyanide poisoning, and is due to the super oxygenated state of the blood (Marris et al., 1996). Cyanide-cellular enzyme binding has been documented to occur within minutes of exposure (Marris et al., 1996).

Some acute health affects after inhaling cyanide are hyperventilation, which as a result increases amount of cyanide inhaled, loss of consciousness, convulsions, and death from cardiac or respiratory arrest (Marris et al., 1996; Karalliedde et al., 2000). Other acute health effects that have been identified are rapid breathing, gasping, tremors, vomiting, rashes, weakness, headaches, and a rapid or an irregular heartbeat (EPA, 1985; USACHPPM, 1996; Greenfield et al., 2002; Karalliedde et al., 2000). Persons exposed to cyanide have also acknowledged a feeling of apprehension, a metallic taste in their mouth, and difficulty breathing. Chronic cyanide poisoning is rare and not thought to be a concern; although, some long-term exposure affects have been documented. Some of these effects are intellectual deterioration, mental confusion, Parkinson's disease, paralysis, weight loss, thyroid effects, nerve damage, and the wasting of the muscles (DHEW, 1976; Marris et al., 1996).

The majority of cyanide that enters the body is eliminated in the urine, while a very small amount is expired into the air. Cyanide is excreted in the form of thiocyanate ( $\text{SCN}^-$ ) and this compound is biodegradable. Researchers have observed that cyanide blood concentrations return to normal within 4 to 8 hours from the time of exposure, depending on the exposure concentration (DHEW, 1976). Fortunately, many antidotes exist for individuals who have been exposed to cyanide which can reverse its effects and these antidotes are readily available to medical professionals (Marris et al., 1996; Sidell et al., 1997; Karalliedde et al., 2000).

### *Exposure Routes*

Contamination of potable water is a concern since people use water for recreation, hygiene, and drinking. Because of drinking waters' many uses, people can be exposed to contaminated water by inhalation, dermal absorption, and ingestion. The exact mass of cyanide required to cause toxicity by these exposure routes is not known; although, some researchers have predicted concentrations using previous poisoning cases and workplace exposure standards.

Consumers can be exposed to volatile cyanides by inhalation during showering, bathing, and cooking (Kim et al., 2001; EPA, 2000). The amount of chemical that volatilizes from water into air depends on a number of factors, most notably the air concentration ( $y$ ), aqueous concentration ( $C$ ), and Henry's Law constant ( $H$ ). In environmental systems chemical volatilization is modeled by using Henry's Law:  $y = H \cdot C$ . Other factors that will influence volatilization of cyanide from water are the chemical's  $\text{pK}_a$  and the water temperature. As water  $\text{pH}$  increases, less  $\text{HCN}$  is available for volatilization as shown in Figure 1. Some researchers have reported that as  $\text{pH}$  is increased from 7 to 9.5 inhalation exposures to  $\text{HCN}$  could be reduced by more than 50% (Kim et al., 2001). Water temperature also affects chemical volatilization in that as water temperature increases the amount of mass transferred to the gaseous phase increases as well.

Cyanide poisoning by dermal absorption of drinking water is not considered a significant health risk (Kim et al., 2001). While dermal exposure is likely (i.e., bathing), large quantities of cyanide will need to be absorbed in order to produce toxic affects. Also,  $\text{HCN}$  and  $\text{CNCl}$  present in water would most likely volatilize prior to dermal exposure. Contact by dermal absorption would occur during bathing and personal hygiene practices.

Ingestion of contaminated drinking water is a noteworthy exposure route. The EPA's maximum contaminant level (MCL) for cyanide in drinking water is 0.2 mg/L. This MCL assumes a lifetime exposure with a sufficient margin of safety, an average intake of 2 liters of water per day, and was determined using hydrogen cyanide toxicity data. The EPA's one-day and ten-day health advisories for a 10-kg child are both 0.2 mg CN/L. Table 2 shows other regulated cyanide drinking water concentrations. Lethal ingestion concentrations are highly variable and will not be discussed in this document.

**Table 2. Regulated Cyanide Drinking Water Concentrations**

<b>Concentration (mg/L)</b>	<b>Regulatory Organization</b>
0.2	U.S. Environmental Protection Agency
0.07	World Health Organization
0.2	Canadian Ministry of Health Services

## AQUEOUS DETECTION

Cyanide can be measured in multiple ways because of its dissociation and complexation properties in water. First, free cyanide is typically measured as HCN and CN<sup>-</sup>. Total cyanide is another measurement, which includes all cyanides present including the metallocomplexes. Lastly, cyanide amenable to chlorination is a measure of simple cyanides and most metallocomplexes with the exception of the iron complexes. The MCL in the U.S. is a measure of free cyanide.

Many analytical methods can be used to detect cyanide in drinking water at concentrations of 0.005-0.020 mg/L (APHA, 1998). Although, these methods are typically lab-based and require numerous measurement apparatus and detection equipment (i.e., spectrophotometer). One disadvantage of these methods is that some water samples might require pretreatment before analysis because interfering chemicals may be present. Another limitation of laboratory-based methods is that several do not measure insoluble cyanide complexes. Some researchers have recently developed and tested a new cyanide detection method with a detection limit of 5 µg/L (Strauss et al., 2002). This method is still under development. The major disadvantage of these laboratory based detection methods is that they are not portable and sample preparation time is lengthy.

A number of portable cyanide detection kits are commercially available. These portable commercial-off-the-shelf (COTS) kits have proven to detect cyanide in drinking water and can also be used to analyze for a number of different chemicals. The USACHPPM has field tested and used the following equipment:

- HACH Company (Loveland, CO) markets color disk test kits that detect cyanide at concentrations of 0-0.3 mg/L and portable handheld colorimeters (0-0.240 mg/L). These tests take approximately 30 minutes to obtain results.
- Another example of a COTS cyanide detection kit is the 10044 EM Quant<sup>®</sup> Cyanide Test (EM Science: Gibbstown, NJ). This colorimetric kit is semi-quantitative and detects cyanide at 4 different levels, 0, 1, 3, 10, and 30 mg/L. The EM Science technical service center declared that this colorimetric kit test takes about 2 minutes to obtain accurate results.
- CHEMetrics (Calverton, VA) also provides a color test kit with a range of detection from 0.005-1.0 mg/L.

As previously reported, the U.S. Environmental Protection Agency formally allocated research funds in December 2002 to begin assessing drinking water cyanide detection technology (AWWA, 2002). Online cyanide detection equipment is available; however, this equipment is very expensive and installation would not be practical at most, if not all, water utilities.

## WATER TREATMENT OPTIONS

Removing cyanic compounds from drinking water depends on a number of factors. These are the (1) form of cyanide present, simple (i.e., HCN) or complex (i.e., CuCN), (2) water pH and temperature, (3) other drinking water constituents present (i.e., hydroxide ions, metals, and organics), and (4) the volume of water contaminated. Generally, particulate cyanic compounds do not readily dissolve in water and can be removed by sedimentation or filtration; on the other hand, soluble forms are more difficult to remove. This treatment discussion will be based on removing soluble cyanides from water.

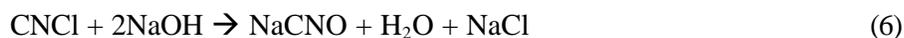
Discussion about water treatment effectiveness will not be covered in this document. Reasons for this include national security. The EPA has identified chlorination, ion exchange, and reverse osmosis as the best available treatment (BAT) technologies for removing cyanide from drinking water (EPA, 1998). Ozonation is another option that is effective but has not been approved by the EPA for removing cyanide (Faust and Aly, 1998). Other options that may be effective include iron coagulation, hydrolysis, aeration, and boiling. No references were found to justify the use of chloramines (combined chlorine), chlorine dioxide, potassium permanganate, ultraviolet radiation (UV), powdered activated carbon (PAC), granular activated carbon (GAC), conventional (multimedia) or ultrafiltration filtration.

### *Free Chlorination*

Free chlorination conducted at  $\text{pH} \geq 10.0$  is a treatment that can be used to destroy cyanide and the resulting byproducts are bicarbonate ions and nitrogen gas. Unlike chlorination used for the inactivation of pathogens where hypochlorous acid (HOCl) is the desired chemical, hypochlorite (OCl<sup>-</sup>) is the desired chlorine species when destroying cyanide ions. During cyanide destruction hypochlorite reacts with the cyanide ion to form cyanate (CNO<sup>-</sup>) (Equation 3). Once formed, the cyanate ion is then reduced to nitrogen, carbon dioxide and water molecules (Equation 4) and this reaction is irreversible (APHA, 1998). The EPA reported that higher pH values could increase the chlorine and cyanide ion reaction rate.



If cyanide destruction is not conducted at a pH greater than 10.0, the destruction effect could be less than desirable. Cyanogen chloride for instance could be produced and cyanogen chloride has been found to be equally if not more toxic than molecular HCN (Pedersen and Marinas, 1995; LaGrega et al., 2001). Equations 5 and 6 illustrate the formation and destruction of cyanogen chloride. The more desirable reaction byproduct is the cyanate ion because cyanate can be sequentially reduced to harmless molecules. Several studies have shown that the breakdown of CNCl is both pH- and time-dependent.



When cyanide is in the form of metallocomplexes, specifically iron and nickel, destruction is more difficult (APHA, 1998; LaGrega et al., 2001). Many of these metallocomplexes do not dissociate and as a result the time required for destruction is greatly increased. Some research indicated an excess chlorine dose of 20% is needed in order to destroy nickel complexes (LaGrega et al., 2001). Additionally, several references indicated that ferrocyanide is converted to ferricyanide during chlorination and additional destruction by chlorine is ineffective. These species are sparingly soluble in water and will be removed during conventional water treatment.

### ***Reverse Osmosis***

Reverse osmosis has proven to reduce cyanide concentrations in the water at elevated pH (EPA, 1985). Reverse osmosis (RO) membranes are also capable of removing many soluble and insoluble salts and metal ions from water including cyanic compounds. Removal of soluble cyanic compounds such as HCN and CNCl and even CN<sup>-</sup> ions is more difficult.

Reverse osmosis is similar to conventional filtration in that water is pushed through a filter, in this case a synthetic membrane, to sieve contaminants. The products of this membrane filtration process are the less concentrated product water (permeate) and highly contaminant concentrated water (brine). The removal efficiency of a membrane is measured as percent of contaminant rejected. This percentage can vary depending on what chemicals are present in the challenge water matrix, pH, temperature, the rate at which water can be filtered per unit area of membrane (permeate flux), and decrease in loss in permeate flux (fouling and colmatage).

### ***Ion Exchange***

Numerous synthetic anion exchange resins have been developed and are currently being used in the water industry. The EPA has approved these units for removing cyanide. Ion exchange units are usually cylindrical in shape and are filled with absorbent or resin beads. Typically, cyanide specific resin beads are presaturated with chloride ions (Cl<sup>-</sup>) are used in ion exchange units designed specifically for cyanide removal. As contaminated water passes through the exchange unit, chloride ions are exchanged for the unwanted CN<sup>-</sup> ions. The product of the ion exchange process is an effluent that has a lower cyanide concentration and a higher chloride concentration.

Much of the research dealing with ion exchange efficiency for removing cyanide is proprietary, although, cyanides are strongly removed by strong base anion exchange resins that are in the hydroxide form. Strong base resins can also remove metal-cyanide complexes. One disadvantage of ion exchange is that over time the resins will become saturated with cyanide anion and cyanide removal will diminish and possibly stop completely. When this occurs resins can either be disposed of or regenerated. The disposal of cyanide saturated resins can be quite costly as this waste now contains a significant amount of cyanide and must be treated as hazardous. Most cyanide saturated resins can be regenerated, although strong base anion exchange resins cannot usually be regenerated efficiently. Regeneration is completed by flowing super concentrated water (containing the presaturant ion, chloride) through the bed. This act forces the cyanide ions to enter the water flow and ultimately be removed. The product of regeneration however, is the highly concentrated waste that must be discarded.

### ***Iron Coagulation followed by Flocculation and Sedimentation, and/or Filtration***

Since iron strongly complexes and forms insoluble precipitates with cyanides, iron coagulation may be helpful when treating contaminated water. Iron salts are some of the most widely used coagulants in the water industry (AWWA, 1999). These coagulants are added during treatment to improve the settling characteristics, filtration performance, and the removal of dissolved species and microorganisms.

The addition of a coagulant allows charged particles to congregate and collide. Without a coagulant, many of these particles will remain suspended in water and will not be removed by settling or filtration processes. While the exact chemistry of iron coagulation and reaction products is not completely understood, the use of this chemical has proven to remove many unwanted contaminants. The EPA, as an acceptable cyanide removal practice, does not approve iron coagulation.

The effectiveness of iron coagulation is highly dependant upon water pH. Generally, the minimum solubility of ferric hydroxide (one type of iron coagulant) occurs at pH 8.0; however, this coagulant has proven to be effective in the pH range of 5.0 to 10.0 (AWWA, 1999). Due to HCN and CN<sup>-</sup> speciation, it may be possible that iron coagulation for the removal of cyanide ions would best occur at pH greater than 9.2.

Effective coagulation and flocculation would be noticed by increased water turbidity or a decrease in water clarity. Once cyanides are in the particulate form settling and filtration processes can be used. Generally, soluble cyanides, particularly CN<sup>-</sup>, would not be removed by settling or filtration alone. Many drinking water treatment plants that serve medium to large installations have coagulation and flocculation processes already in place and would not require major upgrades to implement this process.

Another concern with the iron coagulation process is that effectiveness is highly dependant on the type of treatment processes that follow. The addition of iron coagulant alone will not remove cyanide from water. Particle removal steps, such as flocculation, settling, and filtration must be used to remove the coagulated particles. Depending on the duration, extent, and type of particle loading, the filter can become clogged and experience irreversible damage.

The effectiveness of iron coagulation for the removal of water soluble cyanides is theoretically based and has never been tested on a bench-, pilot-, or full-scale application. Based on the literature review the authors believe that iron coagulation at pH equal to and greater than 9.6 should promote iron-cyanide complexation. The U.S. Army Tank-automotive Research and Development Engineering Command (TARDEC) located in Michigan, USA is currently testing this theory (Li and Downing, 2002).

### ***Ozonation***

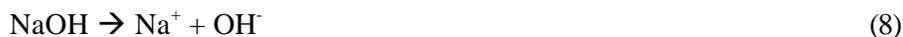
Ozonation is a process that is gaining popularity at many water utilities because of its ability to disinfect as well as remove unwanted tastes and odors from water. During ozonation, gaseous ozone (O<sub>3</sub>) is added to water where it reacts with hydroxide ions (OH<sup>-</sup>) to form hydroxyl radicals. These hydroxyl radicals are mainly responsible for the inactivation of pathogenic organisms, while molecular ozone plays a smaller part.

While not approved for removing cyanide from drinking water by the EPA, one study found that ozone is an effective disinfectant that can destroy cyanide. According to the EPA, cyanide in water at 5-15 mg/L concentrations was completely destroyed using a 1.3 to 1 ozone to cyanide molar ratio (EPA, 1985). The results of this study also indicated that the rate of destruction decreased when cyanide concentrations were less than 5 mg/L. Other research has indicated that ozone reacts with cyanide at a very fast rate, although the reaction products are unknown. The American Waterworks Association (AWWA) reported that during ozonation iron cyanide complexes inhibit cyanide destruction while copper complexes catalyze ozone reactions (AWWA, 1999).

### ***Hydrolysis, Aeration, and Boiling***

Other treatment options for cyanide contaminated waters are hydrolysis, aeration, and boiling. These methods are most effective for removing volatile cyanic compounds such as HCN and CNCl.

Unfortunately these methods are only suitable for small volumes of water. Hydrolysis has proven to reduce the concentration of cyanogen chloride dissolved in water. Hydrolysis is the decomposition of a chemical, such as cyanogen chloride, by reaction with water. Cyanogen chloride has been found to go through hydrolysis using the hydroxide ion (Equations 8 and 9) (Pedersen et al., 1999). Using these stoichiometric equations, approximately, 0.65 mg/L of caustic soda (NaOH) is required to hydrolyze 1 mg/L of cyanogen chloride. One researcher reported that approximately 4 mg/L of soda ash (Na<sub>2</sub>CO<sub>3</sub>) is required for every 1 mg/L CNCl in low alkalinity waters (Sanchis, 1946). No additional data was found that states hydrolysis is effective for removing any other cyanic compounds.



Aeration and/or boiling of HCN and CNCl contaminated water is a feasible alternative, but is dependent on water pH and temperature. Aeration is commonly used in the water treatment industry to strip volatile chemicals out of water. Vigorous aeration conducted at room temperature and at a pH above 9.2 may be somewhat effective for both HCN and CNCl, but aeration below pH 9.2 would be much improved. Aeration conducted at higher water temperatures would also be more effective. In contrast to aeration, boiling contaminated water would increase the rate of cyanide volatilization. By increasing the water temperature the amount of cyanide volatilized would increase as well. Due to energy requirements and costs, this process may only be suitable for small volumes of water. One researchers stated that boiling water is not effective for the removal of HCN in concentrations greater than 200 mg/L in alkaline (pH > 7.0) waters (Sanchis, 1946).

## CONCLUSIONS

Water utilities should follow at least industry standard if not more rigorous security measures to protect against cyanic threat because many cyanic compounds readily dissociate in water and pose a significant risk to consumers. Furthermore, widespread use of cyanide allows it to be easily acquired by people in many different walks of life. Water utilities should understand the capabilities of their treatment system and disinfectant at protecting consumer health.

Consumers may be exposed to cyanide by inhalation and dermal absorption, but the conditions and concentrations required to be lethal are many. The most likely cyanide exposure route is by ingestion. Fortunately, consumers may detect exposure by noticeable water tastes and odors. The odor threshold concentration of HCN is 1 ppm. Because of this fact, consumer complaints must be responded to and handled expeditiously (Whelton and Richards, 2002). One researcher has speculated that water with a 50 mg HCN /L drinking water concentration would be unpalatable to consumers (Sanchis, 1946).

Contamination of the source water (i.e., lake) is practically impossible. The mass of cyanide needed to contaminate a moderate sized reservoir is in the millions of pounds. Transport and dosing of such a large amount of cyanide would likely be dangerous and would even require multiple transport vehicles (i.e., dump trucks). If such an event did occur, there would most likely be a massive fish kill indicating some type of poison in the water.

The EPA has approved free chlorination, reverse osmosis, and ion exchange as acceptable treatment methods for cyanide contaminated drinking water. Other non-EPA approved cyanide removal options that could be effective are iron coagulation, the use of ozone, aeration, boiling, and allowing hydrolysis. The effectiveness of these methods is highly dependant on water pH, temperature, other constituents present in water, and the specific cyanic compound(s) and concentrations present.

Importantly, the pH of water will need to be strictly controlled to obtain good removal/destruction. For small water quantities hydrolysis, boiling, and aeration may be effective. Water utilities may want to consider installing point-of-use (POU) devices on buildings designated of high-importance. These POU's should be proven to remove cyanide to below the MCL.

## RECOMMENDATIONS

Water utilities should consider the following-

- Determine if there is a background cyanide concentration in potable water and in the source water(s).
- Be alert for complaints involving illness, metallic tastes, bitter almond and pepperish odors and integrate consumer complaints into the early-warning system as indications of possible bad water quality.
- Determine typical free chlorine residual concentrations and water pH values throughout the distribution system.
- Continually monitor distribution system free chlorine residual concentration and water pH.
- Increase chlorine residual and pH monitoring frequency and locations in response to elevated threats or system breaches.
- Use approved portable cyanide detection equipment when testing suspect water.
- Estimate the utility treatment effectiveness based on (1) type of cyanic compound present (i.e., simple or complex), (2) water pH, and (3) the volume of water to be treated.
- Install and maintain point-of-use devices on buildings designated of high importance with appropriate treatment equipment similar to those outlined in this paper. These devices should prove effective under different water quality conditions.
- Before treating cyanide contaminated water contact your local and State health officials as well as the EPA. This act should not be executed alone as treatment without concern to water pH could exacerbate the contamination problem.

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