

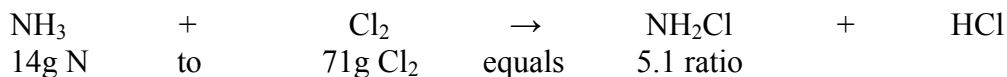
# Chloramine Update Training – Outline

## EBMUD, April 13 and 15, 1999

1. Introduction and Objectives
  - What are chloramines? Why use them?
  - Advantages/disadvantages of chloramines
  - Chemicals used to form chloramine
  - Distribution system disinfectant residual goal
  
2. Chloramine Chemistry
  - Chloramine formation reactions. Breakpoint.
  - Chloramine decomposition reactions
  - Total/free chlorine and ammonia analysis
  - Verification of HACH instruments
  
3. Chloramine Dose Calculations
  - Review of chloramine math
  - Estimating ammonia chemical inventory
  
4. Review of Plant Chloramine Formation
  - Plant by plant review
  - Process diagnostics
  
5. Distribution System Update
  - Long-term water quality trends
  - Nitrification update
  - Where do we go from here?

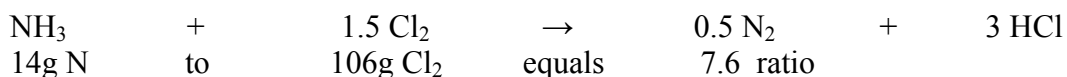
### The “Life Cycle” of Chloramine I – WTPs

#### Monochloramine Formation (5:1 Cl<sub>2</sub>:N ratio)



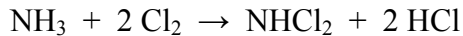
at pH = 7.0 – 9.0 reaction with 0.2 seconds or less – at 25°C  
 temperature slows down reaction to 5 minutes at 0°C

#### Breakpoint Reaction (7.6:1 Cl<sub>2</sub>:N ratio)



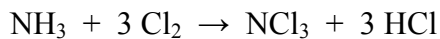
at pH = 9.0 reaction takes hours; faster at pH = 8.0  
pH and water source affects the breakpoint ratio (could be, e.g., 11:1)  
temperature slows down reaction

Dichloramine Formation (10:1 Cl<sub>2</sub>:N ratio)



Only trace levels following breakpoint at pH = 7.0 – 9.0,  
reaction takes hours

Trichloramine Formation (15:1 Cl<sub>2</sub>:N ratio)



Only trace levels following breakpoint  
rarely in routine WTP operations

### WTP – Chloramine Formation & Stability

Below 5:1 Cl<sub>2</sub>:N ratio

- Instantaneous formation of chloramine
- Free ammonia is present
- Free chlorine is not present (false-positive)

Above 5:1 Cl<sub>2</sub>:N ratio

- Gradual loss of total chlorine and ammonia
- Breakpoint reaction is slow at pH > 8.0
- Free ammonia is not present
- Initially free chlorine may be present

Chloramine stability is reduced by:

- Breakpoint and loss of total chlorine
- pH < 8.3
- Lack of free chlorine contact in clearwell at USL and Sobrante
- High ozone doses and peroxide (preliminary results to be verified)

Chloramine stability is not affected much by:

- Chloramine dose
- Cl<sub>2</sub>:N ratio (as long as it is below 5:1)
- Lack of free chlorine contact in clearwell at Aqueduct plants

## The "Life Cycle" of Chloramine II – System

### Monochloramine Reaction with Organics



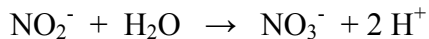
Conceptual reaction simplified after (Harrington et al., 1999)  
1 mg/L combined ammonia releases 1 mg/L free ammonia

### Monochloramine Auto-Decomposition



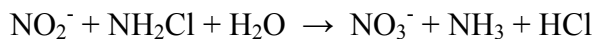
nitrogen gas pathway after (Valentine, 1998)  
1 mg/L combined ammonia releases 1/3 mg/L free ammonia

### Nitrification Microbiological Reactions



Nitrite is formed, oxygen is needed, pH is lowered eventually, reaction goes to nitrate

### Nitrite Reaction with Monochloramine



Simplified complex reaction after (Valentine, 1998; p. 56)  
Chloramine does not react with nitrite (White, 1992; p 227)  
Chloramine and nitrite can be measured in the same sample

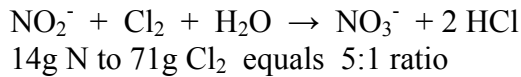
## Distribution System – Chloramine Stability

Chloramine stability is reduced by:

- Presence of natural organics (TOC)  
*TOC reaction releases more free ammonia and occurs soon after chloramine formation*
- Auto-decomposition reaction  
*chloramine will decay at some base rate not much effect of alkalinity observed*
- Release of nitrite during nitrification  
*nitrification rate increases above 15 °C although can occur even at 4 °C if water age is long*

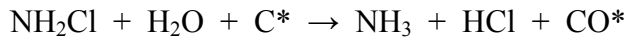
## The "Life Cycle" of Chloramine III – System

### Nitrite Reaction with Free Chlorine (5:1 Cl<sub>2</sub>:N ratio)



free chlorination of nitrified water in the distribution system  
nitrite represents significant chlorine demand (White, 1992; p. 226)

### Dechloramination with GAC



Monochloramine reacts slower with GAC than free chlorine  
carbon surface gets oxidized but not destroyed as with free chlorine

### Dechloramination with Bisulfite



## Process Diagnostics

### Plant Effluent Chloramine Goals

- Total Cl<sub>2</sub> = 2.0 ± 0.1 mg/L Cl<sub>2</sub> – Mokelumne  
Total Cl<sub>2</sub> = 2.5 ± 0.1 mg/L Cl<sub>2</sub> – USL/Sobrante
- Cl<sub>2</sub>:N ratio = 4.5 – 4.7 to 1
- Free ammonia = 0.02 – 0.06 mg/L N

### Process Diagnostics

Free ammonia must be present (within goal)

- If outside goal → verify flows, repeat analysis
  - If zero → increase NH<sub>3</sub>-N or lower Cl<sub>2</sub> dose
  - If high → lower NH<sub>3</sub>-N or increase Cl<sub>2</sub> dose

Free chlorine cannot be present

- If present & free NH<sub>3</sub>-N > 0 → False-positive
  - Verify immediate color against white paper
  - Do not shake, do not place in HACH
  - Use short vial for free Cl<sub>2</sub>
  - Use dedicated vials for free and total Cl<sub>2</sub>
- If present & free NH<sub>3</sub>-N = 0 → Breakpoint
  - Verify flows
  - Increase NH<sub>3</sub>-N or lower Cl<sub>2</sub> dose

Total  $\text{Cl}_2 \geq$  Free  $\text{Cl}_2$  (before ammoniation)

- If not & Free  $\text{NH}_3\text{-N} = 0 \rightarrow$  Breakpoint
  - Verify flows
  - Confirm low total  $\text{Cl}_2$  on 15-min sample
  - Increase  $\text{NH}_3\text{-N}$  or lower  $\text{Cl}_2$  dose

## Strategies to Maintain Chloramine

Implemented – Not long-term solutions

- Breakpoint Chlorinating Reservoirs: short-term, high THMs, customer complaints
- Flushing Pipelines: improved conditions but does not impact reservoirs
- Cleaning Reservoirs: improved hygiene but does not impact reservoirs
- Increased pH to 9.0: helped in Sobrante, may cause precipitation – reduce to 8.7
- Blend Orinda Water: need 50% + ratio, nitrification will return in the summer

Not Implemented – Risky or Unfeasible

- Increase Chloramine Dose: would also increase ammonia
- Reduce Water Age: impractical due to system design, fire flows

Potential Future Implementation

- Further Minimize Free Ammonia: improve control at WTPs; on-line ammonia
- Apply Chlorine Dioxide & Chlorite: experimental – may try next year
- Remove TOC: very expensive – either GAC or membranes

## Calculation Examples

A. Calculate aqua ammonia feed rate in (mL/min)

Ammonia weight percent = 19%  $\text{NH}_3$

Plant rate = 25.3 MGD

Ammonia dose desired = 0.52 mg/L N

1.  $\text{NH}_3\text{-N}$  concentration in stock:  
19% aqua ammonia weighs 7.74 lbs  $\text{NH}_3/\text{gal}$   
$$\frac{(7.74 \text{ lbs } \text{NH}_3/\text{gal}) \times 19\% \times (14 \text{ g N})}{(17 \text{ g } \text{NH}_3)} = 1.21 \text{ lbs } \text{NH}_3\text{-N}/\text{gal}$$
2. Ammonia nitrogen  $\text{NH}_3\text{-N}$  feed rate:  
$$(25.3 \text{ MGD}) \times [(8.34 \text{ lb/M}) (1 \text{ L/mg})] \times (0.52 \text{ mg/L N}) = \underline{109.7 \text{ lbs } \text{NH}_3\text{-N}/\text{day}}$$

3. Aqua ammonia feed rate in (mL/min):  

$$\frac{(109.7 \text{ lbs NH}_3\text{-N/day}) \times (3785 \text{ mL/gal})}{(1.21 \text{ lbs NH}_3\text{-N/gal}) \times (1440 \text{ min/day})} = 238.3 \text{ mL/min}$$

B. Calculate expected free ammonia as N

Total chlorine = 2.0 mg/L Cl<sub>2</sub>  
 Chlorine to ammonia-N ratio = 4.5:1

1. Total NH<sub>3</sub>-N dose:  

$$(2.0 \text{ mg/L Cl}_2) / 4.5 = \underline{0.44 \text{ mg/L NH}_3\text{-N}}$$
2. Combined NH<sub>3</sub>-N in chloramine:  

$$(71 \text{ g Cl}_2) / (14 \text{ g N}) = 5 \text{ Cl}_2 : \text{NH}_3\text{-N ratio in chloramine}$$

$$(2.0 \text{ mg/L Cl}_2) / 5 = \underline{0.40 \text{ mg/L NH}_3\text{-N}}$$
3. Free NH<sub>3</sub>-N expected leaving the plant:  

$$0.44 - 0.40 = \underline{0.04 \text{ mg/L NH}_3\text{-N}}$$

C. Calculate required change in ammonia dose

Total chlorine = 2.0 mg/L Cl<sub>2</sub>  
 Total ammonia dose is 0.67 mg/L NH<sub>3</sub>-N  
 Required Cl<sub>2</sub> : NH<sub>3</sub>-N ratio is 4.5:1

1. Where are you on breakpoint curve?  

$$(2.0 \text{ mg/L Cl}_2) / (0.67 \text{ mg/L NH}_3\text{-N}) = \underline{3:1 \text{ Cl}_2 : \text{NH}_3\text{-N ratio}}$$
 increasing portion of breakpoint curve – OK  
 Ammonia dose needs to be reduced
2. Required NH<sub>3</sub>-N dose:  

$$(2.0 \text{ mg/L Cl}_2) / 4.5 = \underline{0.44 \text{ mg/L NH}_3\text{-N}}$$
3. Required reduction in total NH<sub>3</sub>-N dose:  

$$0.67 - 0.44 = \underline{0.23 \text{ mg/L NH}_3\text{-N}}$$

D. Calculate required change in ammonia dose

Total chlorine = 2.0 mg/L Cl<sub>2</sub>  
 Total ammonia dose is 0.30 mg/L NH<sub>3</sub>-N  
 Required Cl<sub>2</sub> : NH<sub>3</sub>-N ratio is 4.5:1

1. Where are you on breakpoint curve?

$(2.0 \text{ mg/L Cl}_2) / 0.30 \text{ mg/L NH}_3\text{-N} = \underline{6.6:1} \text{ Cl}_2 : \underline{\text{NH}_3\text{-N ratio}}$   
decreasing portion of breakpoint curve – NOT GOOD  
Ammonia dose needs to be increased

2. Required NH<sub>3</sub>-N dose:

$(2.0 \text{ mg/L Cl}_2) / 4.5 = \underline{0.44 \text{ mg/L NH}_3\text{-N}}$

3. Required increase in total NH<sub>3</sub>-N dose:

$0.44 - 0.30 = \underline{0.14 \text{ mg/L NH}_3\text{-N}}$

*Source:* Kirmeyer, et. al., © 1993