Chlorination

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Disinfection

- Destroy or prevent the growth of microorganisms

Sterilization

- Destruction of all living microorganisms, especially those including spores

Inactivation

Destruction of

- Proteins
- Nucleic acids (DNA, RNA)
- lipids (bilayer membranes)

Ideal disinfectant

- Active against all microbes
- Fast and effective
- Nontoxic; soluble, stable, safe
- Compatible with various materials
- Provides residual
- Easy to operate
- Economical

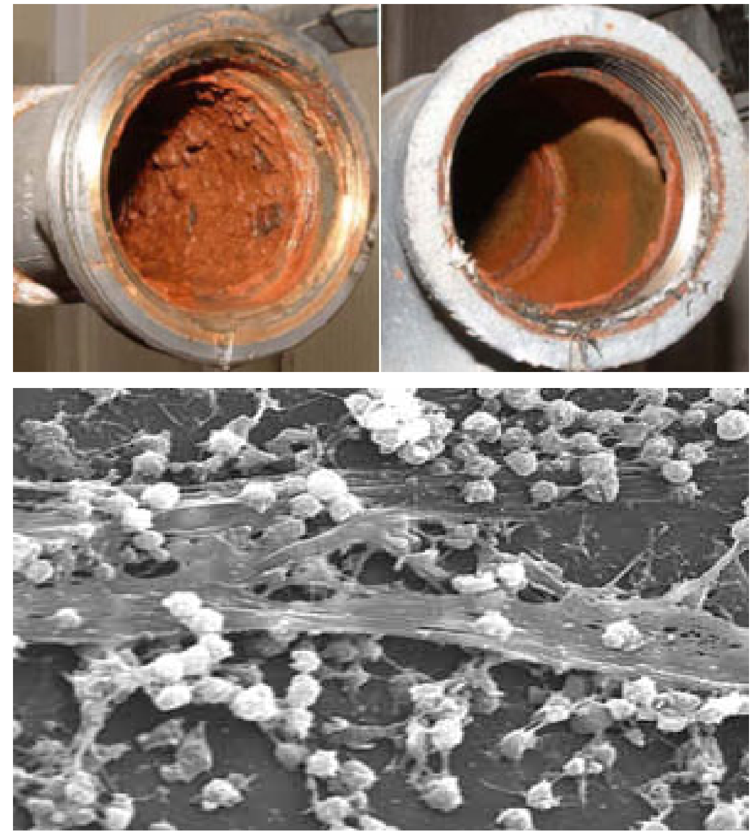
Natural Organic Matter

Problems for conventional treatment processes

- Precursors to chlorination disinfection by-products
  - TTHMs (80 μg/L max)
  - HAA5 (60 μg/L max)
- Binding of heavy metals and pesticides
- Bacterial re-growth potential

Assimilable Organic Carbon (AOC)

- Biological stability parameter
- Bacterial regrowth
- Biofilm formation
- Public health concerns
- Undesirable taste & odour



Source: www.ecogen.ie/DF_Biofilm

Chlorine

- The most widely used disinfectant: effective at low concentrations, cheap, and forms a residual if applied in sufficient dosage.
- Oxidize enzymes that are essential to the cells metabolic processes.
- May be applied as a gas (the most common) or as a hypochlorite.
- The gas is liquefied at 5 to 10 atm and shipped in steel cylinders.
- Recommended maximum residual concentration of free chlorine < 2-4 mg/L (free chlorine)

Free chlorine formation

Cl_2(gas):

$$Cl_2(g) + H_2O \leftrightarrow HOCl + H^+ + Cl^-$$

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

Hypochlorite of calcium (solid):

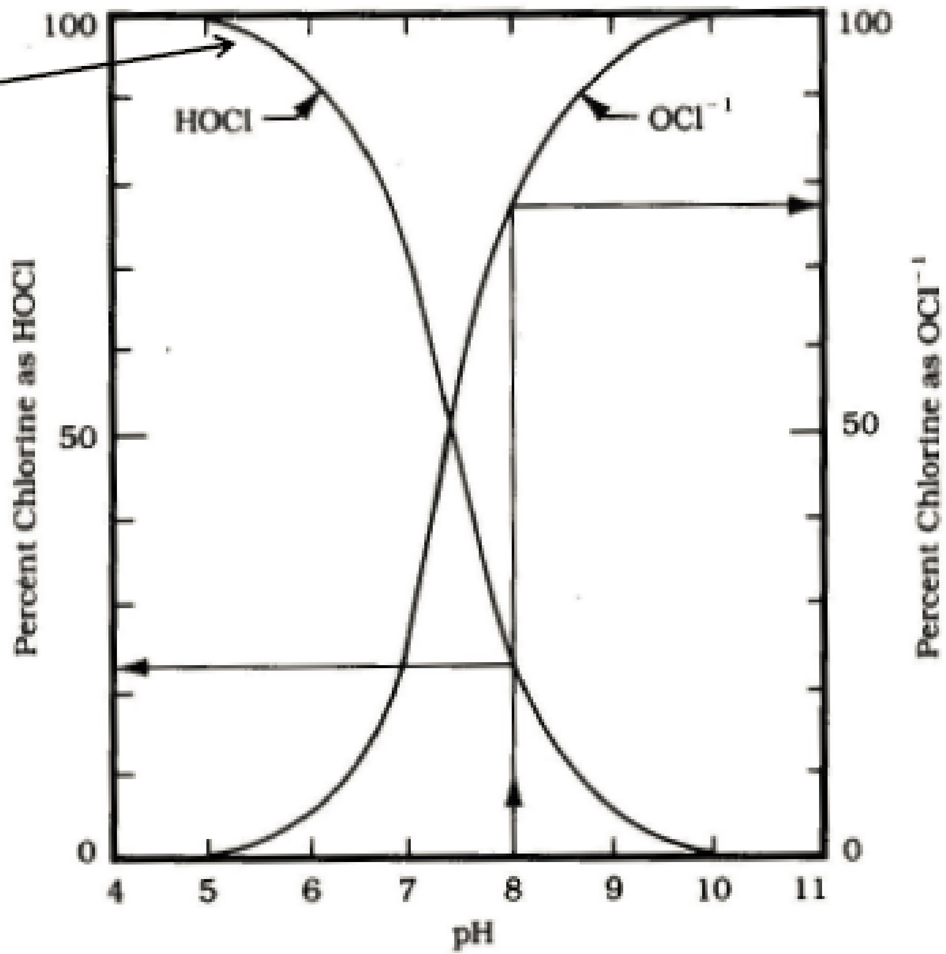
$$Ca(OCl)_2 \rightarrow Ca^{+2} + 2\ OCl^-$$

Hypochlorite of sodium (liquid):

$$NaOCl \rightarrow Na^+ + OCl^-$$

Chlorine

HOCl is more effective



$HOCl \leftrightarrow H^{+} + OCl^{-}$

Microbial inactivation

- Greater microbial inactivation at lower pH (HOCl) than at high pH (OCl^-)
  - o Probably due to greater reactivity of the neutral chemical species with the microbes and its constituents
- Resistance of Cryptosporidium to free chlorine (and monochloramine) has been a problem in drinking water supplies

Microbial inactivation

Main functional targets of inactivation

- Bacteria: respiratory activities, transport activities, nucleic acid synthesis
- Viruses: reaction with both protein coat (capsid) and nucleic acid genome
- Parasites: mode of action is uncertain

Chlorine removal

- Chlorine can be chemically removed using sulfur dioxide (SO_2), Hydrogen peroxide (H_2O_2), Ammonia (NH_3)

- The most used is SO_2

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$H_2SO_3 \rightarrow H^+ + HSO_3$$
$$HSO_3 \rightarrow H^+ + SO_3^-$$
$$SO_3^- + HOCl \rightarrow SO_4^{2-} + Cl^- + H^+$$

- Activated carbon

Chlorine

ADVANTAGES

- Well established technology
- Effective disinfectant against bacteria and most viruses
- Residual can be maintained
- Relatively inexpensive

Chlorine

DISADVANTAGES

- Increased safety regulations, toxic to humans
- Low doses may not inactivate some pathogenic viruses, spores, and cysts
- Release of volatile organic compounds
- By-products formation, toxic effect in receiving waters

Monochloramine

Monochloramine

Alternative disinfectant to free chlorine due to low THM formation potential

More stable disinfectant residual; persists in distribution system

Secondary disinfectant to ozone and chlorine dioxide disinfection to provide long-lasting residuals

Monochloramine

Monochloramine formation:

$$HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O$$

Stable at pH 7-9, moderate oxidation potential

Generation:

mix hypochlorite and ammonium chloride (NH4Cl) solution at Cl_2:N ratio at 5:1 by weight, 1:1 on a molar ratio at pH 7-9

Monochloramine

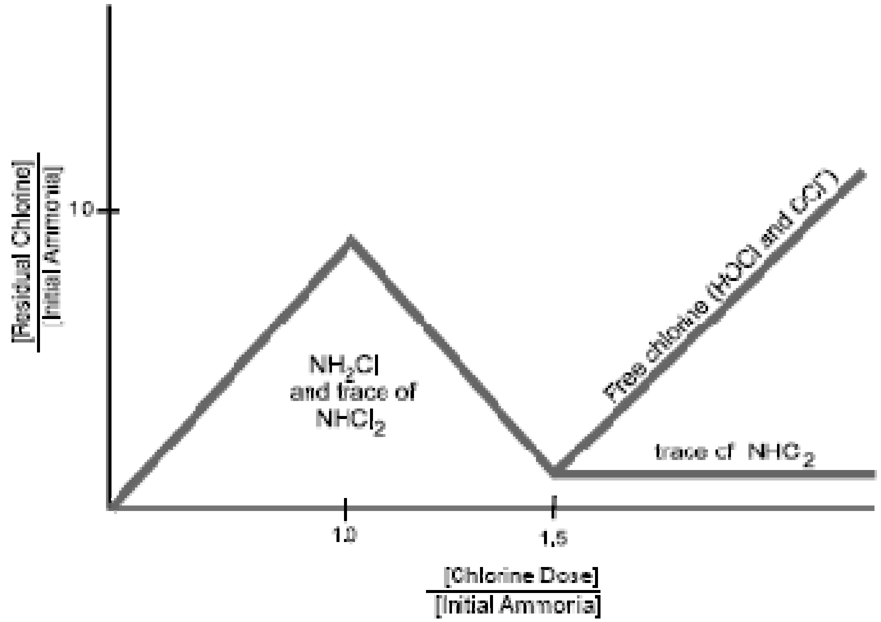
Monochloramine Formation Reaction

This reaction occurs rapidly when ammonia nitrogen is combined with free chlorine up to a molar ratio of 1:1

$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$

Breakpoint Reaction

When excess free chlorine is added beyond the 1:1 initial molar ratio, monochloramine is removed



$2\ NH_2Cl + HOCl \rightarrow N_2 + H_2O + 3\ H^+ + 3\ Cl^-$

Chloramines

Advantages

- Less corrosive than HOCl
- Low toxicity and chemical hazards
- Relatively tolerable to inorganic and organic loads
- No known formation of DBP
- Relatively long-lasting residuals

Disadvantages

- Not so effective against viruses, protozoan cysts, and bacterial spores

Chlorine dioxide ClO_2

Chlorine dioxide ClO_2

ClO_2 is a more powerful oxidant than chlorine

- It is used for bleaching (wood pulp), for odor reduction, iron and manganese removal, and disinfection

- Very soluble in water; generated as a gas or a liquid on-site, usually by reaction of Cl_2 gas with $NaClO_2$

$$2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl$$

Chlorine dioxide ClO_2

- Long lasting residual
- ClO_2 can be removed by aeration and is readily discomposed by exposure to UV radiation
- Recommended maximum combined concentration of chlorine dioxide and it’s by-products < 0.5 mg/L
- Chlorine dioxide is about 5 to 10 times more expensive than chlorine

Chlorine dioxide ClO_2

Advantages

- Very effective against all type of microbes
- Low formation of DBP’s
- Long lasting residual

Disadvantages

- Unstable (must be produced on-site)
- High chemical hazards
- Highly sensitive to inorganic and organic loads
- Expensive