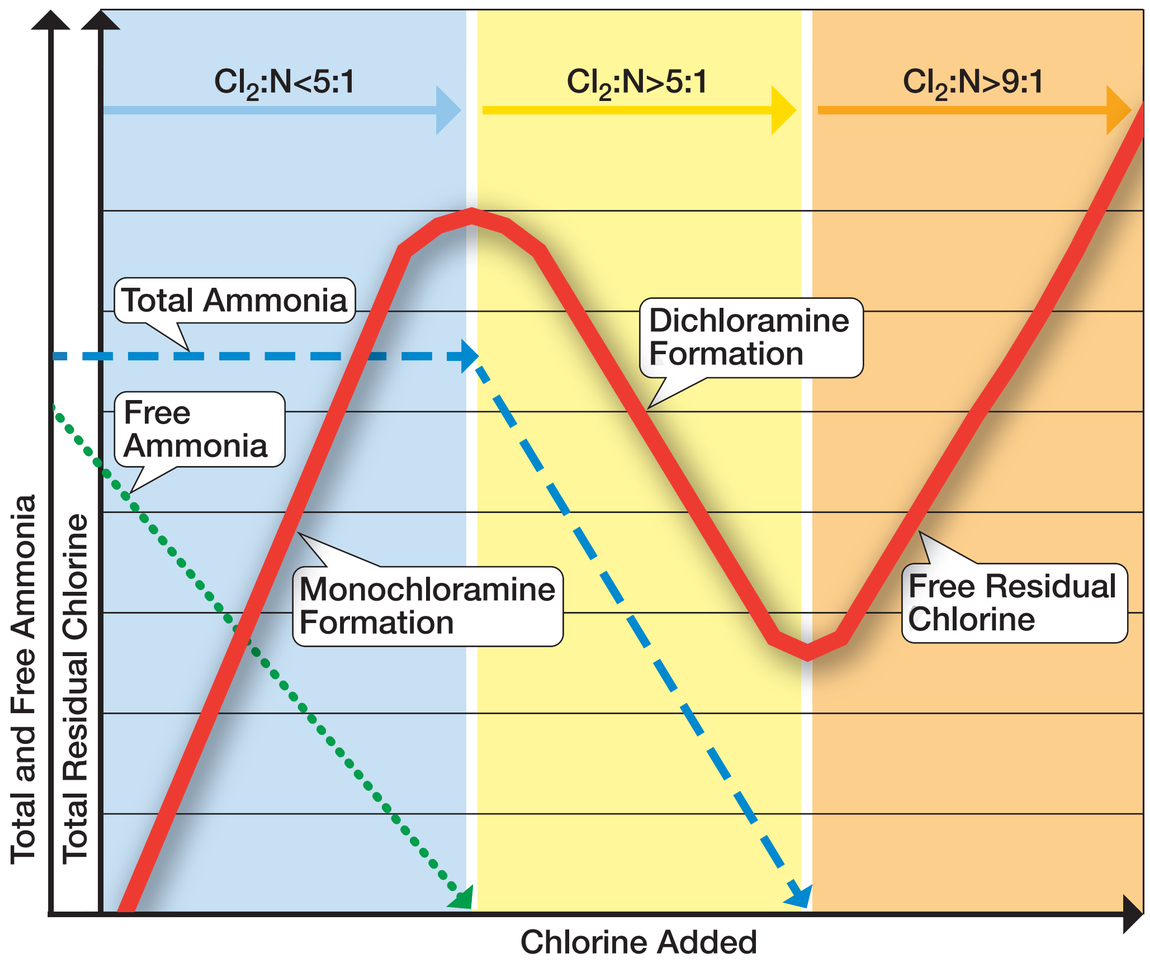
CHLORINATION AND CHLORAMINATION

Breakpoint Curve for Chlorination and Chloramination



Monochloramine, Free Chlorine, Cl_2:N <5:1
(Monochloramine predominates, Free Ammonia > 0)

- Minimizes formation of chlorinated organics, specifically TTHM.
- Less effective disinfection than free chlorine.
- Requires longer contact time and/or greater concentration than free chlorine.
- More stable than free chlorine (long distribution systems).
- Generally does not produce DBPs (this issue is still being studied).
- Must reduce free ammonia to reduce risk of nitrification issues.

Dichloramine & Trichloramine, Cl_2:N >5:1 (Free Ammonia = 0)

- Likely taste and odor issues.

Free Chlorine, Cl_2:N >9:1 (Total Ammonia = 0)

- Most effective disinfection, least taste and odor occurs with free residual chlorine.
- Free chlorine may lead to formation of DBP.

NOTE: Shape of the curve is dependent upon amount of ammonia and other chlorine demand substances in the water, temperature, pH, and contact time.

Key Reactions

1. When chlorine is combined with water, forms hypochlorous (HOCl) and hydrochloric (HCl) acids:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

2. Reaction is reversible. Above pH 4, reaction is to the right.

3. HOCl dissociates to the hydrogen ion* and hypochlorite ion (OCl^-) varying with temperature and pH:

$$HOCl \rightleftharpoons H^+ + OCl^-$$

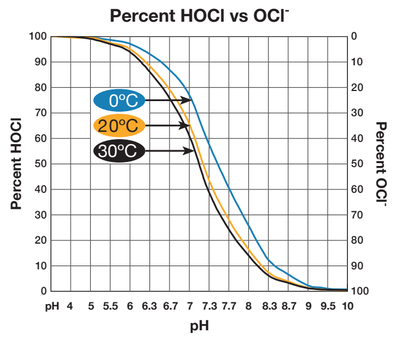
(See Table and Graph to the right.)

4. Chlorine (HOCl and OCl^-) reacts with ammonia to form chloramines, commonly referred to as “combined chlorine.”

5. The predominate species are monochloramine and dichloramine. A small fraction is trichloramine or nitrogen trichloride.

**Hydronium ion, H_3O^+*

Effect of pH on Chlorine Species



Proportions of HOCl and OCl^- at varying temperature and pH levels

pH	HOCl 0°C	OCl 0°C	HOCl 20°C	OCl 20°C	HOCl 30°C	OCl 30°C
4	100	0	100	0	100	0
5	99.85	0.15	99.4	0.6	99.68	0.32
6	98.53	1.47	97.45	2.55	96.92	3.08
7	87.04	12.96	79.29	20.71	75.9	24.1
8	40.18	59.82	27.69	72.31	23.95	76.05
9	6.29	93.71	3.69	96.31	3.05	96.95
10	0.67	99.33	0.38	99.62	0.31	99.69

Chloramine Species

- Monochloramine - NH_2Cl

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O$$

- Dichloramine - $NHCl_2$

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$$

- Trichloramine (Nitrogen Trichloride) - NCl_3

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$$

- Definition of unreacted (free) ammonia:

  NH_3 Free ammonia gas dissolved in water

  and/or

  NH_4^+ The ammonium ion

Nitrification Process

Formation of Nitrate

Conversion of free ammonia to nitrite.

$$NH_3 + O_2 \rightleftharpoons NO_2^- + 3H^+ + 2e^-$$

Ammonia converts to Nitrite

Nitrosomonas, Nitrosococcus, and Nitrosospira

Conversion of nitrite to nitrate.

$$NO_2^- + H_2O \rightleftharpoons NO_3^- + 2H^+ + 2e^-$$

Nitrite converts to Nitrate

Nitrobacter, Nitrospina, Nitrococcus, and Nitrospira

What is Meant by “Free Ammonia?”

- “Free ammonia” refers to ammonia in water that h s not reacted with chlorine to form monochloramine.
- The reaction forming monochloramine is reversible (see Key Reactions). As water age increases the monochloramine can revert to free chlorine and free ammonia.

Signs and Consequence of Nitrification

Early Indicators

Control strategies can be applied.

- ▲ Free Ammonia
- ▼ Monochloramine
- ▲ Nitrite (just detectable)
- ▲ ATP
- ▼ pH
- ▼ DO
- ▼ Alkalinity
- ▲ Temperature

Late Indicators

A significant problem exists and remedial action must be implemented– extensive flushing, cleaning of storage tanks, free chlorine “burnout.”

- ▲ Nitrite
- ▲ Nitrate
- ▲ Turbidity
- ▲ HPC
- ▲ Customer complaints

Effect of Temperature on Nitrification

32°F	50°F	77°F	80 to 100°F	104 to 122°F
Nitrification Ceases	NItrification Slows	Favorable for Nitrification	Most Favorable for Nitrification	Nitrification Slows and Ceases
0°C	10°C	25°C	26 to 39°C	40 to 50°C

Control Strategies

Areas of Control	Action
pH	▲
Free Ammonia	▼
Water Age (flushing, decrease storage level, etc.)	▼
Monochloramine Residual	▲
TOC	▼
Improve Tank Mixing	▲

Use this panel to identify the areas of correction for your distribution system or storage tank when you begin to experience the signs of nitrification.
▲= Increase ▼= Decrease

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