Alternative Technologies - Chloramination

Technology Overview:

- Chemistry of Disinfection
- Areas of Consideration
- Chloramination Generation Technologies
- Potential Byproduct Formation
- Limitations of the Technology
The technology is based on the addition of ammonia to chlorinated water to produce chloramines.

Discovery of the interaction between chlorine and ammonia was first established in the early 1900’s.

Important to understand chlorine chemistry to correctly implement chloramination process.

Offers extended disinfection and is often used to provide residual disinfection in distribution networks.
The Chlorine - Ammonia interaction produces a number of chloramine substances:

- **Monochloramine**
  \[
  \text{NH}_3 + \text{HOCl} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}
  \]

- **Dichloramine**
  \[
  \text{NH}_3\text{Cl} + \text{HOCl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O}
  \]

- **Nitrogen Trichloride**
  \[
  \text{NHCl}_2 + \text{HOCl} \rightarrow \text{NCl}_3 + \text{H}_2\text{O}
  \]
Introduction - Chloramination

As chloramine formation is greatly dependant on the HOCl concentration the formation reactions are dependant on pH.

The greatest formation potential for chloramines exists at a pH of 7.0 to 8.5. - Specifically 8.3.

Addition ratios between chlorine and ammonia are important to understand.

Breakpoint chlorination is an important factor to understanding the interaction between chlorine and ammonia.
Chlorine breakpoint and chloramination.

As the desired effect is to create the monochloramine, as this has the most readily available disinfection capability and contributes the least to taste and odour problems.

Over dosing of ammonia will provide the potential of dichloramine and nitrogen trichloride formation - as well as bacteria growth.

The optimum ratio chlorine:ammonia is 6:1 for disinfection.

The design characteristics of most systems is 3 to 5 : 1
Introduction - Chloramination

Figure 6-1. Theoretical Breakpoint Curve
Introduction - Chloramination

Major Uses -

Extended Disinfection in Distribution Systems

Used for Secondary Disinfection.

Reduce Levels of THM formation in the water treatment process.
Chloramines disinfect by means similar to chlorine, although with a much lesser extent typically 200:1.

Monochloramine readily reacts with the amino acids in the DNA of the bacteria, and inhibits cell metabolism.

Viral inactivation performs in a similar method, the monochloramine attacks the protein coat of the virus to destroy it.
Chloramination is typically used for extending the disinfecting capability within the distribution network.

- **Effects of using Chloramination**
  - Chloramines are not as reactive with organic material as free chlorine in forming THMs.
  - Monochloramine residual is more stable than chlorine and chlorine dioxide.
  - Monochloramine has been shown to be effective against the formation of biofilms in distribution networks.
  - Chloramines can lessen taste and odour concerns by not interacting with organic compounds as readily as chlorine (chlorophenols).
Disinfection-

Typical limits set for chloramination in drinking water distribution systems are 1 to 4 ppm.

Studies have shown that a minimum of 2 ppm should be retained to prevent nitrification from occurring in the network.

Conversion of free chlorine to monochloramine can significantly reduce coliform concentrations in large distribution systems.
Applications - Chloramination

Disinfection-

Chloramines are weak disinfectants against virus and protozoa. CT is extremely difficult to establish using this alternative.
Applications - Chloramination

CT For Desired Giardia Removal

Log Reduction

CT Chloramine
CT Chlorine
Parameters effecting disinfection (pH)-

pH has a direct effect in controlling the proportion of chloramine species in the system.

pH has relatively no implication on disinfection itself rather than the organisms susceptibility to disinfection.
Applications - Chloramination

Figure 6-2. Distribution Diagram for Chloramine Species with pH

Palin, 1950.
Parameters effecting disinfection (Temperature):

Disinfection capability increases with the increase of temperature.

Efficiency dramatically reduces under conditions of high pH and low temperature.

Inactivation of E.coli. Is 60 X slower at pH 9.5 and temp of 2 to 6 C than at pH 7 and temperatures 20 to 25C.
Parameters effecting disinfection (Organic Nitrogen)-

Organic nitrogen will compete with ammonia to produce a variety of organic chloramines.

These compounds do not have the same disinfecting capabilities as inorganic chloramines.

The competing reactions favour the formation of organic chloramines over inorganic.

Special consideration should be given at levels > 0.3 ppm.
Parameters effecting disinfection (Organic Nitrogen)-

Monochloramine will hydrolyze with organic nitrogen to form organochloramines, non germicidal.

After the monochloramine disipates, nitrogen is present again, and is a strong nutrient.

Bacterial fouling can cause taste and odour problems and dirty water.
Points of application for Chloramination-

Typically ammonia is added after chlorination to provide “quenching” of available chlorine to form chloramines.

This is due to the fact that a much longer CT is required if ammonia is added prior to chlorination as the primary disinfectant.
Impact on other treatment processes-

High levels of ammonia present in the water treatment system can provide a food source to nitrifying bacteria, which can lead to increased levels of nitrate formation.

Imbalances in the ratio of chlorine to ammonia will provide breakpoint situations to exist in the distribution network.

Monochloramine upstream of the filtration process can reduce biological growth on the filters. Bad for biologically active filters.
Chloramines are formed with the interaction of chlorine and ammonia.

As a result, implication of a chlorination system, if not already existing and an ammonia feed system is required.

The rate of reaction between chlorine and ammonia is determined by pH.
Time for Conversion to Chloramine vs pH
Chlorination feed systems - An Overview.

Chlorine can be supplied in gas, solid or liquid form.

Upon dissolution hypochlorous acid is formed and contributes to the formation of chloramine when interacting with ammonia.
Ammonia Feed Systems.

Once chlorine in the form of hypochlorous acid is available, ammonia can be added to create the chloramines.

Ammonia can be added in anhydrous form - gaseous, or in liquid form.
Ammonia Feed Systems.

Anhydrous ammonia is supplied in pressurized tanks, and requires similar feed equipment to gas chlorination.

Anhydrous ammonia is fed to the process using an ammoniator; a self contained unit with pressure regulating valve, gas flow meter feed rate control valve and piping to control the flow of ammonia to the process.
Ammonia Feed Systems.

Evaporators are used when large quantities of ammonia are used.

Anti-siphon or check valves should be used to prevent the backflow of water to the ammoniator.
Ammonia Feed Systems.

Ammonia is typically fed directly to process through a number of pressure regulating valves.

This direct feed is typically used for high demand applications - 1000 lb/day.

Lower demand applications work more closely to chlorinator devices and use an eductor with motive water to deliver the ammonia to the system.
Figure 6-6. Anhydrous Ammonia Solution Feed System

Ammonia Feed Systems.

Liquid Ammonia is supplied in a similar fashion to liquid chlorine.

Ammonia is stored in a chemical tank, that should be FRP or stainless steel to prevent deformation from occurring under slight pressures that may be exerted by aqueous ammonia.

A feed system using a chemical metering device can then be used to deliver the ammonia in proportion to demand.
Ammonia Feed Systems.

After the liquid ammonia is added to the process, good mixing should occur as to prevent the formation of dichloramine and nitrogen trichlorine.
Generation Technologies - Chloramination
Figure 6-7. Aqua Ammonia Feed System

DBP Formation potential is determined by a number of factors-

- The point of addition of ammonia compared to chlorine
- Chlorine to Ammonia Ratio
- pH of the reaction
- Extent of Mixing
If chlorine is added prior to ammonia for initial disinfection then the relative production of DBP overall will be determined by the DBPFP of chlorine.

Thus THM and HAA5 formation may still represent a problem.

If ammonia is added first, then chloramines will be formed in place of free chlorine and the result will require longer CT for disinfection, however better control of DBP.
The closer to the breakpoint the water is the more chance there is for DBP formation.

Free chlorine may still be available, and may still react with organics to form DBP.

Chloramination will also result in the formation of other chlorinated byproducts, although not much is understood with regards to these compounds.
Chloramines provide a number of advantages over straight chlorination:

Chloramines are not as reactive with organics as free chlorine in forming DBP.

Monochloramine has a longer residual effect than chlorine.

Potential for formation of taste and odour byproducts is lessened.

Chloramination is inexpensive.

Chloramines are easy to produce.
Limitations and Considerations - Chloramination

Disadvantages-

Disinfecting capabilities are much less than other disinfection methods.

Chloramines will not oxidize iron or manganese.

When using as a secondary disinfectant it may be necessary to periodically switch to chlorine to prevent biofilm build up in the distribution network.
Limitations and Considerations - Chloramination

Disadvantages-

Excess ammonia in the distribution network may cause nitrification, and result in nitrate formation.

Monochloramines are less effective at high pH than low pH.

Dichloramines have treatment and operation problems.

Chloramines must be produced on site.