

EPB 431- Ammonia Fact Sheet

This information sheet is intended to assist the waterworks designer, owner, manager or operator in understanding the complexity in dealing with source water containing high ammonia levels, available treatment options, and the related requirements of the Water Security Agency.

What is ammonia?

Ammonia (NH_3) is a colorless, alkaline gas at ambient temperature and pressure, with a distinct pungent odor. Ammonia is very soluble in water and forms the ammonium cation (NH_4^+) on dissolution in water. In the pH range of most natural waters nitrogen exists principally as NH_4^+ . Ammonia may be present in groundwater as a result of the degradation of naturally occurring organic matter or manmade sources. Natural ammonia levels in groundwater and surface water are usually below 0.2 mg/L, but many regions throughout the world have high levels of naturally occurring ammonia. Ammonia may also originate from nitrogen-fertilizer application, livestock operations, industrial processes, sewage infiltration, and cement mortar pipe lining. During 1998 to 2010, samples from 393 private water wells in Saskatchewan were analyzed for ammonia and it was detected in more than 87% of the samples with an average value of 1.19 mg/L.

Are ammonia and its derivatives regulated in drinking water?

A health based guideline has not been developed for ammonia levels in drinking water. However, the World Health Organization suggests that at a concentration above 1.5 mg/L ammonia can cause odour and taste problems. Ammonia can also compromise disinfection efficiency, increase oxidant demand, cause the failure of filters for the removal of manganese, and corrode copper alloy pipes and fittings. Moreover, a major concern with ammonia in drinking water is nitrification associated with the formation of nitrites and nitrates. Nitrites and nitrates can cause health problems; although, this risk is relatively low in Saskatchewan waterworks because of low operating temperatures most of the year. Another health concern is the formation of chloramines when chlorine is added to water systems.

At present, the Water Security Agency (WSA) does not establish standards or objectives for ammonia levels in drinking water. The WSA does regulate the maximum acceptable concentration (MAC) of 45 mg/L (10 mg/L as nitrate nitrogen) for nitrate. Where nitrate and nitrite are determined separately, levels of nitrite should not exceed 3.2 mg/L (1 mg/L as nitrite-nitrogen). Health Canada sets a MAC of 3 mg/L for total chloramines which is based on a risk evaluation for monochloramine. The WSA is currently reviewing this MAC for adoption.

What is the concern over chlorine disinfection of ammonia-bearing water?

Ammonia in raw water interferes with the chlorine disinfection process and free chlorine residual maintenance in the distribution system. This is due to the rapid reaction of ammonia with chlorine once contacted, which impedes the achievement of adequate CT values (residual disinfectant concentration multiplied by contact time) for the inactivation of microorganisms. Decreased disinfection efficiency as well as taste and odor problems are to be expected if drinking water containing more than 0.2 mg/L of ammonia is chlorinated, as the added chlorine may react with the ammonia and become unavailable for disinfection. Required disinfection may not be achieved in water containing ammonia unless breakpoint chlorination is reached prior to distribution.

What is the normal strategy to deal with ammonia-bearing water and what is its problem?

Breakpoint chlorination (also known as super-chlorination or shock-chlorination) is one of the essential treatment techniques for the removal of ammonia in raw water. Ammonia, when in contact with chlorine, will react rapidly to form chloramines. Chlorine will first react with NH_3 to form monochloramine (NH_2Cl). Additional free chlorine then reacts with monochloramine to form dichloramine (NHCl_2), and then trichloramine (nitrogen trichloride, NCl_3), before the breakpoint is achieved. Further dosage of chlorine passing the breakpoint will result in free chlorine residual. Breakpoint chlorination is thus the addition of chlorine to water until the chlorine demand has been satisfied to reach the breakpoint. Chlorination can then be achieved by using chlorine-based disinfectants, such as chlorine gas and sodium hypochlorite.

Although breakpoint chlorination is considered a cost effective strategy under low ammonia levels, high ammonia levels may greatly increase the chlorine demand. The presence of 1 mg/L of ammonia nitrogen in raw water may require 8 to 10 mg/L of chlorine dose to achieve breakpoint chlorination. It can be difficult and expensive for water treatment facilities to add enough chlorine to provide satisfactory levels of disinfecting compounds in the water and have reactions proceed at a rapid enough pace. A high amount of chlorine may result in a high concentration of total chloramines that exceeds the MAC level of 3.0 mg/L set by Health Canada and interferes with the DPD (i.e. N, N-diethyl-p-phenylenediamine) test method for free chlorine. Trihalomethanes (THMs), halogenated acetic acids (HAAs), bromates, chlorates, and chlorides are other concerns with high dosage of chlorine-based disinfectants.

Can we use as much disinfectant as needed for achieving breakpoint chlorination?

No. The WSA regulates that only NSF Certified Drinking Water Treatment Chemicals can be used in drinking water, and the max use level (MUL) of each chemical product must conform to the latest version of *NSF/ANSI Standard 60: Drinking Water Treatment Chemicals - Health Effects*. An MUL indicates the maximum amount of a packaged chemical product (in the form that it is delivered) that can be added to the entire process train per liter of water being treated. Please note that, the MUL for each hypochlorite product is based on 10 mg Cl_2 /L unless specifically stated. For chlorine gas, levels up to 30 mg Cl_2 /L are acceptable for short-term applications such as shock chlorination and disinfection of new installations. Listings of NSF certified chemical products at their MULs can be found at <http://www.nsf.org/Certified/PwsChemicals/>. The manufacturer and trade name of each product must be obtained to search the respective MUL. It is not allowed to overdose chemicals beyond the MUL at any time.

What options do we have if breakpoint chlorination is not suitable?

When sodium or calcium hypochlorite is applied, breakpoint chlorination may not be achieved in water with more than 1 mg/L of ammonia nitrogen based on the MUL limits. When chlorine gas is used, such a concentration threshold of ammonia nitrogen may be increased to 3 mg/L. These values should be lowered when reducing agents that react rapidly with chlorine are present in water, such as iron and manganese which are very common in Saskatchewan's groundwater. It therefore has to be emphasized that the above values derived from theoretical calculations are approximate and for reference only. Chlorine demand is determined by factors such as the amount of interferences, pH, contact time and temperature, and should be determined through developing a site-specific breakpoint chlorination curve. Besides the consideration on MUL limits, breakpoint chlorination may also become inapplicable due to compliance concerns over chloramines, THMs, etc. When breakpoint chlorination is considered inappropriate, options such as removal of ammonia from raw water and use of alternative disinfectants can be considered. The choice of strategy to be adopted should be based on site-specific technical and economic analyses.

What treatment techniques are available for ammonia removal?

One of the reasons ammonia should be removed during drinking water treatment is to ensure adequate disinfection with a low chlorine dose. Generally, conventional water treatment processes (i.e., coagulation, flocculation, and filtration) are not effective in ammonia removal from drinking water. Ammonia may be removed by biological nitrification or physicochemical processes (such as ion exchange, membrane filtration and air stripping). Reverse osmosis has been installed and is being considered by some communities in Saskatchewan. The selection of a treatment technology depends on many factors, such as the characteristics of raw water, the source and concentration of ammonia, the operational conditions of the specific treatment method, and the utility's treatment goal. A brief discussion on effectiveness and cost factors of these techniques can be found in the WSA's publication EPB311 "*Strategies for Dealing with Groundwater Treatment Systems Having High Natural Ammonia*".

What alternatives are available to disinfect water containing ammonia?

While chlorine is the most commonly used disinfectant, alternative disinfectants (e.g., chlorine dioxide) or combined disinfectants (e.g., chlorine dioxide followed by chloramines, and ozone followed by chloramines) may have to be considered for inactivating microorganisms and maintaining a stable disinfectant residual when the source water contains high ammonia levels. The screening of disinfection strategies should include consideration of factors such as disinfectant efficacy, raw water quality, disinfection by-products (DPBs), Maximum Residual Disinfectant Levels (MRDLs), and cost. Chloramines, ozone, and chlorine dioxide are discussed below. Currently, the applications of other disinfectants are rare in Saskatchewan communities.

Chloramines

Chloramines are an attractive secondary disinfectant for water containing ammonia as indigenous ammonia in raw water can be removed while being utilized for chloramination. Chloramines are not as reactive with organics as free chlorine in forming THMs and HAAs. Monochloramine is the most useful chloramine species and conditions employed for chloramination are designed to produce only monochloramine. Current practice is to use a Cl₂:N ratio by weight in the range of 3:1 to 5:1, with a typical value of 4:1. High chlorine dose would cause taste and odor problems associated with the formation of di- and tri-chloramines. Monochloramine is more stable and longer lasting than free chlorine or chlorine dioxide, which makes it attractive for secondary disinfection (i.e., protection against bacterial regrowth in the distribution system). However, due to its relatively weak disinfection properties for inactivation of viruses and protozoa pathogens it is extremely difficult to meet the CT criteria for primary disinfection (i.e., inactivation of microorganisms in the water treatment plant) considering the very long contact times required. The WSA requires at least a 4-log reduction of viruses by disinfection in groundwater systems and at least a 0.5-log reduction of *Giardia* by disinfection in surface water or GUDI (groundwater under the direct influence of surface water) systems.

In systems where chloramines are used for secondary disinfection, it is strongly recommended by the WSA that a total chlorine residual of no less than 0.5 mg/L is maintained in the water entering the distribution system and in the water throughout the distribution system. The permittee of waterworks using chloramination shall ensure that owners of kidney dialysis equipment, as well as other groups that can be significantly affected by chloramines, are notified in writing regarding the presence of chloramines in the water.

It should be noted that in systems where chloramination is implemented, there will still be free ammonia in the system which can create nitrification problems that have to be considered. Good operational practices can help prevent nitrification, such as limiting excess free ammonia entering the distribution system to concentrations below 0.1 mg/L, and preferably below 0.05 mg/L, measured as nitrogen.

Chlorine dioxide

Chlorine dioxide is more effective than chlorine and chloramines for inactivation of viruses, *Cryptosporidium*, and *Giardia*. It oxidizes iron, manganese, and sulfides and does not react with ammonia. Chlorine dioxide requires careful handling in the interests of worker and user safety. Chlorine dioxide is less persistent in the distribution system than free chlorine or chloramines. Concerns about possible taste and odor complaints may limit the use of chlorine dioxide as a secondary disinfectant. Consequently, drinking water suppliers that are considering the use of chlorine dioxide for oxidation and primary disinfectant applications in ammonia-bearing water may want to consider chloramines for secondary disinfection. In this case, monitoring for the residual of total chloramines in the water entering and throughout the distribution system will be included in the Permit to Operate a Waterworks. If chlorine dioxide is used to provide a disinfectant residual in the distribution system, the minimum chlorine dioxide level in water entering the distribution system and in water throughout the distribution system shall be 0.1 mg/L, unless otherwise set out in the permit.

Treatment plants using chlorine dioxide as primary disinfectant shall not exceed a maximum feed dose of 1.2 mg/L without approval from the WSA. The MRDL of chlorine dioxide in water within the distribution system is 0.8 mg/L. Using chlorine dioxide for drinking water disinfection can form by-product chlorite and chlorate which must be monitored. As set by Health Canada, MACs for chlorite and chlorate are both 1 mg/L. Pilot plants in Saskatchewan have shown chlorine dioxide is difficult to employ unless water quality is good and experts are involved over a period of months to years.

The owner of a facility using chlorine dioxide shall notify any facility where kidney dialysis is practiced of the use of chlorine dioxide as a water disinfectant and shall confirm that advisement in writing. For more information on chlorine dioxide and its related regulations, please refer to the WSA's publication EPB 416 "*Chlorine Dioxide*".

Ozone

Ozone is another alternative to disinfect ammonia-bearing water, given that a secondary disinfectant such as free chlorine or chloramine is used for ensuring complete system disinfection. Ozone gas is highly corrosive and toxic, requiring a high level of maintenance and operator skill. Although ozone is a strong oxidant and disinfectant, it should not be relied upon as a secondary disinfectant since it decays rapidly and does not remain in water for any significant amount of time. The rapid reactions of ozone with organic and inorganic compounds cause an ozone demand in the treated water, which should be satisfied during water ozonation prior to developing a measurable residual.

Ozone residual must be monitored at the outlet of every tank where CT credits are awarded for disinfection. It is recommended that ozone residual monitoring be conducted on a continuous basis. As each tank and water quality is different, the minimum ozone residual required will vary from location to location. An engineering consultant must be hired to set an appropriate ozone residual level for each tank where disinfection is occurring. Bench- or pilot-scale studies must be conducted to assist designers with setting an appropriate ozone dosage for the water treatment plant, and to determine the required ozone residual in the contacting tanks to ensure that adequate disinfection is taking place. An ambient air ozone monitoring plan is also required.

A major issue with the use of ozone for disinfection purposes is the formation of bromate when the water to be treated contains bromide. Health Canada sets an interim maximum acceptable concentration (IMAC) of 10 ug/L for bromate in drinking water. The Permit to Operate a Waterworks for the system will include routine bromate testing where bromide is present in the raw water. WSA's publication EPB 429 "Ozone" contains more detailed information on ozone and the related regulations.

Do we need a permit to construct or alter our water treatment plant to treat ammonia-bearing source water?

Yes. A Permit for Construction of Waterworks must be obtained from the WSA before starting construction of such works. It is recommended to submit an Application for Permit to Construct, Extend or Alter Existing Works at least 45 business days before the planned construction date, which must include the prescribed forms, engineering reports, and design plans sealed by a professional engineer. The plans must be complete for the purpose of regulatory review, and may be marked as "for regulatory review only", "preliminary", or "not for construction". Please refer to Section 1 of the WSA's publication EPB 501 "*Waterworks Design Standard*" for a list of information required for approvals. The WSA reviews the application and issues a Permit for Construction of Waterworks once provincial requirements are met. The issued permit contains conditions of the construction and adds value in the areas of human health protection and environmental protection.

Who can assist us in dealing with ammonia in drinking water?

The handling of ammonia in drinking water is a complex topic. Additional information on proper design and operation of waterworks using ammonia-bearing source water can be obtained from municipal engineering consultants, chemical suppliers, and equipment suppliers.

Additional information on the regulations concerning waterworks where the source water contains ammonia is available from Environmental Project Officers (EPOs) and Approval Engineers of the Water Security Agency. To speak to an EPO or an Approval Engineer, please call 306-787-6504.

The WSA's publications mentioned in this fact sheet are available for download at <http://www.saskh20.ca/DWBinder.asp>.