OSORNO

NEWSLETTER February 2015

Water Disinfection (Part 1): Chlorination

Chlorination History

In 1854, a severe outbreak of cholera occurred in the Soho district of London, England. The physician John Snow studied the outbreak and discovered that cholera is spread by contaminated water. He proved it by (illegally) removing the pump handle to the local well. People could no longer get water from the well and the outbreak ceased. However, it took some time before water disinfection was implemented to prevent future disease outbreaks.

A paper published in 1894, formally proposed the idea of adding chlorine to water to render it "germ-free." Two other authorities endorsed this proposal and published it in several papers in 1895. Early attempts at implementing water chlorination began in 1893 at a water treatment plant in Hamburg, Germany. The town of Maidstone, England was the first to treat their entire water supply with chlorine in 1897.

Permanent water chlorination began in 1905, when a faulty slow sand filter and a contaminated water supply led to a serious typhoid fever epidemic in Lincoln, England. Dr. Alexander Cruickshank Houston used chlorination of the water supply to stem the epidemic. His installation fed a concentrated solution of calcium hypochlorite (bleaching powder) to the water. Chlorination of the water supply helped stop the epidemic and as a precaution, the chlorination was continued until 1911 when a new water supply was instituted.

Prior to water disinfection, the danger of epidemics was unabated. In June 1832, the Carrick, a ship from Ireland reached Quebec with a few feverish immigrants on board. By the end of that year, the epidemic had claimed 9,000 lives. Over 190 years later, the headline in the Vancouver Sun read "*Typhoid fever on track to break B.C. Record*" (May 26, 2008). The article began "*Typhoid and paratyphoid fever cases in B.C. are on pace to shatter all previous incidence rates of the past several years as 44 cases of both have already been diagnosed so far this year.*" The only reason that this recent typhoid outbreak did not spread further is due to modern water disinfection treatment. Clearly, disrupting the infection chain is critical, and water disinfection is the primary tool to achieve that.

Since chlorination was first introduced more than 120 years ago, several new products have been introduced to achieve disinfection: chlorine gas, sodium hypochlorite ("bleach"), electrolytically generated chlorine / hypochlorite, dichloroisocyanuric acid (also known as dichlor, marketed as troclosene), and trichloroisocyanuric acid (also known as trichlor). In all these cases, the active disinfection compound is hypochlorous acid, not chlorine, contrary to common belief.

Chlorine and Hypochlorous Acid

In 1946, the Journal of the American Chemical Society published an article under the title "*The Mechanism of the Hydrolysis of Chlorine*" (page 1692, author: J. Carrell Morris) which began "*A few years ago Shilov and Solodushenkov ... succeeded in measuring the extremely rapid*

Osorno Enterprises Inc. ● 976 Elgin Ave. ● Winnipeg MB R3E 1B4
Phone: +1 (204) 488-1538 ● Fax: +1 (204) 488-1566 ● Internet: http://www.osorno.ca

rate of hydrolysis of chlorine. They found the reaction to be substantially complete in less than a second even at 1 °C." We can simplify this statement to "***chlorine in water does not exist***", despite common terms like "free chlorine" in water testing, when in fact the measured quantity is free hypochlorous acid and its anion hypochlorite.

The interesting product of this rapid hydrolysis is hypochlorous acid. An equal amount of hydrochloric acid is also formed in this reaction, but is immediately neutralized under the conditions of water treatment, and therefore plays no further role.

Unfortunately, hypochlorous acid is an unstable chemical compound, sensitive to light and elevated temperatures. Even at room temperature, it decomposes at a rapid rate, forming toxic compounds (chlorite, chlorate) and non-toxic chloride. Our tests of commercial hypochlorite that was rated at 12% concentration have shown that it is not uncommon that the actual measured concentration was only 3% or less, owing to its relatively short shelf life. The obvious and sad news is that the balance between 12% and 3% are decomposition products, meaning undesirable and potentially toxic chemical.

Electrolytically Generated Chlorine

Given the short shelf life of hypochlorite solutions, it is tempting to generate it fresh on site through simple electrolysis, which requires only common table salt and electricity. Unfortunately, the freshly created hypochlorite has its highest concentration at the anode, where it competes with chloride for oxidation. This competition leads to the formation of toxic chlorite, which in turn is oxidized at the anode to toxic chlorate, and ultimately to the extremely toxic perchlorate. Perchlorate is an endocrine disruptor which interferes with the hormone production of the thyroid.

The amount of perchlorate formed depends largely on the electrode (anode) material, as a German professional organization (DVGW), has found. The two types of electrodes commonly used in this equipment are either mixed metal oxide (MMO electrodes), or boron-doped diamond (BDD). As the DVGW research report shows, none of the BDD-based equipment satisfies acceptable standards for perchlorate contamination. Interestingly, manufacturers usually do not indicate what type of electrodes they use. Both MMO and BDD based electrolysis systems generate chlorate and perchlorate, as well as bromate, the latter through the oxidation of bromide that is found in small amounts in most natural waters. Bromate is a suspected carcinogen.

All electrolytic equipment requires electrode maintenance at least once per month; the amount of undesirable by-products increases over time since the last electrode maintenance.

Disinfection By-products

Disinfection by chlorination can be problematic. Any disinfectant produces compounds known as disinfection by-products (DBPs). Chlorine reacts with naturally occurring organic compounds found in the water supply to produce DBPs, the most common of which are trihalomethanes (THMs) and haloacetic acids (HAAs). Among the THMs created from chlorination are several which are considered health hazards. Chronic exposure to THMs can cause liver and kidney cancer, heart disease, unconsciousness, or at high doses - death. Due to the potential carcinogenicity of these compounds, drinking water regulations across the developed world require regular monitoring in the distribution systems of municipal water systems.

When DBPs are a concern, as they commonly are, alternatives to chlorination should be considered. Osorno can provide advice on alternative water disinfection processes.

Summary

Despite the obvious benefits of water treatment through chlorination, there are significant disadvantages, including the formation of toxic disinfection by-products. Future newsletters will provide additional information on water treatment, including safe alternatives to the use of chlorine.

(continued in the next newsletter)

Osorno Enterprises Inc. ● 976 Elgin Ave. ● Winnipeg MB R3E 1B4
Phone: +1 (204) 488-1538 ● Fax: +1 (204) 488-1566 ● Internet: http://www.osorno.ca