THE TIES THAT BIND: FORMING CHLORAMINES THAT LAST

David W. Sloan, P.E., BCEE
Freese and Nichols, Inc.
4055 International Plaza, Suite 200
Fort Worth, Texas 76109-4895

ABSTRACT

Conventional wisdom has been that chlorine and ammonia have a strong mutual attraction: put them both in water, and they're bound to pair up. In reality, it's not quite so simple. Chlorine has a wandering eye, reacting with other partners before or after meeting up with ammonia. And both chlorine and ammonia are fickle prospects, with dual, pH-dependent personalities. The mutual attraction is limited to a relatively narrow pH range. When the partnership fails, the result is often nitrification.

More and more water systems are discovering nitrification problems and loss of disinfectant residual. Depending on the conditions, several strategies are useful in prevention, including water age management, unidirectional flushing, tank mixing, free chlorine shocking, and booster chlorination. Chloramine chemistry is typically oversimplified, and pH effects are often ignored. This paper will use several case studies to explain common misconceptions and present approaches for more consistent chemical dosing to form stable chloramines.

KEYWORDS

Chloramine formation, nitrification, pH effects, disinfection.

CHLORAMINES AND NITRIFICATION

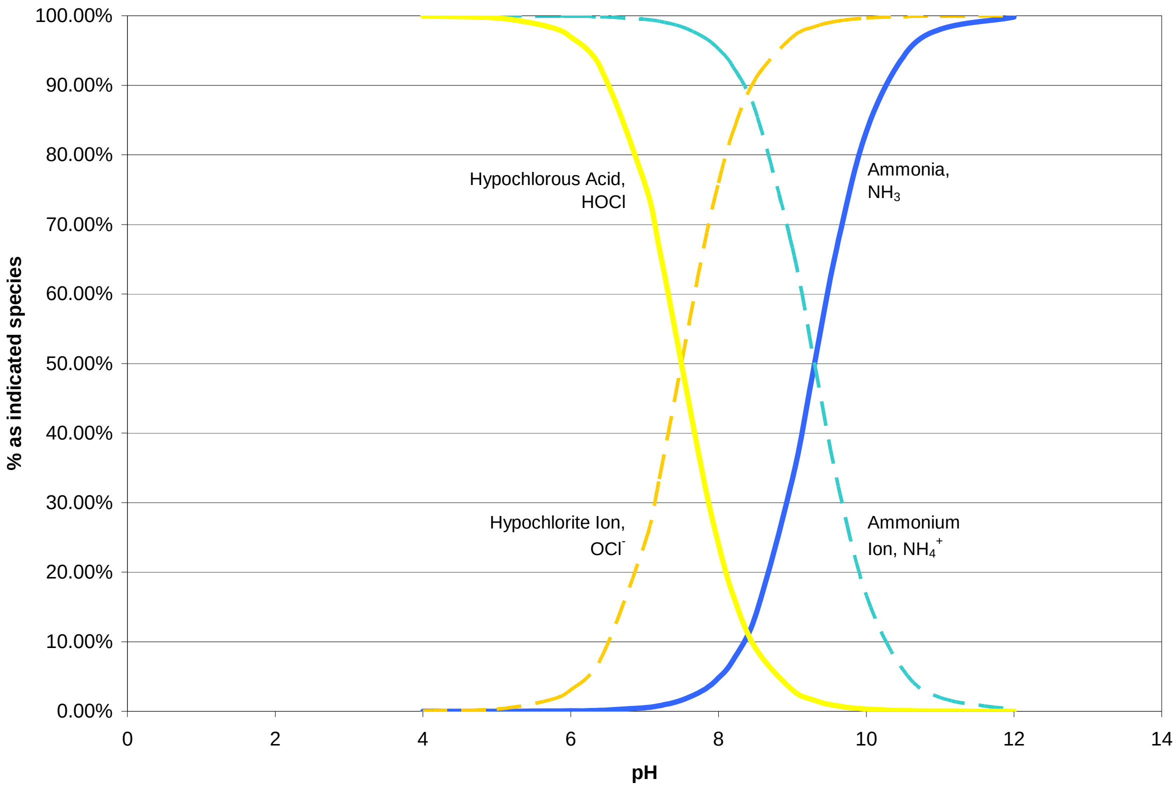
Most of us know something about chlorination history; there are some good books and articles which trace the discovery of its disinfecting properties and its importance in the fight against waterborne diseases. However, in the 1970s trihalomethanes, or THMs were discovered and determined to be probable carcinogens. The use of ammonia to "tie up" the available chlorine became an effective strategy to reduce THM formation. Chloramines had some other advantages as well: they tend to decay more slowly, and have a less pronounced flavor than free chlorine. The disadvantages of chloramines are the significantly reduced disinfection potency compared to free chlorine and the tendency in many water distribution systems to develop episodes of nitrification.

Nitrification is the biological conversion of ammonia to nitrite, and then to nitrate. It is commonly encouraged in wastewater treatment to reduce the oxygen demand on the receiving streams, but its prevalence in water distribution systems is very unwelcome. Nitrification is associated with the loss of chlorine residual, positive bacterial samples, and potentially with waterborne disease outbreaks. Excess ammonia is the raw material for nitrification; although several factors affect the process, the surest way to limit nitrification is to minimize concentrations of free ammonia. This requires an understanding of the chemistry of chlorine, ammonia and chloramine formation and decay.

Chlorine

Chlorine is a common element which takes numerous forms, but the form of interest in water disinfection is hypochlorous acid, a weak acid formed when elemental chlorine gas is dissolved in water. Hypochlorous acid, HOCl, exists in water in equilibrium with its alter ego, hypochlorite ion, OCl^-. These two species have markedly different properties, but can shift quickly with changes in the solution pH, and the term free chlorine is defined as the sum of the two forms. At a pH of approximately 7.5 (depending on temperature), they are equally balanced; below this pH, hypochlorous acid dominates, while hypochlorite ion dominates at higher pH values. Figure 1 illustrates the shift in species with solution pH.

Figure 1 – Chlorine and Ammonia Species vs. pH



HOCl is the form desired for drinking water, but is often in short supply. This form is a much stronger oxidant, is more reactive, and is 100 times stronger as a disinfectant. This is the basis for the variation with pH in disinfection credit for free chlorine. Due to the neutral electrical charge of HOCl, it is more likely to penetrate bacterial surfaces and contact solid particles with a negative surface charge. **Critical to the practice of chloramination, HOCl will react with ammonia to form chloramines, while OCl^- will not.** However, as the acid form is depleted through various chemical reactions, some of the ionic form will shift to maintain the equilibrium.

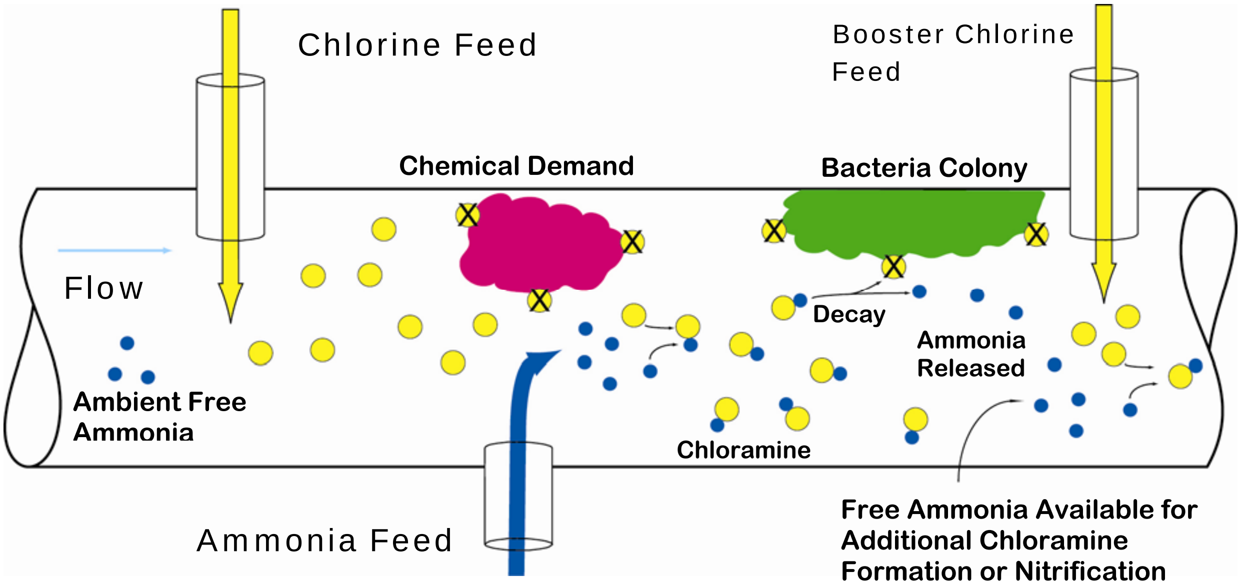
Ammonia

Ammonia also exists as a neutral form, aqueous ammonia (NH_3), and an ionic form, ammonium (NH_4^+). The crossover pH for ammonia is approximately 9.3. Ammonium ion dominates below this level, while neutral ammonia is the predominant form at higher pH. Since its only function in drinking water is as a partner to chlorine in forming chloramines, the neutral form is the one desired. The equilibrium shift with pH for the two ammonia species is also illustrated in Figure 1.

The Zone of Mutual Attraction

At first glance it might appear that chloramine formation is hopeless since the two partners don't frequent the same venues from a pH standpoint. However, from Figure 1, at pH 8.3 each of the desired species is present at about 10% of the total concentration. This allows significant chloramine formation, and as hypochlorous acid and ammonia pair up, additional partners are created as each chemical shifts to maintain equilibrium. There is a range of pH where sufficient activity is present for this to proceed, but the optimum condition is around 8.3, with some variation due to temperature.

Figure 2 – Chloramine Formation and Decay



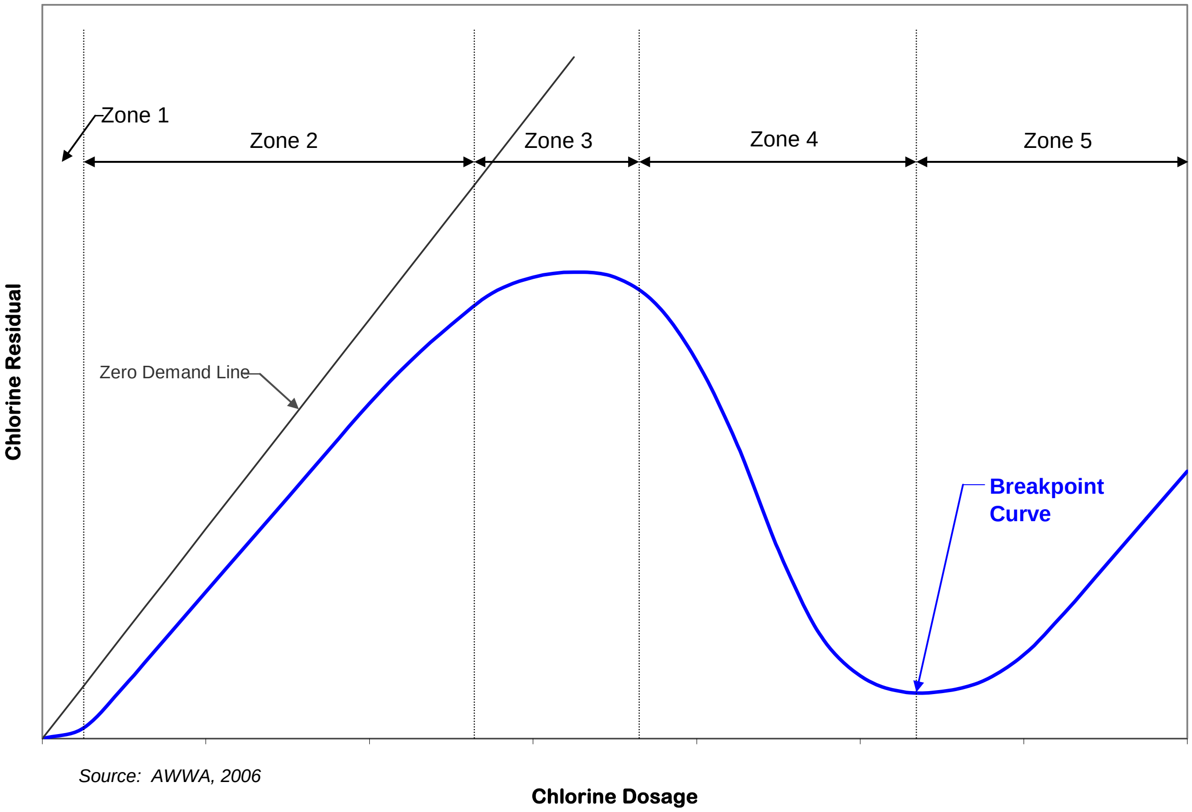
Given favorable conditions, hypochlorous acid and ammonia will form monochloramine, the most common and desirable product. Monochloramine, NH_2Cl, results from the combination of a single molecule of hypochlorous acid with a single molecule of ammonia. If sufficient chlorine is available, it will react with monochloramine to form dichloramine, $NHCl_2$. Dichloramine is somewhat more potent as a disinfectant, but has a stronger taste and is less stable. Greater excess chlorine can also form nitrogen trichloride, NCl_3, which has even stronger taste and odor, but is unstable and does not persist long in water.

Once formed, chloramines retain the oxidizing capacity of chlorine, but in a weaker configuration. When the chlorine component participates in an oxidation reaction, its valence is changed and it is of no further relevance as a disinfectant. The ammonia is released and is available to attach to more chlorine, or to nitrify. Figure 2 is a simplified illustration of chlorine and ammonia interactions in a water system.

THE BREAKPOINT REACTION

Another phenomenon of chlorine and ammonia interaction is known as the breakpoint reaction, represented by the breakpoint curve, illustrated in Figure 3. The recently published *AWWA Manual M20, Water Chlorination/Chloramination Practices and Principles* contains a very good discussion on the breakpoint reaction, which is observed as an alternately rising and falling chlorine residual with progressively higher chlorine dose. At low doses chlorine is first

Figure 3 – Breakpoint Chlorination Curve



Source: AWWA, 2006

consumed by chemicals which exert an immediate demand (zone 1). The remainder will react with ammonia to form monochloramine, illustrated as the rising line in zone 2. As the available ammonia is depleted, dichloramine formation predominates, and the total residual levels off in zone 3. Additional chlorine causes the formation of nitrogen trichloride, which rapidly decomposes, causing the rapid loss of residual observed in zone 4. Eventually, the breakpoint is reached, where most of the ammonia is driven off and additional chlorine results in a free chlorine residual (zone 5).

REAL LIFE EXAMPLES

The chemistry of chlorine and ammonia is fascinating to a few, but confusing to most of us. A couple of examples from water utilities in Texas illustrate how some of these characteristics intrude on the real world.

The Softening Plant

A water plant practices conventional softening. It employs two chlorine feed points, and one ammonia feed point. A portion of the required chlorine is added to the plant influent, and ammonia is added immediately downstream to limit THM formation. Following treatment, additional chlorine is added as necessary to meet the needs of the distribution system. Late summer nitrification is an annual event, resisting repeated efforts to control it. Despite normal ratios of chlorine:ammonia, there is an abundance of ammonia in the finished water leaving the plant.

The chlorine:ammonia ratio in this case is based on both chlorine feed points, but when water arrives at the second chlorine point, the pH is elevated from the softening treatment. In this condition, almost all the chlorine is in the OCl^- form, so few additional chloramines are formed. The ammonia targeted for chloramine formation simply goes out the plant as free ammonia. A free chlorine test will indicate significant free chlorine residual, which might be expected to stave off bacterial activity and nitrification, but with almost all of this residual in the ionized form, its disinfecting powers are weak.

The Customer City with Severe Nitrification

A medium-size city buys its water from a large system. The large system keeps pH high (near 9) to increase the staying power of its chloramine residual. In early fall, a rapid fall-off in system demand results in high water age, triggering widespread nitrification in the customer city system. Heavy flushing and booster chlorination fail to stop the loss of residual, and several positive bacteriological samples are reported. Desperate to turn things around, the customer city agrees to “shock” the system with free chlorine. However, with no plant of its own, the only way to achieve free chlorine on its own is to add sufficient chlorine to achieve breakpoint. Temporary facilities are placed, chlorine is added, and initial results are promising, but as the area to be shocked widens, the results are disappointing. The nitrification seems to dissipate, but ammonia persists, even as the measured free chlorine rises, and taste and odor complaints mount.

The simultaneous presence of free chlorine and free ammonia seems to contradict our simplistic notions about chloramine formation, but when the pH is figured in, it starts to make sense. The added chlorine is almost all in the form of hypochlorite ion, and is unavailable for chloramine formation.

CONCLUSION

When chlorine and ammonia go their separate ways, nitrification will often result. In fact, an AWWA study estimated that over two thirds of systems using chloramine as a distribution disinfectant experience nitrification. Contributors to the problem include long water age, organic content and aging water lines. These factors may be controlled to varying degrees, and there are some effective tools to prevent and combat nitrification, including targeted flushing programs, system hydraulic optimization, and others. However, a holistic approach to the problem includes understanding the chemical processes involved. By creating conditions for proper chloramine formation and minimizing free ammonia, nitrification can prevented or reduced.

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