By Pat McCool, KRWA Consultant

Feeding Ammonium Sulfate to Form Combined Chlorine Residual

Many Kansas public water supplies (PWSs) add ammonia to react with free chlorine in the water to form combined chlorine. Not adding enough ammonia will result in a decrease ("residual loss") in chlorine residual. Adding too much ammonia will result in waste of chemical and more "food" for nitrifying bacteria.

Ammonia addition

Ammonia is added for two reasons. First, ammonia is added to stop the reactions of free chlorine that form trihalomethanes (THMs) and haloacetic acids (HAAs). Ammonia is added to change the free chlorine residual to combined chlorine residual because combined chlorine does not form THMs and HAAs.

Second, ammonia is added to maintain combined chlorine residual in the distribution system. Ammonia is added at treatment plants, at wells, and at rechlorination locations in the distribution systems.

There are mainly three different ammonia chemicals that can be added. Most PWSs serving less than 15,000 persons add ammonium sulfate. Larger systems add either ammonium hydroxide ("aqua ammonia") or ammonia gas. Ammonium sulfate is chosen because it avoids safety issues, some feeding problems, and possibly larger capital costs. Aqua ammonia and ammonia gas are cheaper chemicals but the cost savings for small systems are insignificant when compared to the advantages of using ammonium sulfate.

Free chlorine and ammonia reactions

In water the possible reactions of free chlorine (HOCl) and ammonia (NH_3) can be represented by the following:

- $HOCl + NH_3 \rightarrow NH_2Cl$ (monochloramine) $+ H_2O$ (1)
- $NH_2Cl + HOCl \rightarrow HNCl_2$ (dichloramine) $+ H_2O$ (2)
- $NHCl_2 + HOCl \rightarrow NCl_3$ (trichloramine) $+ H_2O$ (3)

In water treatment it is important to add ammonia according to the first reaction to form monochloramine. The last two reactions forming dichloramine and trichloramine (also called nitrogen trichloride) are to be avoided because these two reactions also result in a decrease in chlorine residual.

In calculating the ammonia feed rates, the amounts of the free chlorine and ammonia reacting to form monochloramine must be specifically addressed. The formation of monochloramine has also been written as follows:

- $HOC1 + NH_4^+ \rightarrow NH_2C1 + H_3O^+$ (4)

Free chlorine residual is measured with testing equipment and the results are reported as mg/l of Cl_2. That is, the residual is measured and reported as free chlorine in the water is in the Cl_2 form, which it is not. Free chlorine in the water is in the forms of HOCl and OCL-, the proportion of each depends on the pH of the water.

This photo shows ammonium sulfate solution feed equipment for a 500 GPM water treatment plant. The solution is made from purchased granular ammonium sulfate in 25 pound bags. The solution strength is determined by the plant operators.

Definitions of "Ammonia"

When discussing or addressing "ammonia" it is very important to be knowledgeable and specific as to which of the three ways "ammonia" is meant. The three possible ways are:

1) ammonia (NH_3); or
2) ammonium ion (NH_4^+); or
3) ammonia-nitrogen (NH_4-N).

Ammonia and ammonium ion can be used interchangeably because their molecular weights are very close at 17 and 18, respectively. However, the molecular weight of ammonia-nitrogen (that is, the nitrogen in ammonia or in ammonium ion) is 14 and that is a substantial difference with the other two ways of reporting "ammonia".

"Chlorine-to-ammonia ratio"

The "chlorine-to-ammonia ratio" unfortunately has different definitions to different operators and thus different numerical values or "ratios". This causes confusion and misunderstandings in determining ammonia dosages. The "chlorine-to-ammonia ratio" should address the matter of chlorine and ammonia reacting as in reactions (1) or (4) so as to form monochloramine.

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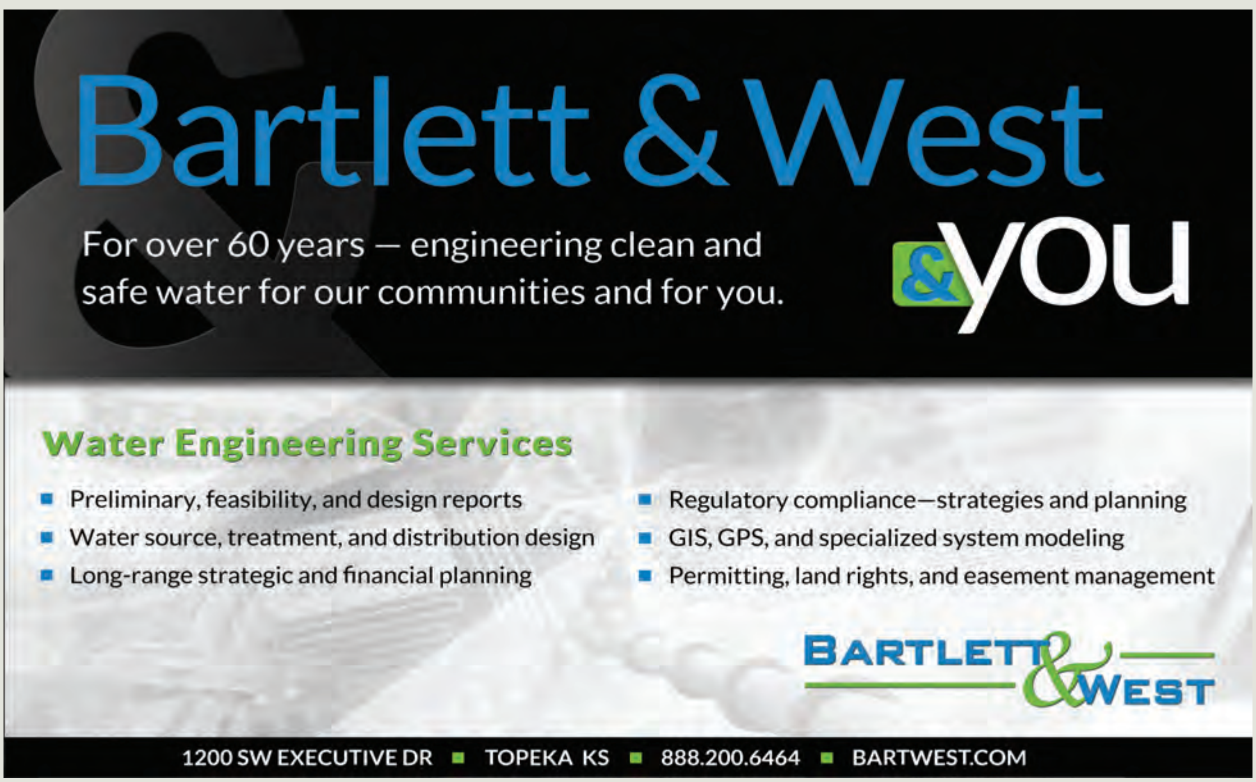
The following definition is used by many and KRWA. It is: The "chlorine-to-ammonia ratio" is the ratio of the free chlorine (in the water just before the ammonia is added) to the ammonia (calculated as ammonia and not ammonia-nitrogen) added to the water to form monochloramine without providing excess, "free", un-reacted ammonia in the water.

When using NH_3 in reaction (1) or NH_4^+ in reaction (4), the ratio is 3.9 or 4.2, respectively, or approximately 4.1. If ammonia-nitrogen is used as the basis of "ammonia", then the ratio is approximately 5.1.

This ammonium sulfate solution feeding equipment is used in a 1,000 GPM water treatment plant. The plant purchases the solution already mixed.



Feeding Ammonium Sulfate Solution

KRWA has worked with operators at many locations in setting up ammonia addition, in trouble-shooting operational problems, in optimizing ammonia addition, and in correcting residual loss. The equation KRWA uses when adding ammonia sulfate solution is explained in the sidebar at right.

The equation has worked in all situations except initially in a few situations that have special circumstances that cause the formation of monochloramine to be "inefficient". Such situations include poor mixing of chlorine or ammonia in the water, over-chlorination downstream of ammonia addition, and too much ammonia addition due to automatic controls.

Also, it is beneficial to add more ammonia (approximately 0.1 – 0.3 mg/l) than necessary for monochloramine formation. The additional "free", un-reacted ammonia in the water results in a (chlorine and ammonia reaction) system that is more "forgiving". That is, if the free chlorine residual increases there will be ammonia for reaction and the residual will not decrease.

Equation and definitions

$$\text{gph} = \frac{(\text{mg/l}) \times (\text{GPM}) \times 1.9}{(\#/\text{gal}) \times 1{,}000}$$

gph = gallons per hour (pumping rate of ammonium sulfate solution feed pump)

GPM = gallons per minute (water flow to which ammonia is being added)

mg/l = ammonia dosage in milligrams of ammonia per liter (ammonia as NH_4^+ or NH_3)

#/gal = pounds of ammonium sulfate per gallon (ammonium sulfate solution)

1.9 is a conversion factor

1,000 is a conversion factor

These two conversion factors are chosen for simplicity and are a combination of the following four factors: molecular weights ratio, grams per pound, minutes per hour, and liters per gallons.

The equation is used for determining ammonium sulfate solution pump sizes and feed rates; sizing solution feed tanks; determining dosages; estimating "free" ammonia; determining solution mixing rates; and other pertinent operational and quality control factors.

For small systems that purchase granular ammonium sulfate in bags and make solutions, the (#/gal) is usually in the range of 0.25 to 1.5 depending on solution pump sizing and GPM being treated. If commercial 38 percent ammonia sulfate solution is being used, check with supplier for (#/gal) or use 3.9 if information is unavailable.

For most all systems, the (mg/l) dosage is usually in the range of 0.5 to 1.5 depending on chlorine residual goal and desired "free" ammonia levels.

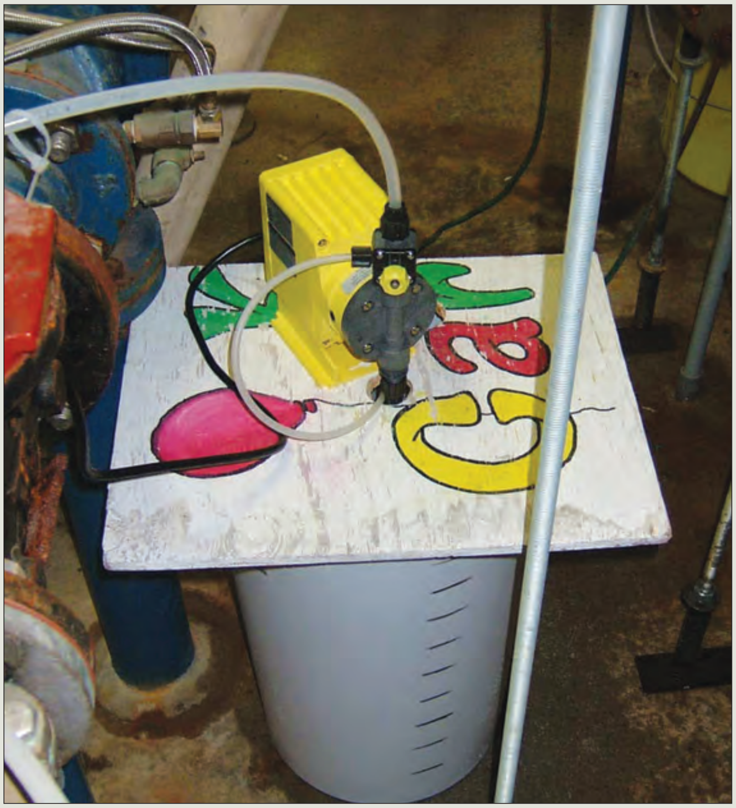
When calibrating solution pumps it should be remember that 1.0 gph = 63.08 ml/min (milliliters per minute) or 63 ml/min.

Rechlorination

Many PWSs are rechlorinating water in the distribution system that has combined chlorine residual. As shown in the chlorine and ammonia reactions, to form monochloramine there must be enough ammonia in the water to react with the chlorine. Otherwise, the "excess" chlorine will react with monochloramine in reaction (2) and chlorine residual will decrease. Thus, ammonia addition at rechlorination locations is needed when "free", un-reacted ammonia in the water is insufficient for rechlorination.

Ammonia addition "Forget-Me-Nots"

Some chemistry, knowledge, and operator experience are necessary to add ammonia in correct amounts. However, if there is one important fact that all operators must remember, it is this: When forming and maintaining combined chlorine residuals, sometimes the correction of chlorine "loss" / decrease involves doing what is the opposite of what is intuitively or logically thought to be the correction.



This ammonium sulfate feed system is for a very small 60 GPM flow at a rechlorination system at a pump house in a distribution system. Ammonium sulfate is purchased in 25 pound bags and mixed at only 0.25 pounds per gallon of feed solution. Rechlorination and ammonia addition are only needed in this system the summer and early fall months. The chemistry and the chemical reactions are the same regardless of the size of the feed systems.

For instance, in some situations where chlorine residual is decreasing, the solution could be to decrease the chlorine dosage or increase the ammonia dosage. Another situation, increasing chlorine dosages may make chlorine residuals decrease. However, all instances can be explained by the knowledge of the chlorine and ammonia reactions.

The most frustrating problem encountered when adding ammonia is the decrease of chlorine residual or as many say, chlorine "loss". The most common correction is adding the correct amount of ammonia and that usually is more ammonia than is presently being added.

If any reader believes his/her water system may have such problems, please contact KRWA as KRWA staff are available to discuss or help troubleshoot and correct chlorine and ammonia dosages.

In the July 2016 issue of *The Kansas Lifeline*, I will present actual examples concerning use of the equation to determine ammonia dosages and other suggestions how to monitor, evaluate, and adjust dosages.

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