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The Truth About Cyanide Toxicity at MGP Sites

Bruce Coulombe, GEI Consultants, Inc.

Few manufactured gas residuals grab attention the way that cyanide does. Yet as our industry researches the cyanide issue, we find that MGP-related cyanide is usually of little concern, posing insignificant risk to human health and the environment.

To understand why cyanide is rarely the risk driver when evaluating MGP sites, we need only to look at its chemistry. A cyanide compound contains the cyano radical, which consists of a carbon atom joined by a triple bond to a nitrogen atom (CN^-). Cyano radicals do not exist on their own in nature because they are negatively-charged free radicals, and must bond with other elements. Consequently they can form a wide array of more complex compounds. The number of natural and man-made inorganic and organic cyanide compounds is large, ranging from simple compounds such as hydrogen cyanide (HCN), to complex organic compounds created in plants and animals, such as fungi and more complex organisms like fruit trees. However, for our discussion of cyanide at MGP sites we will only look at the cyanides associated with manufactured gas.

What is Cyanide?

Inorganic cyanide compounds are grouped into three classes: free cyanide, simple cyanide, and metal-complexed cyanide. As the complexity increases, reactivity and toxicity decreases. Free cyanide, or hydrogen cyanide (HCN), is the simplest and most toxic of all cyanide compounds and it poses an acute risk to life. Hydrogen cyanide is the combination of hydrogen with the cyano radical (CN^- anion). It is highly toxic because it is a weak acid which readily breaks down to release CN^- when it goes into solution. When the CN^- radical is released or enters the human body, it binds with the iron-rich hemoglobin in red blood cells in an irreversible way, and at sufficient concentrations, that can lead to death. Generally, when non-practitioners hear the word "cyanide", it is the toxic hydrogen cyanide, with its faint scent of almonds that comes to mind.

The simple cyanides include those compounds where the CN^- binds with the alkali metals, sodium (Na), potassium (K), and lithium (Li). These compounds are more complex than free cyanide but can

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What's News

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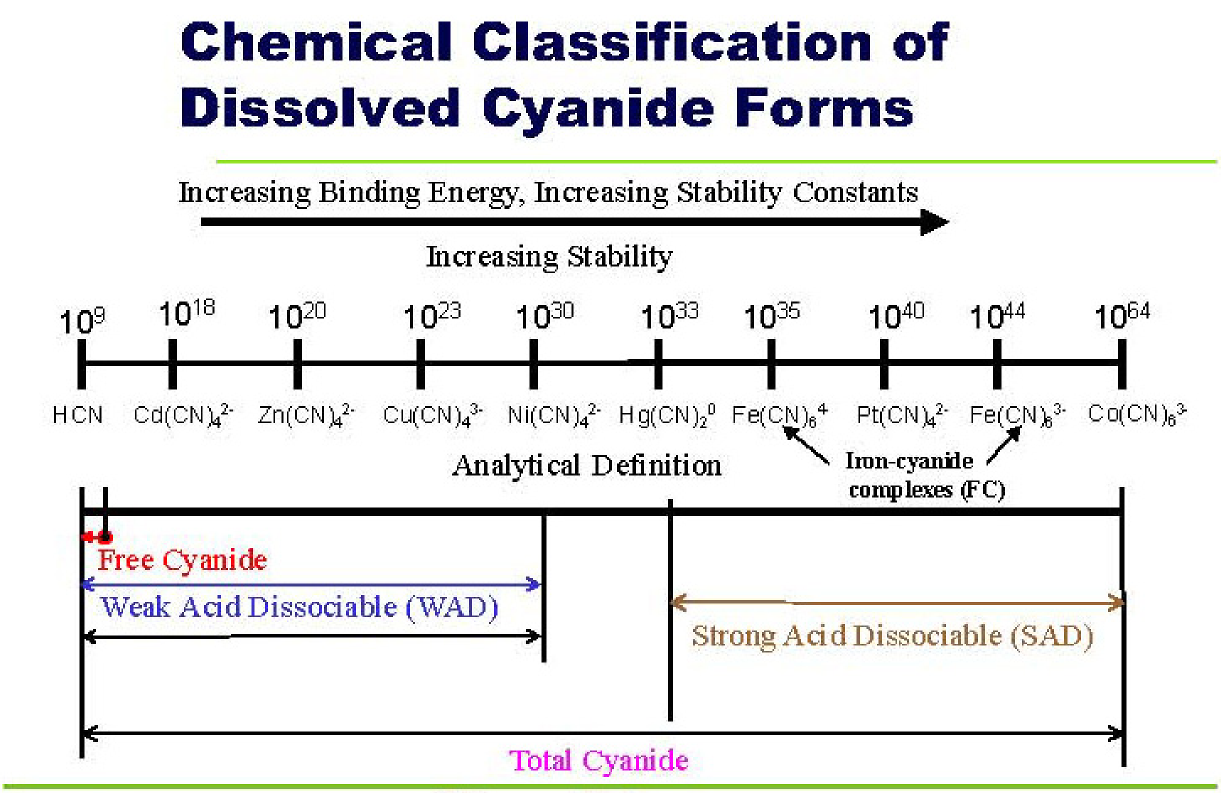
also be toxic since they also can release the cyano anion when in solution. Therefore, they too are regarded as a human health risk.

When we talk about testing for free cyanide, or the environmental or health risks of cyanide, we are commonly grouping the free and simple forms of cyanide together. Though highly toxic, the good news is that these forms of cyanide, if present at all, are typically present at very low concentrations in nature and at MGP sites. Instead, at MGP sites, we must look at the third general category of cyanide compounds.

The third general category of inorganic cyanides are the metal-complexed cyanide compounds. Under normal environmental conditions, these compounds form stable bonds with transition metals such as iron, cobalt and gold, and are highly non-reactive and non-toxic. This is because they will not release the CN^- anion except under very unusual circumstances that are not found in the environment, i.e., these compounds are not solubilized except at a pH approaching 10 and higher, after which they must be exposed to ultraviolet light. These are the most common cyanide compounds at MGP sites, formed in the past by the practice of using iron oxide impregnated wood chips (shavings) in purifier boxes to help with the removal of hydrogen sulfide, hydrogen cyanide and other impurities from the gas. The dominant compound found is ferric ferrocyanide (FFC) or "Prussian blue". This is the compound which gives purifier wastes and materials in contact with them their signature blue color. Prussian blue is quite stable and has been used for centuries as a blue pigment. Prussian blue is also used to make blueprints. As an indication of its lack of toxicity under controlled doses, the US Food and Drug Administration (FDA) has ruled that Prussian blue can be administered in 500 mg capsules for the treatment of internal poisoning by radioactive thallium or cesium (FFC binds with the radioactive elements and is passed out of the body through the intestines).

The figure below presents the range of inorganic cyanide compounds that may be present at an MGP site. Moving from free cyanide to simple cyanide to metal-complexed cyanide (from left to right), the binding energy of the compounds increases by orders of magnitude, reducing the propensity to release the toxic CN^- anion. The iron-complexed cyanide compounds are dominant at MGP sites because of the iron that was used in gas purifier media (and is also abundant in many soils).



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Editorial

Cyanide, The Blue Herring

Dennis Unites, GEI Consultants, Inc.

Back in the 80's when we started poking around manufactured gas plants, cyanide associated with purifier waste was a perceived issue, with lots of mythology surrounding it. "If it gets mixed with acidic material there will be a toxic cloud!" "If it's exposed to sunlight, cyanide gas will be released."

And there were lots of questions about cyanide analytical methods and results. As one step in trying to decipher the mythology, the Gas Research Institute (GRI) sent split samples of purifier waste to a number of laboratories. The labs were instructed to analyze for total cyanide using USEPA Methods, and note significant variations in application of the methodology. The results ranged over three orders of magnitude. The highest result was still two orders of magnitude below the "true" value determined in two university laboratories.

We're glad that the state of knowledge has improved greatly. But the state of understanding amongst many regulators and decision-makers in our industry remains rooted in the dark ages. Free cyanide is the main concern with respect to risk, but numerous regulations continue to call for measurement of total cyanide.

Dzombak et al (2006) shed light and dispel a lot of the mythology. Hopefully our feature article will encourage decision makers to request appropriate analytical methods so we can quit squirming in the morass.

David A. Dzombak, R. S. Ghosh, G. M. Wong-Chong. 2006. Cyanide in Water and Soil: Chemistry, Risk, and Management. CRC Press. Boca Raton, FL.

MGP Reporter

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***The GEI MGP Reporter** is a quarterly newsletter covering selected environmental issues in the electric and gas industry. The newsletter staff welcomes articles and comments from members of the industry. When contractor and/or vendor names are listed anywhere in this publication, it is for information only and does not imply any endorsement whatsoever on the part of GEI or its co-sponsors.*

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Speak Up

MGPs Around the World

Submitted by Russel Thomas, UK

Gasworks - English UK
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Gaswerk - German
usines à gaz - French
gasfabrieken - Dutch
officina del gas - Italian
fábrica de gás - Portugeese
εργοστάσια παραγωγής αερίου - Greek
gasverk - Swedish
газовый завод - Russian
havagazı fabrikası - Turkish

Coal Tar History: Bee Hive Coke Ovens

John Ripp, GEI Consultants, Inc.

During an attempt to disappear and get my mind off of MGPs for a while last summer in the mountains of Colorado, I stumbled across the historic site of the Colorado Fuel and Iron Company Redstone Coke Ovens. The "bee hive" ovens there took coal from a mine 12 miles up the mountain and converted it into coke. They operated between the late 1890s and 1908.

Coke is made when low-ash, low-sulfur bituminous coal is heated to drive off volatile matter and moisture in the absence of oxygen. The coke product was used for the most part as an industrial heating fuel. The coke was shipped to Pueblo via the Standard Gauge Crystal River Railroad.

Coal tar is not usually associated with beehive ovens because exhaust gases were vented to the atmosphere. At MGP operations, the gas stream was captured and cooled to condense the coal tar by-products.

My wife thought I was crazy when I told her I've been waiting years to be able to get inside a bee hive coke oven.

Read Up

Dense Nonaqueous Phase Liquids at Former Manufactured Gas Plants: Challenges to Modeling and Remediation

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Abstract: The remediation of dense non-aqueous phase liquids (DNAPLs) in porous media continues to be one of the most challenging problems facing environmental scientists and engineers. Of all the environmentally relevant DNAPLs, tars in the subsurface at former manufactured gas plants (FMGP's) pose one of the biggest challenges due to their complex chemical composition and tendency to alter wettability. To further our understanding of these complex materials, we consulted historic documentation to evaluate the impact of gas manufacturing on the composition and physicochemical nature of the resulting tars. In the recent literature, most work to date has been focused in a relatively narrow portion of the expected range of tar materials, which has yielded a bias toward samples of relatively low viscosity and density. In this work, we consider the dissolution and movement of tars in the subsurface, models used to predict these phenomena, and approaches used for remediation. We also explore the open issues and detail important gaps in our fundamental understanding of these extraordinarily complex systems that must be resolved to reach a mature level of understanding.

http://www.sciencedirect.com/science/article/pii/S0169772208002155
Journal of Contaminant Hydrology
Volume 105, Issues 3-4, 1 April 2009, Pages 81-98

ANNOUNCING

Announcing The 4th International Symposium and Exhibition on The Redevelopment of Manufactured Gas Plant Sites (MGP 2012)

CALL FOR PAPERS

MGP 2012 will be held at the Palmer House Hilton Hotel in downtown Chicago from March 27-30, 2012. Visit **http://www.mgp2012.com** for instructions on submitting an abstract and for all symposium information.

Abstracts are due September 30, 2011.

Please consider signing up for a **Sponsorship or Exhibit Booth.** Based on past MGP symposia, we expect a high turnout so don't delay in making your decision to participate in this timely and informative meeting. Exhibit space is limited and availability will be on a first come first serve basis.

Future updates on MGP 2012 will be posted in the MGP Reporter and through separate email announcements.

Coal Tar & Pavement Sealers (Part 5)

Our Winter 2011 issue reminded readers of USGS studies that point to coal tar based driveway sealers as a primary source of PAHs in sediments. USGS is also reporting that a main source of PAHs in house dust is coal tar based driveway sealers. You can review their study here: http://tx.usgs.gov/. You can also download and listen to a "Corecast" interview with one of the researchers here: http://www.usgs.gov/corecast/details.asp?ep=116.

At http://www.truthaboutcoaltar.com/ you can review opposing viewpoints in the matter. The website owner is not listed at the site, but when we first reported about it in 2007 the phone number provided on the webpage led to Cooper's Creek Chemicals, a refiner of crude coal tar.

Based largely on the USGS studies, the State of Washington voted on May 5, 2011 to ban coal tar based driveway sealants. This is a first in the United States. http://www.msnbc.msn.com/id/42917004/ns/us_news-environment/t/state-bans-coal-tar-sealants-big-win-foes/

Web Finds

More Coal Tar on the Internet

Take a look at http://coaltar.org/. If you can figure out who developed this site and why, please let us know. The text below the "Coal Tar Epoxy" page is particularly strange and useless.

We didn't poke around this website enough to really nail the connection between coal tar and Lewis and Clark, but someone thinks there is one. You are welcome to look for yourself at http://lewis-clark.org/content/content-article.asp?ArticleID=550.

Here's a misleading coal tar page. http://healthychild.org/issues/chemical-pop/Coal_tar_dyes. Follow the link and read the first sentence. These dyes, the site asserts, are not healthy but are no longer manufactured from coal tar. However, they are still called coal tar dyes. That's really helpful……….

Look at http://coaltarfreeamerica.blogspot.com. We weren't able to determine who the blogger is, and following links to join or support the cause led us to equally anonymous Facebook pages.

If you are sentence-challenged, check out this page: http://sentence.yourdictionary.com/coal-tar. What will they think of next?

Truth About Cyanide (continued from page 2)

Analytical Methods

It is difficult to perform laboratory testing to measure all forms of cyanide. The laboratory test for "total" cyanide does not identify or quantify the variety of individual cyanide compounds that may be present, and it provides little meaningful information on the environmental significance of the result. All that can be said is that if little or no total cyanide is detected, then the concentration of the more toxic free cyanide must also be low.

In general, the analytical tests for cyanide compounds can be broken into two categories – those that dissociate using strong acids and those that dissociate using weak acids. The strong acid dissociable (SAD) compounds are the most inert and least toxic and include the iron-complexed cyanide compounds found at MGP sites. Because these compounds are inert and non-toxic, the calculation of SAD (total cyanide minus WAD = SAD) is not typically performed for MGP media.

WAD cyanides include free cyanide, simple cyanides and those metal–complexed cyanides that will readily release their CN^- anion under weak acid conditions. WAD testing includes the toxic free cyanide and simple cyanides, excluding the iron cyanides. As such, it provides a more environmentally significant measure of environmental risk – though it is still a very conservative measure. For the purposes of site management, WAD concentrations do represent a step in the right direction.

WAD cynaide can be measured by an ASTM International (ASTM) method, but it is not an EPA-approved method and cannot routinely be used to assess compliance with state or Federal permit requirements. The cyanide amenable to chlorination and available cyanide methods are EPA-approved and they generate results similar to the WAD method. However, the cyanide amenable to chlorination method is rarely used because of its known lack of precision. The available cyanide method is more precise, but overestimates the concentrations of free and simple cyanide compounds.

Until recently, there has not been an EPA-approved analytical method for free cyanide, alone. This lack of a free cyanide-specific test was a problem because the Federal drinking water standard and most state water quality standards are based on the concentration of free cyanide alone.

In 1995, the ASTM published a method for measuring free cyanide (CN^-) using a microdiffusion method (ASTM D 4282-95). In 2010, based on research sponsored by National Grid, the Northeast Gas Association and Alcoa, the USEPA adopted this method, without changes, as EPA Method 9016 (http://www.epa.gov/waste/hazard/testmethods/pdfs/9016.pdf). This new EPA method finally allows us to measure how much of the total cyanide at MGP sites is in the form of metal complexed cyanides and how little is present as free cyanide.

Labs that were already running the ASTM method appear to be capable of running the equivalent EPA method. The cost of the analysis is typically less than $100 per sample and may go lower as more labs bring the method on-line. Because the new EPA method follows the same procedure as the ASTM method, data from both tests are directly comparable.

Unfortunately, many regulations remain based on total cyanide concentrations in soil or water. Unless regulations are revised to account for differences between free and complex cyanides it will be necessary at some sites to use both total and free cyanide tests in order to assess the environmental compliance and risks.

Where to Find Out More

A comprehensive overview of cyanide in the environment is the 2006 book "Cyanide in Water and Soil – Chemistry, Risk, and Management", by Dzombak, Ghosh, and Wong-Chong. A recent summary of cyanide issues as they pertain to MGP sites is the 2010 EPRI publication "Understanding Cyanide at Manufactured Gas Plant Sites: Presence and Risk". ASTM also offers their document D6696-10, "Standard Guide for Understanding Cyanide Species".

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