

**The Islamic University of Gaza- Environmental Engineering Department
Water Treatment (EENV-4331)**

Lecture 3: Disinfection and Oxidation

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Disinfection:

is killing or inactivate of pathogenic organisms. It is necessary if the water to be used for drinking water is not hygienically reliable.

In water treatment, aimed at the production of drinking water, disinfection is the most important treatment step.

Purpose of disinfection:

To make Drinking water free of any disease causing bacteria and microbes.

Methods of disinfection:

There are many used disinfection methods at large scale.

- **HEAT:** boiling of water at least one minute inactivates all pathogenic organisms. It is only applicable for small amount of water in emergency cases.
- **ULTRAVIOLET RADIATION:** The absorption capacity of UV-rays (200-310 nm) in water is limited. Moreover other substances (organics and turbid matter) influence the efficiency. In practice it is only applied for small amounts of water to be treated.
- **β - RADIATION:** It has the same disadvantage as UV-rays. Moreover the presence of a radioactive source at the site of the water treatment is not appreciated. Therefore under normal conditions application is not likely.

- **METAL IONS:** like Ag and Cu have only bactericidal action, so unless for general disinfection. Moreover health aspects have to be considered: the addition of metals to water. Generally not suitable for water.
- **CHEMICAL METHODS:** disinfection can be carried out efficiently by application of oxidants like Cl_2 , $\text{Ca}(\text{OCl})_2$ and O_3 . The chemical disinfection is most often applied in water treatment.

Disinfection efficiency depends on:

- Type and concentration of the micro-organism
- Type and dosage of the disinfectant
- contact time
- clarity of water
- Presence of other chlorine consuming compounds
- temperature
- pH

Chlorination

- The most important oxidant used for disinfection is chlorine Cl_2 .
- Chlorine is one of the halogens.
- At a normal temperature and pressure chlorine is a yellow-green gas
- It is heavier than air and can be liquefied.
- Chlorine is rather soluble in water: solubility decrease at rising temperature.

Temperature (°C)	Solubility (kg Cl_2 /m ³ of water)
0	14.4
20	7.25
40	4.6

- In presence of water chlorine affects all metals. In dry state the reactivity is much less with regard to metals, then it affects plastic materials.

Chlorine is one of the most widely used disinfectants.

It is very applicable and very effective for the deactivation of pathogenic microorganisms.

Chlorine can be easily applied, measures and controlled. It is relatively cheap.

However, we only started using it as a disinfectants on a wider scale in the nineteenth century, after Louis Pasteur discovered that microorganisms spread certain diseases.

Chlorine has played an important role in lengthening the life-expectancy of humans.

Chlorine can be used as a disinfectant of the following forms:

- **Gaseous form Cl_2 .**
- **Bleaching solution (NaOH):** Bleach consists of chlorine gas dissolved in an alkali-solution, such as sodium hydroxide (NaOH). Chlorine reacts with sodium hydroxide to sodium hypochlorite (NaOCl).
- **Bleaching powder Ca(OCl)_2 :** This is produced by directing chlorine through calcium hydroxide (CaOH). The benefit of bleaching powder is that it is a solid.

1 . Reactions of the different forms in water:

1.1 Gaseous form Cl_2 : When chlorine is added to water, underchloric acids (hypochloric acid) is formed:



The driving force for this reaction is the ultraviolet radiation from the sunlight (UV), as this UV firstly decomposes the Cl_2 to two chlorine radicals and also decomposes the water to hydroxyl radical and oxygen radical. Then one of the chlorine radical releases one electron to form the positive ion which combines with the hydroxyl radical to form the underchloric acid (HOCl). The released electron instantaneously complete the last orbit of the chlorine to form the negative ion which combine with the positive hydrogen from water to form the hydrochloric acid in its ionic form



1.2 Bleaching solution (NaOH):

As we know that all Na salts are soluble and ionized in water, so the NaOCl is ionized easily to the Na positive ion and the hypochlorite negative ion according to the first equation:



Now once the hypochlorite ion is formed it runs into chemical equilibrium (acid base reaction) with its conjugate acid HOCl according to the following equation:



1.3 Bleaching powder($\text{Ca}(\text{OCl})_2$):

When bleaching powder dissolves, it reacts with water to Calcium hydroxide and chlorine according to the following equation:



Then the chlorine hydrolysis in the water in the same procedure as in case (1.1) the gaseous form.

How does chlorine act?

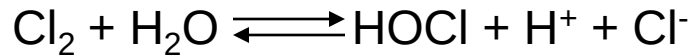
Free “active” chlorine = Hypochloric acid (HOCl) & hypochlorite ion (OCl⁻).

Hypochloric acid is the most reactive and a stronger disinfectant because it's neutral.

Hypochloric acid is able to oxidize microorganisms in seconds while the hypochlorite ion can take up to 30 minutes for the same effect.

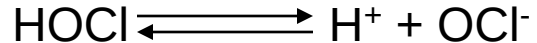
Liquid form – NaOCl (bleach)	$\text{NaOCl} \rightarrow \text{Na}^+ + \text{OCl}^- \leftarrow \text{Hypochlorite ion}$ $\text{OCl}^- + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{OH}^-$
Powder form – Ca(OCl) ₂ (pool tablets/powder)	$\text{CaOCl}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{Cl}_2$ $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$ $\text{HOCl} \rightarrow \text{HCl} + \text{O} \uparrow \leftarrow \text{Hypochloric acid}$
Gaseous form – Cl ₂	$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^-$ $\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}_3\text{O}^+ + \text{Cl}^-$ $\text{HOCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OCl}^-$ $\text{OCl}^- \rightarrow \text{Cl}^- + \text{O}$

- When chlorine dissolved in water the following reaction will take place within a second: (Hydrolysis reaction)



$$K_H = \frac{(\text{HOCl})(\text{H}^+)(\text{Cl}^-)}{(\text{Cl}_2)}$$

- After the hydrolysis reaction dissociation of HOCl will immediately follow:



$$K_A = \frac{(\text{H}^+)(\text{OCl}^-)}{(\text{HOCl})} \longrightarrow \frac{K_A}{(\text{H}^+)} = \frac{(\text{OCl}^-)}{(\text{HOCl})}$$

T (°C)	0	5	10	15	20	25
K_H	$1.5 * 10^{-4}$	$1.8 * 10^{-4}$	$2.4 * 10^{-4}$	$3.0 * 10^{-4}$	$3.7 * 10^{-4}$	$4.5 * 10^{-4}$
K_A	$2.0 * 10^{-8}$	$2.3 * 10^{-8}$	$2.6 * 10^{-8}$	$3.0 * 10^{-8}$	$3.3 * 10^{-8}$	$3.7 * 10^{-8}$

The amount of free Cl_2 dissolved in water during treatment can be neglected.

The amount of OCl^- (less-effective form of active chlorine for disinfection) can be calculated too, starting from the K_A - value for HOCl as the following example:

For 25°C $K_A = 3.7 \times 10^{-8}$	$\frac{K_A}{(\text{H}^+)} = \frac{(\text{OCl}^-)}{(\text{HOCl})}$
$\text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^-$	
$\text{HOCl} + \text{OCl}^- = 100\%$	

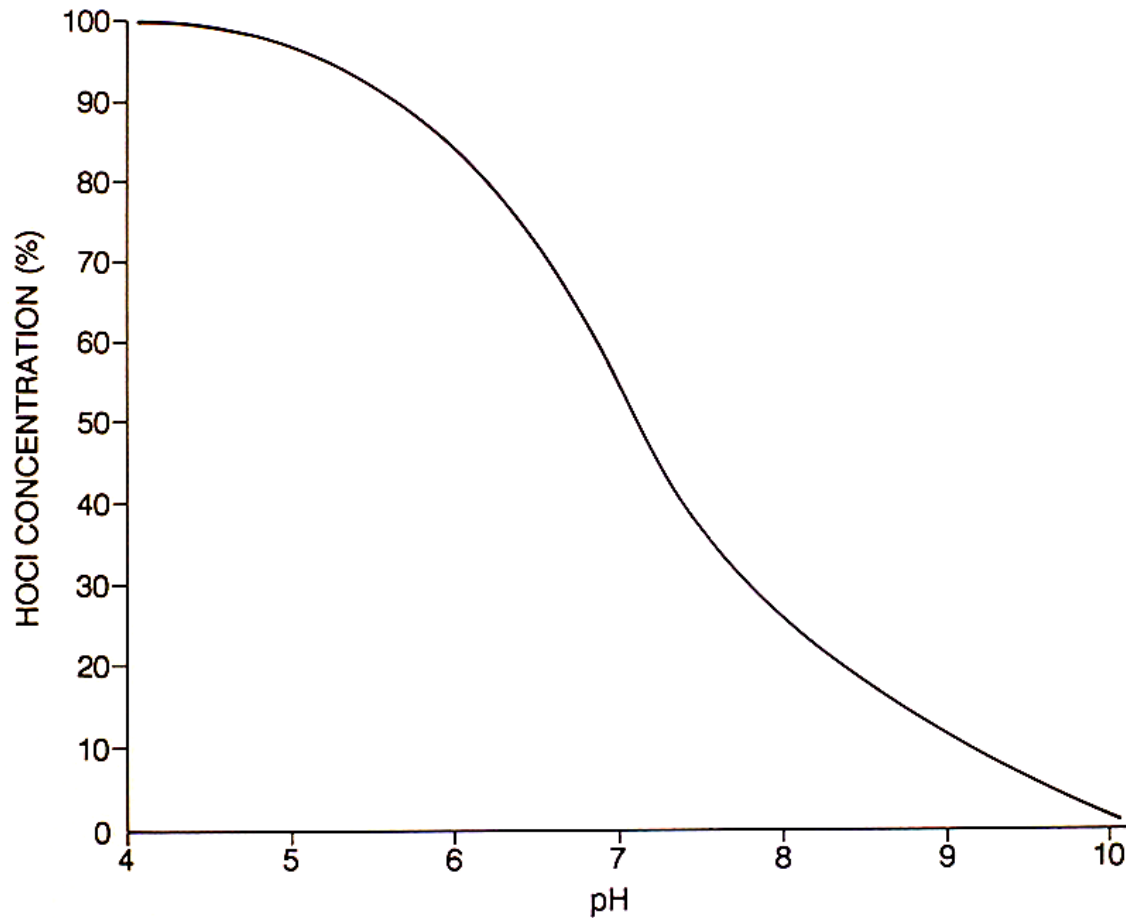
pH = 8 $(\text{H}^+) = 10^{-8}$	$\frac{3.7 \times 10^{-8}}{(10^{-8})} = \frac{(\text{OCl}^-)}{(\text{HOCl})} = 3.7$
$\text{HOCl} = 21.3\%$, $\text{OCl}^- = 78.7\%$	

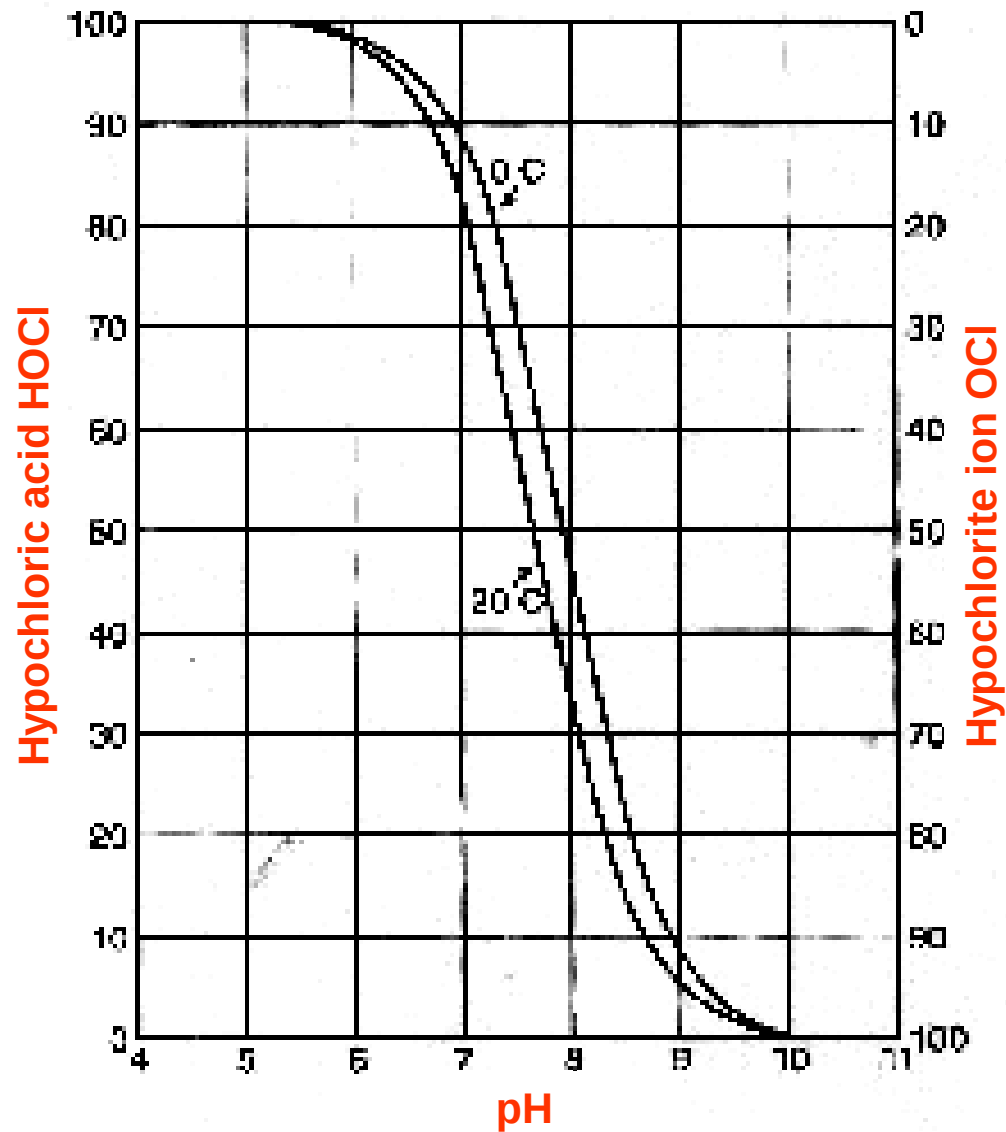
pH = 7 $(\text{H}^+) = 10^{-7}$	$\frac{3.7 \times 10^{-8}}{(10^{-7})} = \frac{(\text{OCl}^-)}{(\text{HOCl})} = 0.37$
$\text{HOCl} = 73\%$, $\text{OCl}^- = 27\%$	

pH = 6 $(\text{H}^+) = 10^{-6}$	$\frac{3.7 \times 10^{-8}}{(10^{-6})} = \frac{(\text{OCl}^-)}{(\text{HOCl})} = 0.037$
$\text{HOCl} = 96.4\%$, $\text{OCl}^- = 3.6\%$	

Chlorination and pH

The water pH determines if free Cl_2 becomes hypochlorite (OCl^-), or (HOCl) which kills organisms 40-80 times more effectively.





Hypochlorous acid (HOCl) & hypochlorite ion (OCl⁻) varies according to pH and temperature

The chlorination process

- Chlorine readily combines with chemicals dissolved in water, microorganisms, small animals, plant material, tastes, odors, and colors.
- These components "use up" chlorine and comprise the **chlorine demand** of the treatment system.
- It is important to add sufficient chlorine to the water to meet the chlorine demand and provide residual disinfection.

The chlorination process Conti.

1. **Chlorine demand** is the amount of chlorine required to kill bacteria, oxidize iron or other elements in the water.
2. **Free available chlorine residual** is the amount of chlorine remaining in the water after the chlorine demand has been met.
3. **Contact time** is the amount of time that the chlorine is present in the water. The combination of chlorine residual and contact time determines the effectiveness of the chlorination treatment.

Reaction of chlorine with ammonia-Breakpoint chlorination

When chlorine is added to water containing ammonia the following reaction take places

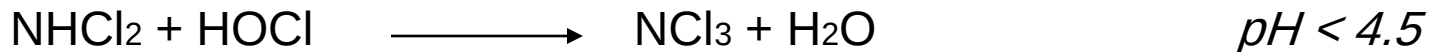
Monochloramine:



Dichloramine:



Trichloramine or nitrogentrichloride:



Chloramines: effective vs. bacteria but NOT viruses.

additional free chlorine + chloramine = H_2 , H_2O , and N_2 gas which will come out of solution.

What will happen depends on four parameters:

a) The ration $\frac{(\text{Cl}_2)}{(\text{N H}_4^+)}$

At low ratio mainly monochloramine is formed; by increasing the ratio more dichloramine and trichloramine will be produced.

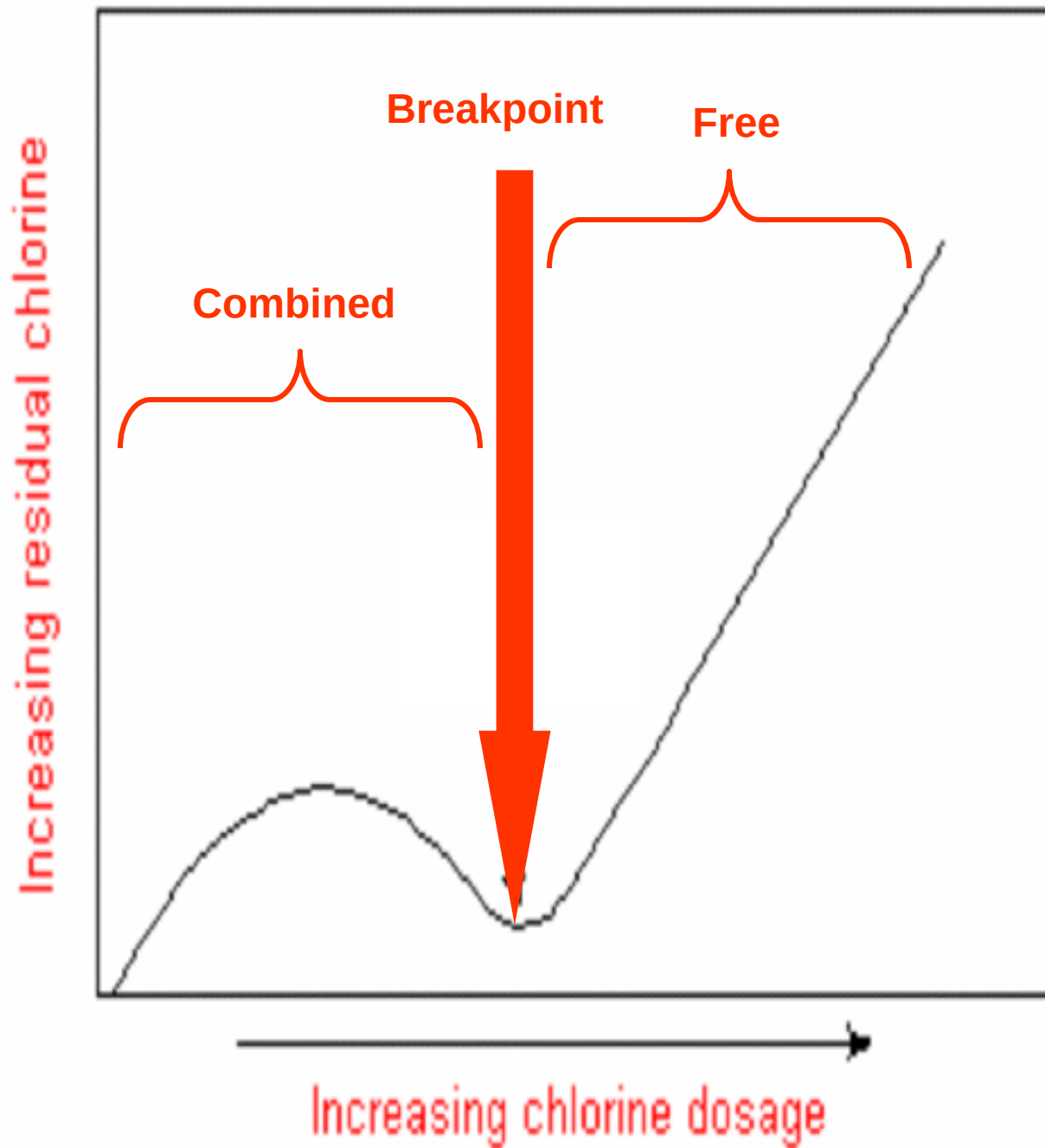
b) pH-value

At a pH value greater than 7.5 (and a low chlorine-ammonia ratio) in principle only monochloramine is formed. The lower the pH value the more NHCl_2 resp. NCl_3 is produced.

c) Temperature and contact time

The rate of formation of monochloramine for concentration of ammonia normally present in water is relatively high. About 90% is formed within one minute at normal pH.

The rate of formation of dichloramine is considerably lower than that of monochloramine at normal pH values.



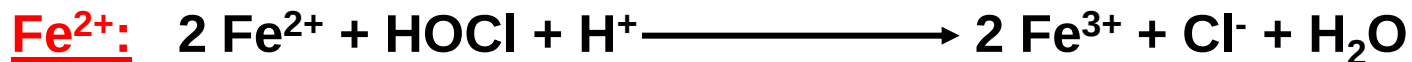
Reaction of chlorine with other inorganic compounds

HOCl is a strong oxidant and has the tendency to react with oxidizable substances in water. The Cl^+ present in the hypochlorous acid molecule is reduced to Cl^- by accepting two electrons coming from the substance to be oxidized.



Examples of inorganic compounds which can be oxidized by chlorine are:

Fe^{2+} , Mn^{2+} , NO_2^- , H_2S , H_2SO_3 .



At normal pH-values hydrolysis will take place:



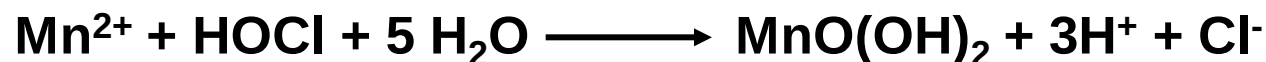
The oxidation of ferrous ions by chlorine is sometimes applied in cases where the iron is present in a complexed form or in cases where ferrous sulfate $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ is used as coagulant.

Oxidation in the latter case is essential for proper coagulation at normal pH-values.

Mn²⁺ In dependence of the dose of chlorine two reactions are possible.



or



Commonly both reactions occur at the same time.

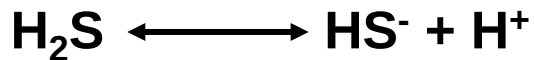
At higher dosages of chlorine the second reaction prevails. In this case the overall reaction equation is given (oxidation and hydrolysis).

The complete oxidation of manganese ions is only applicable at pH-values higher than 7.5.



H₂S or HS⁻

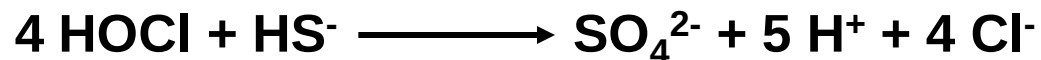
H₂S is a weak acid and - in dependence of pH - only partially dissociated at normal pH-values.



The following reactions are possible: $\text{HS}^- + \text{HOCl} \longrightarrow \text{S} + \text{H}_2\text{O} + \text{Cl}^-$

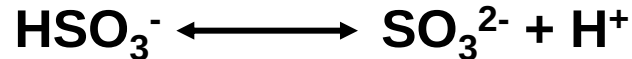
The sulfur formed will precipitate and can be removed easily by the coagulation process.

When an excess of chlorine is present:

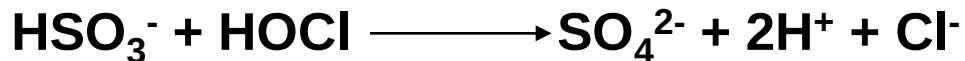


H₂SO₃ Or HSO₃⁻

Sulfurous acid is a weak acid and only partially dissociated at normal pH-values.



The sulfite ions are oxidized by chlorine according to the following reaction equation:



Sulfite is sometimes used for de-chlorination of water. Mostly one starts with sulfur dioxide SO₂ as gas, which can be dissolved in water forming sulfurous acid or sulfite ions:

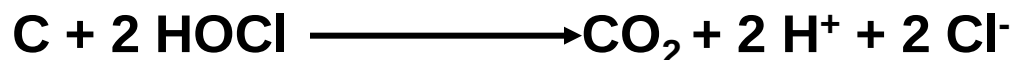


Reaction of Chlorine with Organic Matter

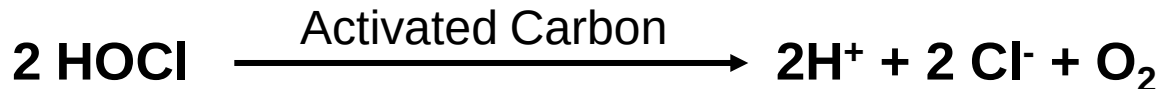
Oxidation of Activated Carbon:

Activated carbon can be considered as an amorphous form of carbon, prepared from certain organic substances, with a high porosity and a high specific surface area (100 - 1500 m²/g). It is an excellent adsorbent for specific organic compounds.

Activated carbon can react with chlorine in the following way:



At the same time a catalytic reduction of hypochlorous acid can take place



Next to the application of sulfur dioxide or sulfite-ions this is a second way for **de-chlorination** of water.

Oxidation of Organic Nitrogen compounds:

The analysis of organic nitrogen compounds is generally aimed at the analysis of **albuminoid** nitrogen (protein soluble in water), consisting of mainly simple amino acids, and the total concentration of organic nitrogen compounds or TON.

Both concentrations are expressed in g NH_4^+ /m³. The origin of NH_4^+ in polluted water is mostly domestic.

By biodegradation proteins are converted to finally ammonium which can be nitrified.

proteins → peptones → polypeptides → dipeptides → α-amino acids →
ammonia, fatty and other acids → CO_2 and water

In case chlorine has been applied to water containing organic nitrogen, the TON reduction gives an impression of the reduction of TON by chlorine.

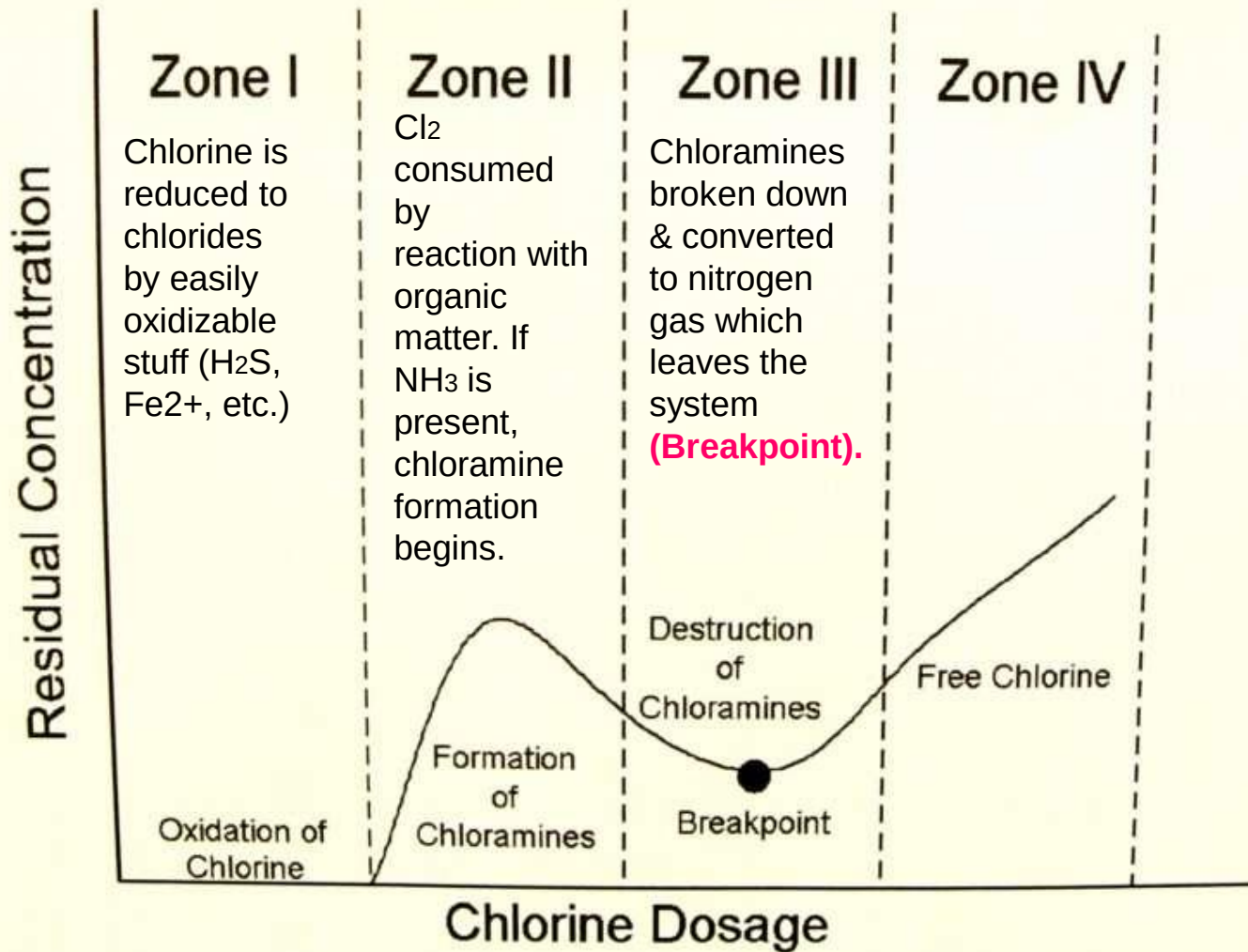
The albuminoid-N reduction gives an impression of the reduction of amino acids by chlorine.

The reduction of proteins is very limited.

Reduction of albuminoid nitrogen up to 75% within one hour is possible with sufficient chlorine.

The organic matter content can be reduced by the application of the coagulation process.

Surface water: Use of a high concentration of chlorine (combined residual x10) to oxidize unwanted nitrogenous pollution (ammonia and chloramines) from water.



Getting to Breakpoint

Total chlorine residual = free available chlorine + combined available chlorine.

Total residual should not be significantly $>$ free residual
(i.e. a total 1.0 mg/l and a free 0.2 mg/l).

When this occurs, indications are that breakpoint chlorination has not been met and additional chlorine should be applied

Free residual test should ideally be = or slightly $<$ total chlorine residual
(i.e. a free 0.8 mg/l and a total 1.0 mg/l).

These test results indicate that breakpoint chlorination

Therefore, testing for TOTAL chlorine *in addition to* FREE chlorine can help!!

Example 1: Chlorination

A surface water contains 0.8 mg NH_4/l .

Chlorine is available as Cl_2 .

A dosage of 8 mg $\text{Cl}_2/\text{mg NH}_4$ is required for the complete oxidation (breakpoint chlorination).

$$\text{HCO}_3^- = 130 \text{ mg/l}$$

$$K_1 = 4.15 \times 10^{-7}$$

$$\text{CO}_2 = 15 \text{ mg/l}$$

$$K_2 = 4.2 \times 10^{-11}$$

Calculate the pH after the breakpoint chlorination.

Solution:

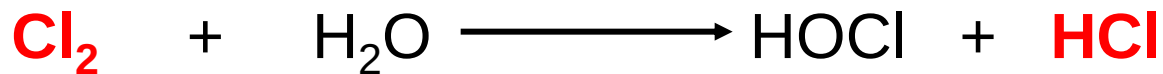


needed $0.8 \times 8 = 6.4 \text{ mg Cl}_2/\text{l} = 6.4 \text{ g Cl}_2/\text{m}^3$

Dosage = Demand + residual

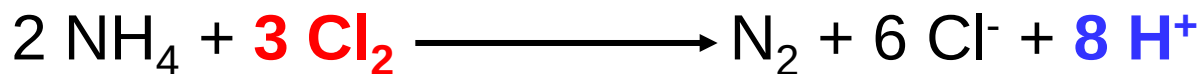
$$6.4 = \text{Demand} + 0.5 \longrightarrow \text{Demand} = 5.9 \text{ mg Cl}_2/\text{l}$$

$$5.9 / 71 = \text{moles Cl}_2 / \text{m}^3 = 0.08 \text{ moles} / \text{m}^3$$



$$0.5 / 71 = 0.007 \text{ moles / m}^3$$

$$0.007 \text{ moles / m}^3$$



$$5.9 / 71 = 0.083 \text{ moles/m}^3$$

$$0.231 \text{ moles/m}^3$$

$$\text{In total (H}^+) = 0.231 + 0.007 = 0.24 \text{ moles H}^+/\text{m}^3$$



$$0.24$$

$$0.24$$

$$0.24$$

Before:

$$\text{HCO}_3^- = 130 \times 10^{-3} / 61 = 2.13 \times 10^{-3} \text{ mole/l}$$

$$\text{CO}_2 = 15 \times 10^{-3} / 44 = 0.34 \times 10^{-3} \text{ mole/l}$$

After:

$$\text{HCO}_3^- = (2.13 - 0.24) \times 10^{-3} = 1.91 \times 10^{-3} \text{ mole/l}$$

$$\text{CO}_2 = (0.34 + 0.24) \times 10^{-3} = 0.58 \times 10^{-3} \text{ mole/l}$$

$$K_1 = \frac{(H^+)(HCO_3^-)}{(CO_2)} \quad 4.15 \times 10^{-7} = \frac{(H^+)(1.19 \times 10^{-3})}{(0.58 \times 10^{-3})}$$

$$H^+ = \frac{(0.58 \times 10^{-3} \times 4.15 \times 10^{-7})}{(1.19 \times 10^{-3})} = 1.26 \times 10^{-7}$$

$$pH = -\log 1.26 \times 10^{-7} = 6.9$$

Post-chlorination

The presence of biodegradable organic matter and/or ammonia in drinking water results in the development of bacteria in the distribution system (mineralization of organic matter; nitrification).

Bacterial activities will ask for oxygen, which is only in a limited amount present in the water, so anaerobic conditions can develop.

After depletion of the oxygen in water oxidized substances - present at the inner-wall of the pipelines or in the water -will be reduced rendering the water colored with often a bad smell.

The development of an excessive growth of bacteria can be prevented by the application of a water treatment system proper for taking out the nutrients necessary for bacterial growth and by the maintenance of a free chlorine residual in the water to be distributed.

In post chlorination so much chlorine is added to the already disinfected water that drinking water entering the distribution system contains a free chlorine residual of 0.3 to 0.5 g Cl₂/m³.

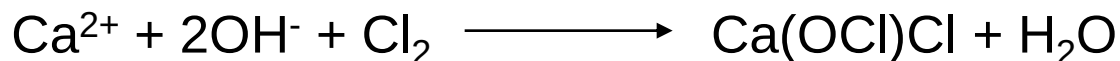
Higher chlorine residuals will result in a disagreeable taste of the water, which can be objectionable for the consumers.

Choice of the type of chlorine compound in water disinfection

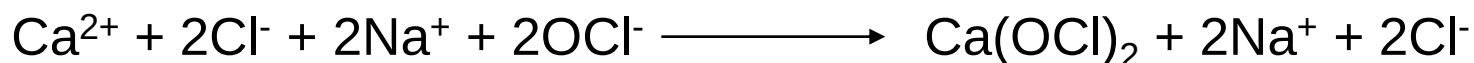
Chlorine is available commercially in three forms:

- Liquefied Cl_2
 - As a solution of NaOCl
 - As solid in the form of calciumhypochlorite Ca(OCl)_2
- Generally in case water supply is larger than $25 \text{ m}^3/\text{hr}$. liquefied chlorine has to be preferred.
 - For smaller supplies it is more convenient to use solution of NaOCl or one of the solid compounds after the dissolution in water.
 - The main disadvantage of the application of a solution of NaOCl are the limited stability of the chlorine compound (natural decomposition which can be enhanced by heat and /or light) and a large volume of water containing NaOCl to transport.
 - The commercial hypochlorite solution can contain 0.25 kg Cl_2 per liter.

Bleaching powder or chlorinated lime is prepared in the following way:



Calciumhypochlorite is commercially available under different trade names like PERCHLORON, PITTCHLOR or HTH (High Test Hypochlorite) in a palletized, granular or agglomerated form. It is produced according the following reaction equation.



The solid products are stable under normal conditions, however calcium salts have a limited solubility.

How chlorine kills/deactivates

Chlorine disinfects water through two mechanisms:

- oxidizing power of free oxygen
- chlorine substitution reactions

Oxidizing powers

- Free oxygen is produced by the breakdown of chlorine compounds in water



- Oxygen attacks the lipids in cell walls and destroys the enzymes and structures inside the cell which either destroys or inactivates it.

Dying of bacteria is often described by the law of Chick:

$$-\frac{dN}{dt} = KN$$

N = the number of organisms at time t

K= a rate constant

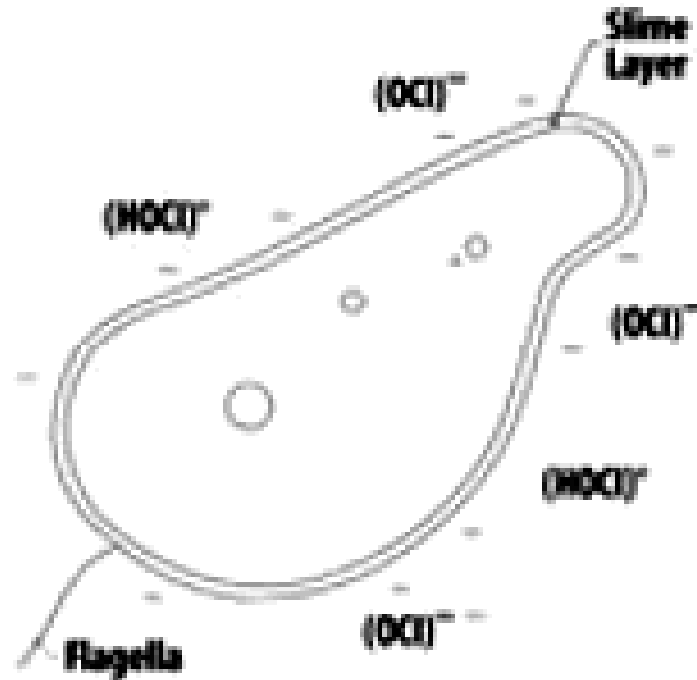
In disinfection often the concentration of the oxidant (disinfectant) is included:

$$-\frac{dN}{dt} = KNC$$

After integration:
$$-\log \frac{N}{N_0} = \frac{k}{2.3} \int_0^t C dt = \frac{kD}{2.3}$$

D is a measure for the amount of disinfection to be dosed. Calculation is only possible if k(t) and C(t) are known.

Chlorine substitution



- Chlorine breaks chemical bonds in enzyme molecules and replace some hydrogen atoms with chlorine.
- This changes the shape or destroys the molecules and makes it difficult for the enzymes to function properly.
- Without effective enzymes, the cell either dies or is unable to reproduce

Affectivity of chlorine

Chlorine concentrations, contact time, temperature, pH, number and types of microorganisms, organic matter

disinfection time with water containing a chlorine conc. of 1 mg/l (1 ppm)
when pH = 7,5 and T = 25 °C

Disinfection time of fecal pollutants with chlorinated water	
<i>E. coli 0157 H7 bacterium</i>	< 1 minute
<i>Hepatitis A virus</i>	about 16 minutes
<i>Giardia parasite</i>	about 45 minutes
<i>Cryptosporidium</i>	about 9600 minutes (6,7 days)

The chlorine dosing equipment should be sufficient enough firstly to allow not less than 30 minutes of contact with the water before use and secondly to maintain chlorine residual of at least $0.3\text{-}0.5 \text{ g Cl}_2/\text{m}^3$ after that time.

There exists a certain relation between chlorine demand and contact time. The mathematical formulation of that relation gives information about the nature of the compounds:

$$D = K t^n$$

D: chlorine demand ($\text{g Cl}/\text{m}^3$)

t: contact time (hours)

K: chlorine demand after one hour

n: constant

The higher the n, the more complicated the system.

For groundwater containing mainly $\text{NH}_4^+\text{-N}$: $n = 0.01\text{-}0.05$

For surface water treated $n = 0.10\text{-}0.20$

Water meter

PLAN

Main connection

Hypochlorite tank

Discharge hose

ELEVATION

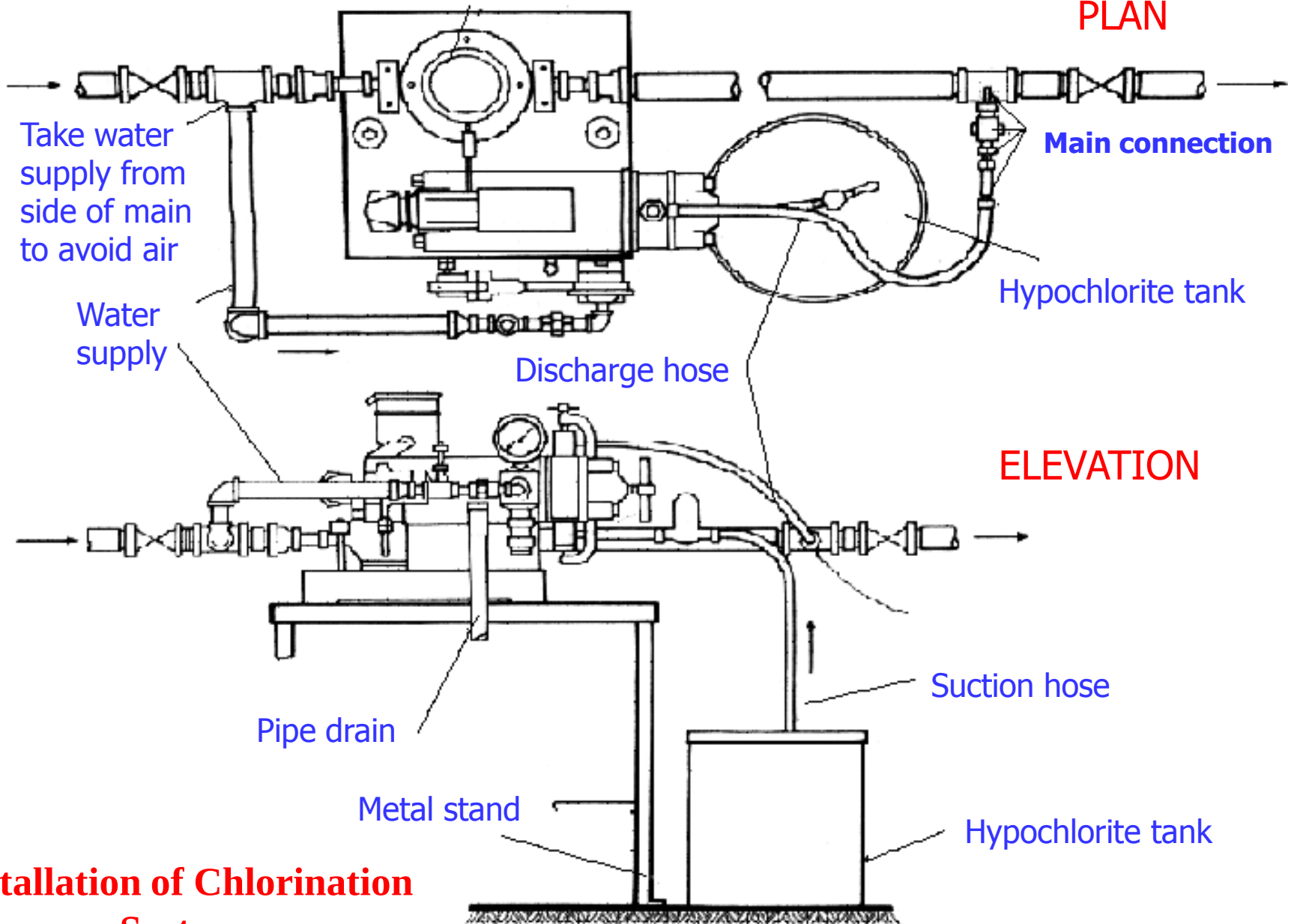
Suction hose

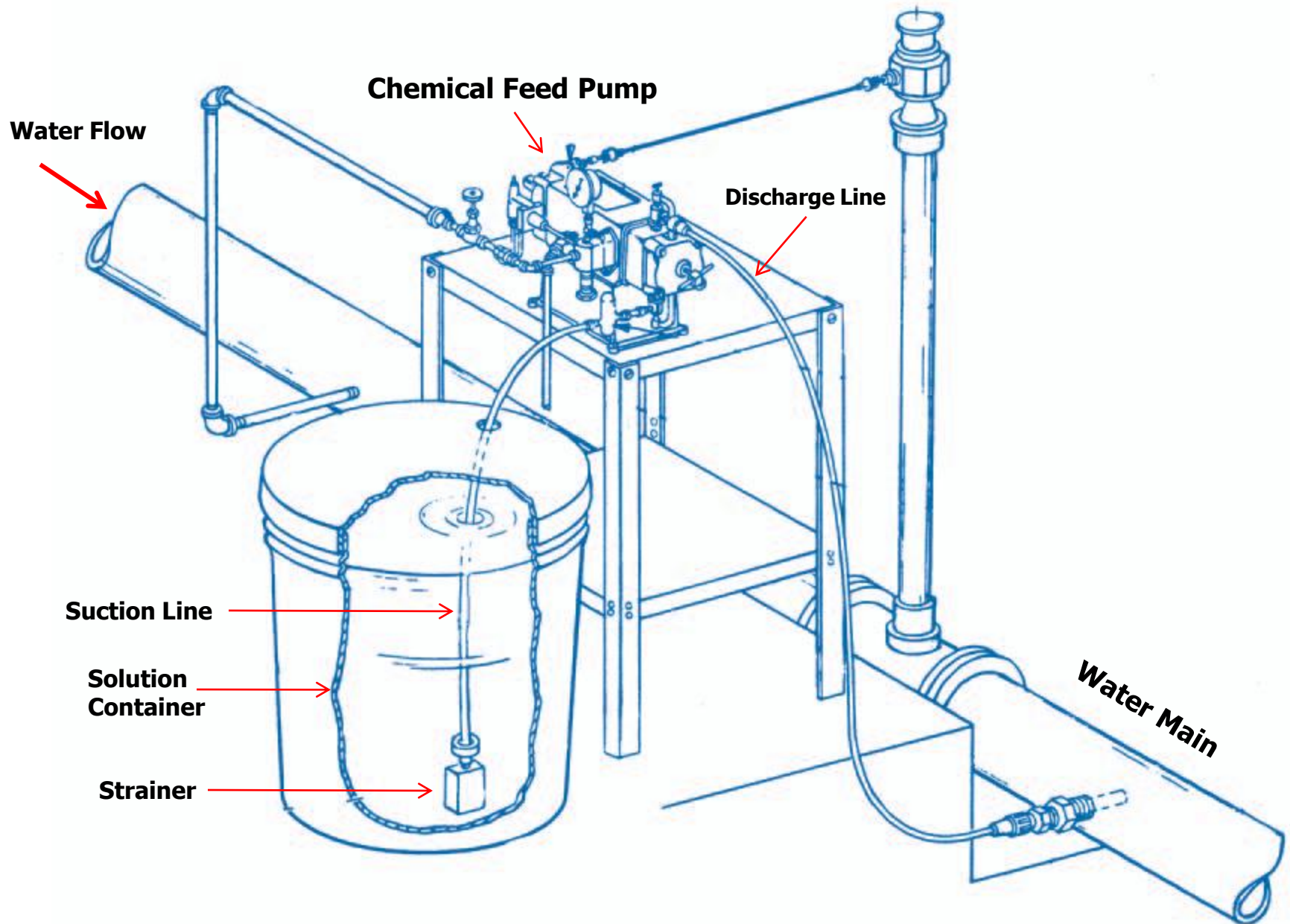
Pipe drain

Metal stand

Hypochlorite tank

Installation of Chlorination System





Chlorine Dose (Example)

The required chlorine dose can be calculated by determining the desired residual, the volume of flow, and chlorine demand.

For example, to disinfect 2000 m³ per day of water and produce a chlorine residual of 0.6 mg/L with water having a 1.0 mg/L chlorine demand.

The chlorine dose rate in kilogram per day would be calculated as follows:

Chlorine, kilogram/day = 2000 m³/day x 1.6 mg/L x 10⁻⁶ (kg) x 10³ (m³) = 3.2 kg/day

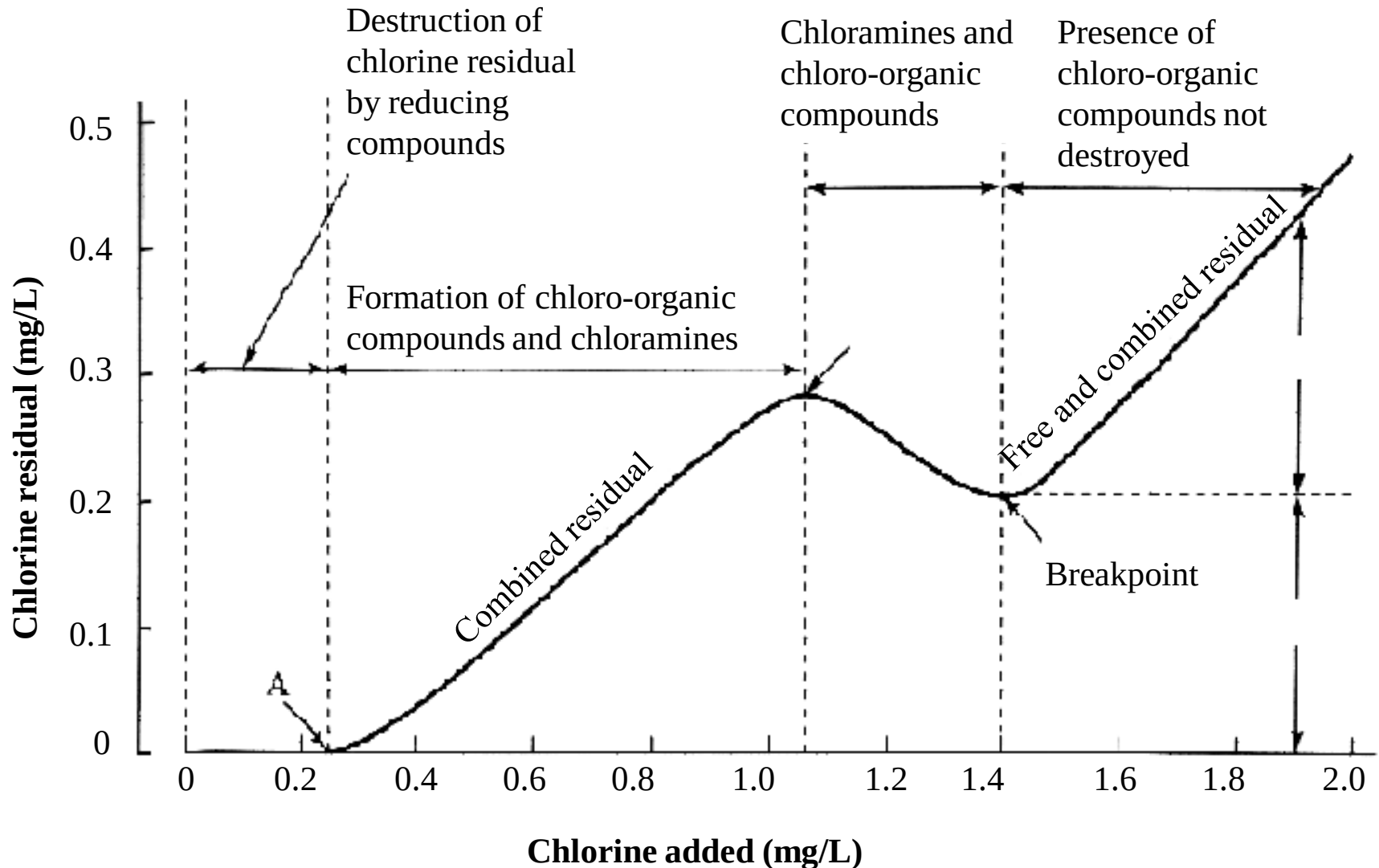
Chlorine pump dosing rate would be calculated as follows:

The commercial hypochlorite solution can contain 0.25 kg Cl₂ per liter

The required volume of hypochlorite solution = (3.2 / 250) x 10³ L = 12.8 liter

Hypochlorite pumping rate = 12.8/24 = 0.53 L/hour.

Example: Referring to Figure, if a dosage of 1.8 mg/L is administered, determine: the amount free chlorine residual that results, the amount of combined residual that results, and the amount of combined ammonia chloramine residual that results.



From the figure,

The concentration of residual chlorine at a dosage of 1.8 mg/L = 0.38 mg/L.

The concentration of the residual at the breakpoint = 0.20 mg/L. Therefore,

free chlorine residual = $0.38 - 0.20 = 0.18$ mg/L

amount of combined residual = 0.20 mg/L

amount of combined ammonia chloramine ~0