

Chapter 5

Disinfection



Section 5.1

Introduction



清华大学环境学院

Water and Wastewater Treatment Engineering

Physicochemical Technology

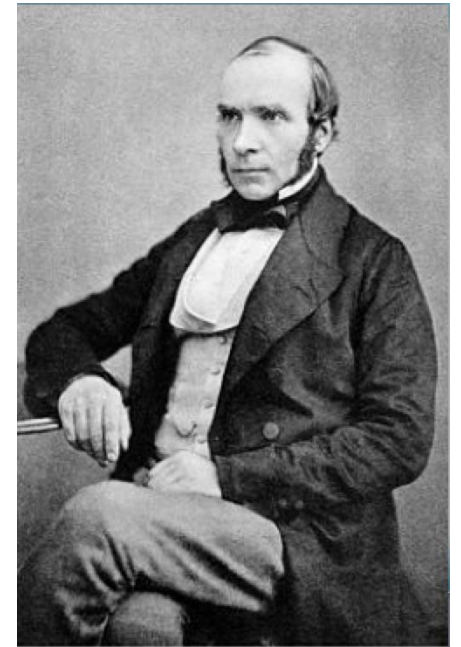
1. A brief history of disinfection



Picture from internet

In 1854, **Cholera** took over 500 lives within 10 days in London.

English physician **John Snow** found out the cause was related to **polluted drinking well water**.



Picture from internet



1. A brief history of disinfection

- 1886, Koch discovered that chlorine could kill bacteria.
- 1902, Belgium first applied chlorine in disinfection of public water treatment.
- 1908, Jersey City in USA started to apply chlorine disinfection in municipal water plants.

In other countries, chlorine disinfection has also been widely used as an important sanitation guarantee of drinking water.



2. Definition of disinfection

Disinfection:

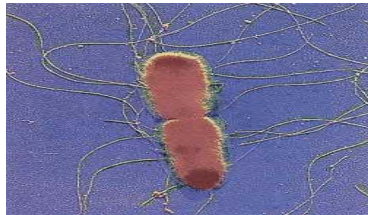
To eliminate most of **pathogenic microorganisms** which are harmful to human health in water, so that the hazardous risk can be reduced to the acceptable level and therefore the water-borne diseases is avoided.

- Bacteria
- Protozoan oocysts and cysts
- Viruses (e.g. infectious hepatitis virus, choriomeningitis virus)



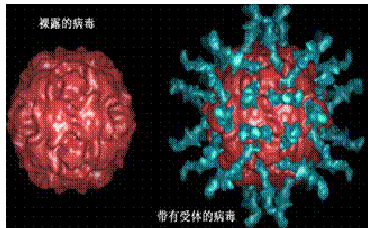
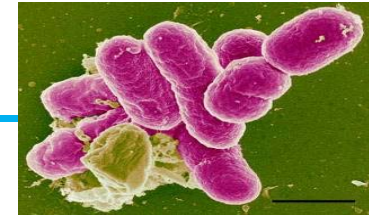
2. Definition of disinfection

Pathogenic microorganisms in water



- **Bacteria**

- ✓ 0157 bacteria
- ✓ Salmonella



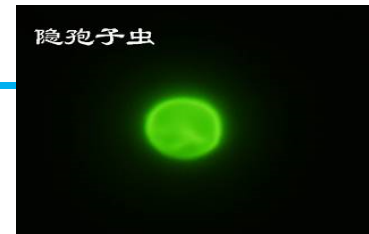
- **Virus**

- ✓ Coxsackie virus
- ✓ Poliovirus



- **Protozoan**

- ✓ Cryptosporidium parvum
- ✓ Giardia (Giardia lamblia Stiles)



- **Parasite**



2. Definition of disinfection

- Difference between disinfection and sterilization:

Sterilization is to **kill all living organisms**, while disinfection only **reduce the pathogenic microorganisms to a safety level**.

- **Drinking water disinfection**: After disinfection, microbiological indices of drinking water should reach the **drinking water quality standards**.

- **Wastewater disinfection**: After disinfection, microbiological indices should meet the **Drinking water microbiology indices** (*Standards for drinking water quality, GB5749-2006*)

The total number of colonies: 100 CFU/mL

“Discharge standards of pollutants for municipal wastewater treatment plant” (GB18918-2002)

Fecal coliform: No more than $10^3/\text{L}$ (I-A)

“The reuse of recycling water -Water quality standard for urban miscellaneous water consumption”

(GB/T18920-2002)

Total coliforms: No more than 3/L



3. Methods of disinfection

- Chlorine disinfection
- Chlorine dioxide disinfection
- Ozone disinfection
- UV disinfection
- Other disinfection methods
(Heating; non-oxidative chemical reagents; radiation, etc.)



4. Mechanisms of disinfection

The mechanism of disinfection is relatively complex, and it may involve the following aspects:

- Breaking the cell wall.
- Damage to the biochemical activity of cell membrane.
- Inhibition of essential metabolic functions and enzyme activity.
- Alteration of organism DNA or RNA.



Section 5.2

Factors of Disinfection

Contact time

Concentration of disinfectant

Temperature



1. Contact time

Given a constant concentration of disinfectant, the reduction rate of microorganism concentration is linearly correlated to the concentration of microorganisms

Chick's law

(1908)

$$\frac{dN_t}{dt} = -kN_t \xrightarrow{\text{Integration}} \frac{N_t}{N_0} = e^{-kt}$$

$$\ln \frac{N_t}{N_0} = -kt$$

(In usual logarithm)

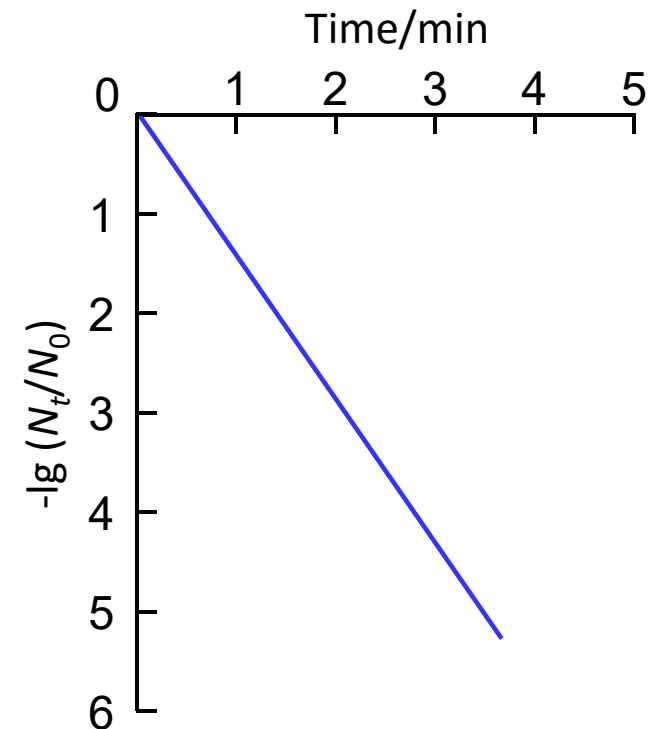
$$\lg \frac{N_t}{N_0} = -\frac{kt}{2.303}$$

(In natural logarithm)

N_t : Concentration of microorganism
at time t

k : Inactivation rate constant

t : Reaction time



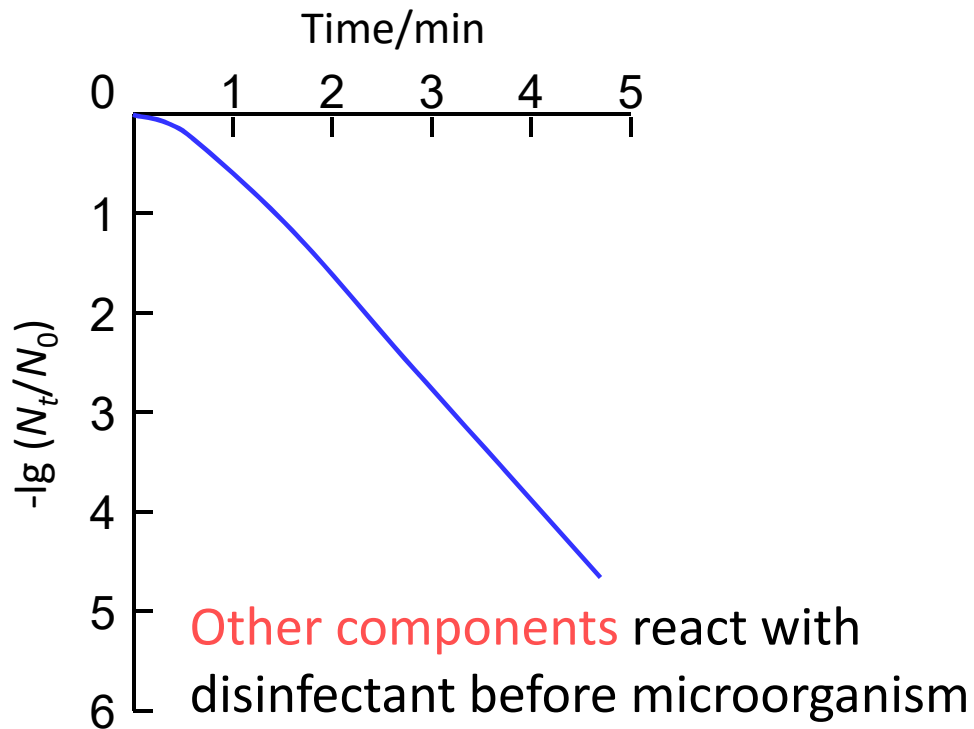
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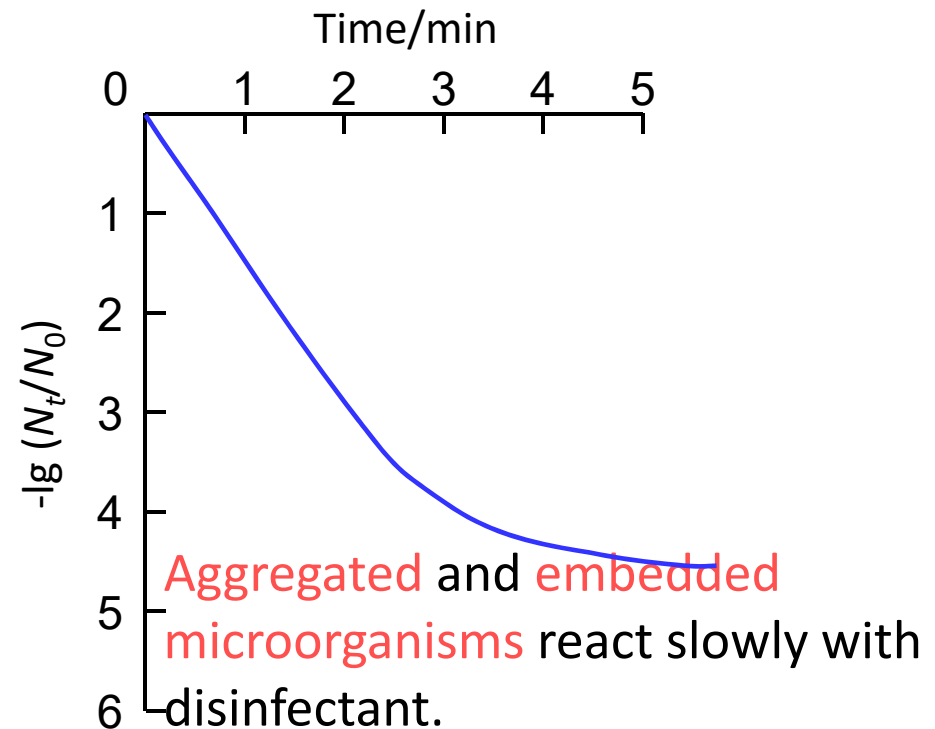
Physicochemical Technology

1. Contact time

Practical inactivation curve



Curve hysteresis



Curve smearing



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2. Concentration of disinfectant

Relation between inactivation rate constant and concentration of disinfectant:

$$k = k' C^n$$

k' : die-off constant
 C : disinfectant concentration
 n : dilution coefficient

$$\frac{dN_t}{dt} = -k N_t$$

Chick law

$$\frac{dN_t}{dt} = -k' C^n N_t$$

Chick-Watson law

Integration

$$\frac{N_t}{N_0} = e^{-k' C^n t}$$

Logarithm

$$\ln \frac{N_t}{N_0} = -k' C^n t$$

$$\lg \frac{N_t}{N_0} = -\frac{k' C^n t}{2.303}$$

For a certain inactivation level,
 $C^n t$ is a constant.

$$\lg C = -\frac{1}{n} \lg t + \frac{1}{n} \lg \left[\frac{2.303}{k'} \left(-\lg \frac{N_t}{N_0} \right) \right]$$

Logarithm

Given a **certain inactivation ratio**, on log-log plot,
 C is linear with t , and the slope is **n** .



2. Concentration of disinfectant

C^nT :



CT

- $n=1$ C and t are equally influential
- $n>1$ C is more influential
- $n<1$ t is more influential

C : Residual concentration of disinfection, mg/L

T : Contact time.

(t_{10} : contact time that 90% water in clean-water reservoir can achieve)

For certain inactivation ratio, " $C \cdot t$ " is a constant.

Normally n is assumed as 1.

- Index of the performance of disinfectant.
- Changes with disinfectants, microorganisms, temperature, pH, et al.
(For a certain inactivation requirement)
- The smaller CT is, the better the disinfectant is.
(For a certain inactivation requirement under same conditions)



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2. Concentration of disinfectant

CT values for 99.9% inactivation of Giardia

Temperature	5°C	10°C	20°C
2 mg/L free chlorine (pH=7)	165	124	62
Chlorine dioxide	26	23	15
Ozone	1.9	1.4	0.72
Chloramines	2200	1850	1100

CT:

Ozone < Chlorine dioxide < Free chlorine < Chloramines

Disinfection ability:

Ozone > Chlorine dioxide > Free chlorine > Chloramines



2. Concentration of disinfectant

Contact time t_{10}

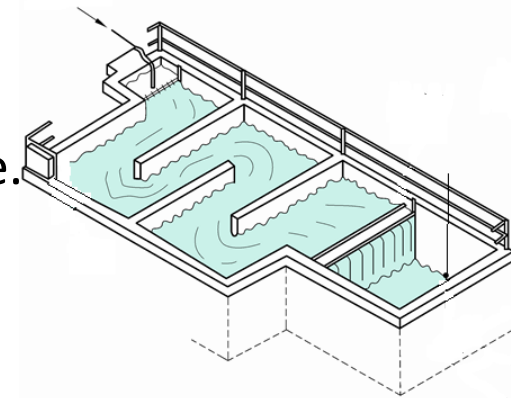
Clean-water reservoir in water plant is usually used to meet the requirement of contact time after the disinfectant is dosed

Flow isn't ideal plug flow.

Part of the water has less retention time than the average.

Design of clear-water reservoir should ensure 90% water in it meet the required retention/contact time.

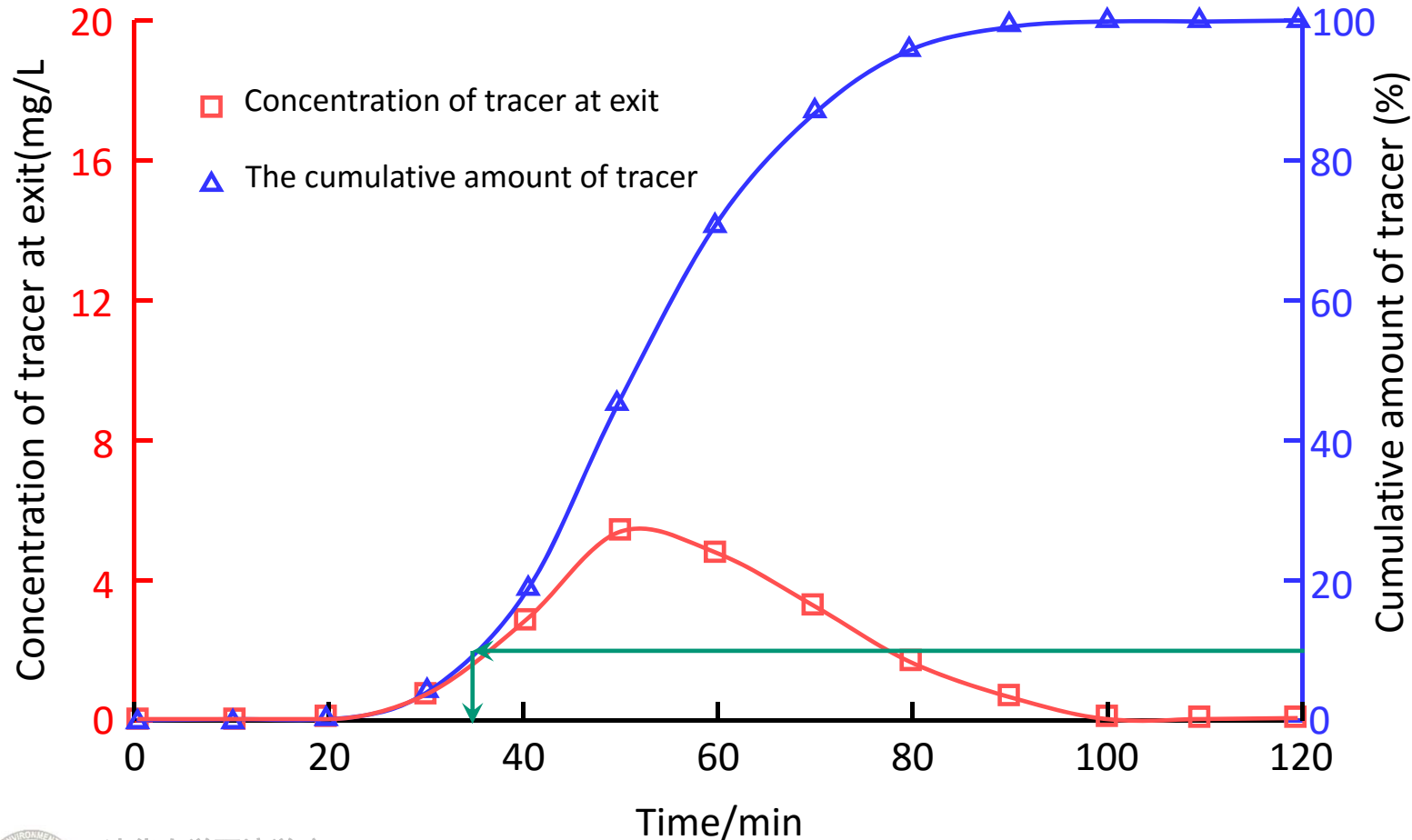
The t_{10} should be used in verification of CT value



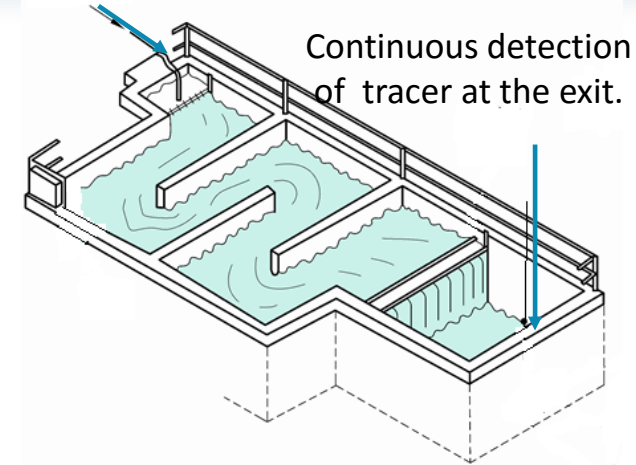
Over 90% of the water can meet the CT requirement



2. Concentration of disinfectant



Dose Tracer when $t=0$



Contact time t_{10}

$$t_{10} = \beta T = \beta \frac{V}{Q}$$

t_{10} : contact time that 90% water in clean-water reservoir can achieve.

β : Effective coefficient.

Good plug flow: 0.65-0.85

T : theoretical retention time of clean-water reservoir's

V : Volume of clear-water reservoir



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2. Concentration of disinfectant

Improve the plug flow in clear-water reservoir.

$$t_{10} = \beta T = \beta \frac{V}{Q}$$

- Add baffles, reduce short flow
- ⇒ Increase β
- ⇒ Get higher CT value

Relation between CT and logarithmic removal of microorganisms

$$CT = -\frac{2.303}{k'} \lg \frac{N_t}{N_0}$$

For a certain species of microorganism:

$$\frac{CT_2}{CT_1} = \frac{\lg \left(\frac{N_t}{N_0} \right)_2}{\lg \left(\frac{N_t}{N_0} \right)_1}$$

- Increasing CT value:
 - ⇒ Higher microorganism's logarithmic removal.
 - ⇒ Higher microorganism's concentration removal.



3. Temperature

$$\lg \frac{k_2}{k_1} = \frac{E}{2.303R} \times \frac{(T_2 - T_1)}{T_1 \cdot T_2}$$

Arrhenius' formula

K_1, K_2 : Inactivation rate constants under temperature T_1, T_2

R : Universal gas constant, 8.314 J/(mol K).

E : Activation energy, J/mol.

Generally:

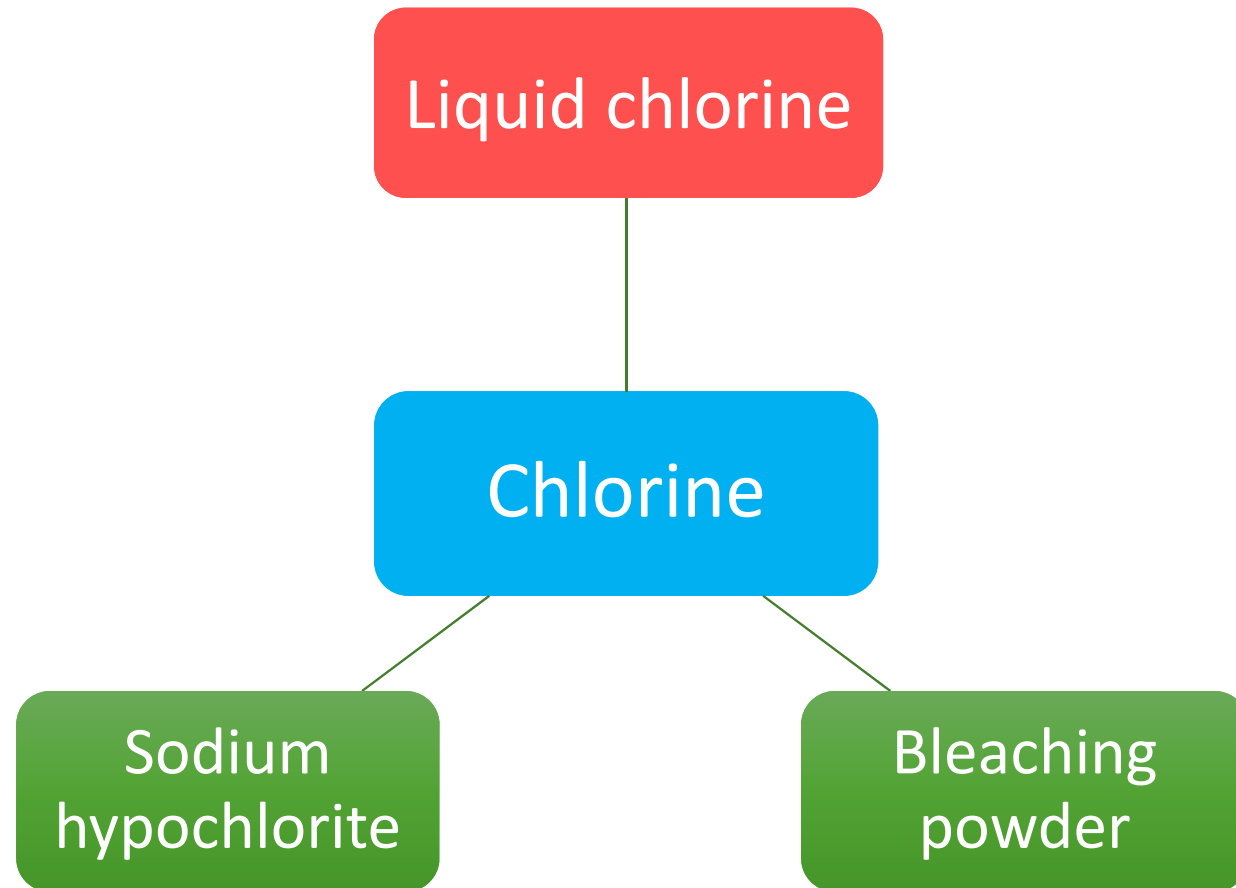
Temperature $\uparrow \rightarrow$ Disinfection rate constant $\uparrow \rightarrow$ Disinfection performance $\uparrow$



Section 5.3

Disinfection with Chlorine





1. Reactions in disinfection with chlorine

(1) Free chlorine

Chlorine is soluble in water, the following reaction occurs instantly in water:



Hypochlorous acid will further dissociate:



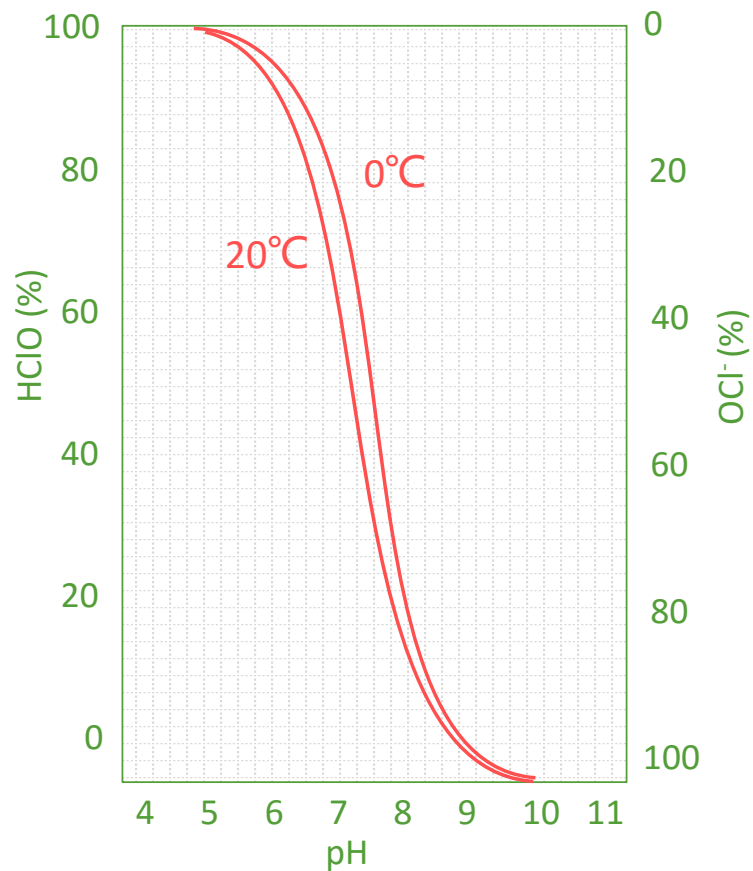
Dissociation equilibrium constant:

$$K_i = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HClO}]}$$

➡ Temperature depended



1. Reactions in disinfection with chlorine



HClO, OCl⁻ fractions are related to **temperature and pH**.

At 20 °C:

pH>9, mostly OCl⁻

pH<6, mostly HClO

pH=7.5, HClO and OCl⁻ each takes 50%



1. Reactions in disinfection with chlorine

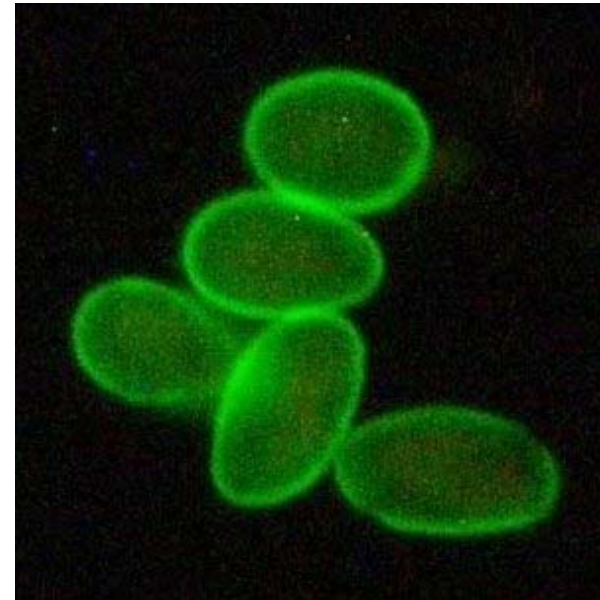
- Disinfection with chlorine is the process of **oxidation**;
- Both **HClO** and **OCI⁻** have oxidation and disinfection capabilities.
- HClO, which is a **neutral molecule**, can easily spread to the bacterium's surface and penetrate into it. Thus it has a strong disinfection capability.
- Under low pH values, HClO takes large proportion, which is good for disinfection;
- When HClO is consumed, OCI⁻ will transfer into HClO, due to the chemical equilibrium between HClO and OCI⁻, and the disinfection continues.
- Both OCI⁻ and HClO are counted in the calculation of disinfectant amount and existing forms. They are called **free available chlorine**, or **free Chlorine** for short.



The chlorine can't effectively inactivate Protozoan cysts/ oocytes.
(1993, US, over 400,000 person infected)



Giardia lamblia
(8-12 μm X 7-10 μm)



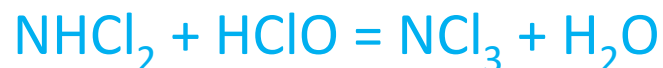
Cryptosporidium oocysts
(4-6 μm)



1. Reactions in disinfection with chlorine

(2) Combined chlorine

If ammonia is present in natural water, chlorine reacts with ammonia and produces chloramines.



The proportions of chloramine species depend on the ratio of chlorine and ammonia, as well as pH:

$\text{Cl}/\text{NH}_3 \leq 5:1$, pH 7-9: Basically mono-chloramine.

$\text{Cl}/\text{NH}_3 \leq 5:1$, pH 6: mono-chloramine $\approx 80\%$.

pH < 4.5: Tri-chloramine exists.



1. Reactions in disinfection with chlorine

(2) Combined chlorine

- Chloramines are oxidative, and have disinfection ability.
- Less oxidation capability than free chlorine.
- Disinfection mechanisms:
 - Direct reaction with microorganism;
 - Disinfection by **free chlorine** through chemical equilibrium with HClO
- Chloramines are called **combined available chlorine**.



2. Dosage of chlorine

Chlorine dosage = Chlorine demand + Residual chlorine



2. Dosage of chlorine

$$\text{Chlorine dosage} = \text{Chlorine demand} + \text{Residual chlorine}$$

Chlorine demand

Within the designed contact time, the **chlorine consumption** for killing the microorganisms and oxidation of organic matter and reductive substances.

Residual chlorine

After the designed contact time, the **remaining chlorine** in water.



2. Dosage of chlorine

Free chlorine disinfection:

Contact time $\rightarrow \geq 30$ min;

Residual chlorine $\rightarrow$ free chlorine ≥ 0.3 mg/L in effluent,
 ≥ 0.05 mg/L in the water at the end of pipelines.

Chloramine disinfection:

Contact time $\rightarrow \geq 2$ h;

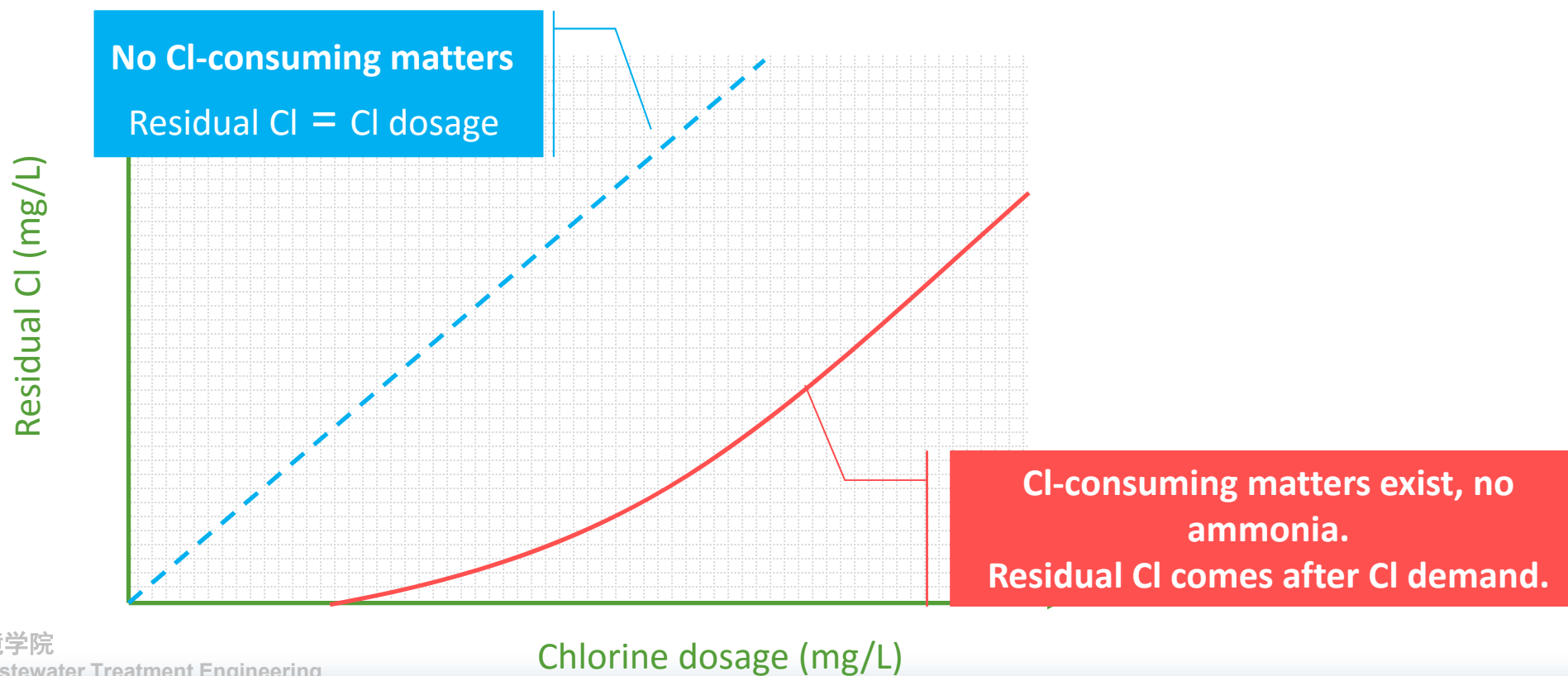
Residual chlorine $\rightarrow$ total chlorine ≥ 0.5 mg/L in effluent,
 ≥ 0.05 mg/L in the water at the end of pipelines.



2. Dosage of chlorine

The chlorine dosage could be obtained through experiment or experience.

Chlorine dosage curve—Relationship curve between chlorine dosage and residual chlorine.



No residual chlorine

Cl + Ammonia
→ chloramines

Chloramines dissociate
Residual Cl decreases

Additional Cl exists
as free chlorine

Residual Cl (mg/L)

Section
1

Section
2

Section
3

Section
4



H (peak)

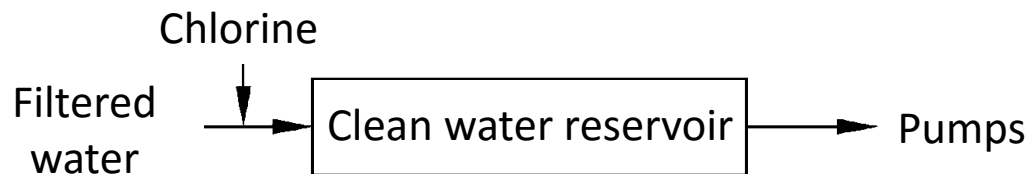
B (breakpoint)

Cl dosage (mg/L)



3. Chlorine disinfection in practice

(1) Disinfection with free chlorine

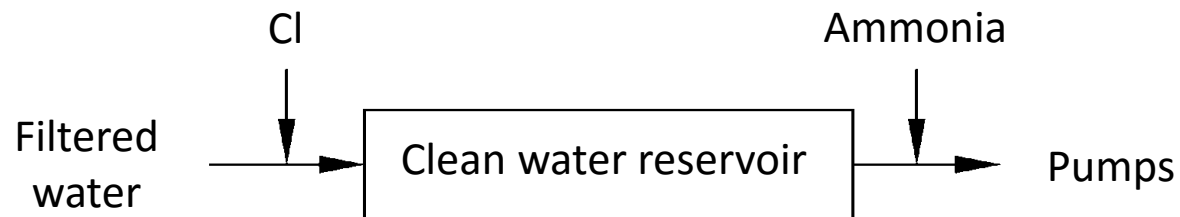


- **Breakpoint chlorination** is usually applied for water with low ammonia concentration (<0.2 mg/L);
- Good disinfection, can remove some **odor** and **organic matter**;
- Water has heavy chlorine smell; when treating polluted water, toxic byproducts would be formed, like **trihalomethanes**, **haloacetic acids**, which are mutagenic, carcinogenic and teratogenic.



3. Chlorine disinfection in practice

(2) Cl-before and ammonia-after chlorine disinfection

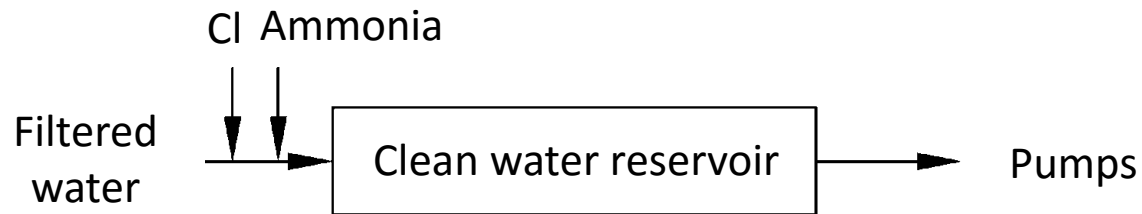


- Effluent by breakpoint chlorination has **strong chlorine smell**, and free chlorine has limited existing time in the pipelines due to its fast decomposition.
- Cl is firstly dosed according to break point chlorination. Then ammonia is dosed at the **secondary pump station** before water **is pumped out**.
- Free Cl turns into residual combined Cl, with less odor and longer residential time.
- $\text{Cl}:\text{NH}_3 = 3:1 \sim 6:1$



3. Chlorine disinfection in practice

(3) Chloramine disinfection

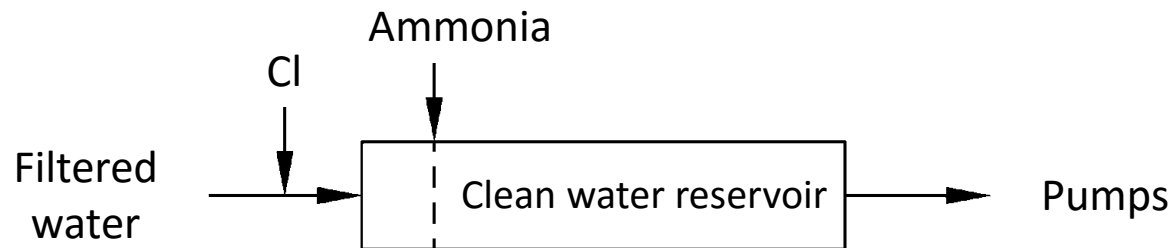


- Less disinfection efficacy than free chlorine;
- Stable, long existing time, little scent of chlorine and chlorophenol;
- Less health-threatening byproducts like trihalomethanes, haloacetic acids, etc.;
- Low disinfection rate, long contact time (≥ 2 h);
- For filtered water with high ammonia concentration:
combined chlorine disinfection (section 2 on the curve);
- For filtered water with low ammonia concentration:
dose both chlorine and ammonia.



3. Chlorine disinfection in practice

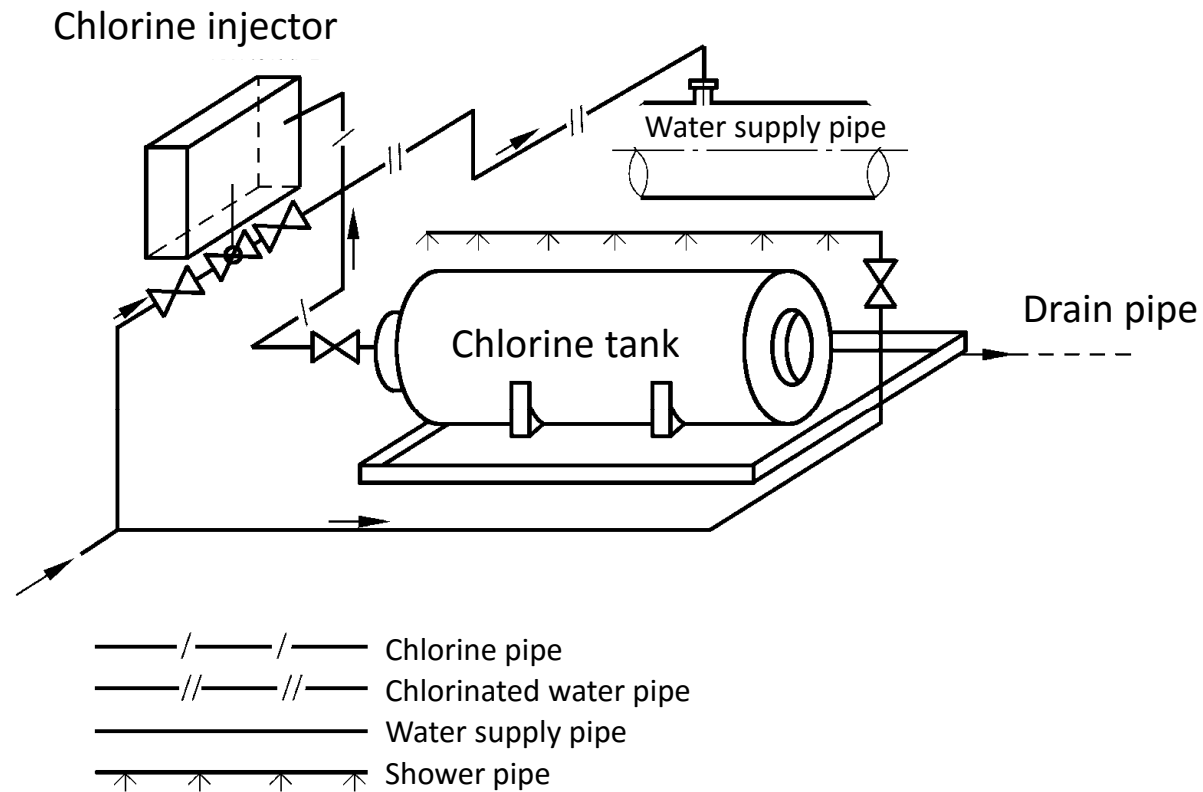
(4) Short free chlorine-before & chloramines-after disinfection



- Dose chlorine at **the inlet of clean water reservoir**, contact for 10-15 min, to achieve short time **free chlorine disinfection**;
- Then dose ammonia, with the retention time of water in clean water reservoir $\geq 2\text{h}$, to achieve the **chloramines disinfection**;
- $\text{Cl}:\text{NH}_3$ usually is 4:1
- Owning characters of both free chlorine and chloramines, control both **microorganism** and **disinfection byproducts**.



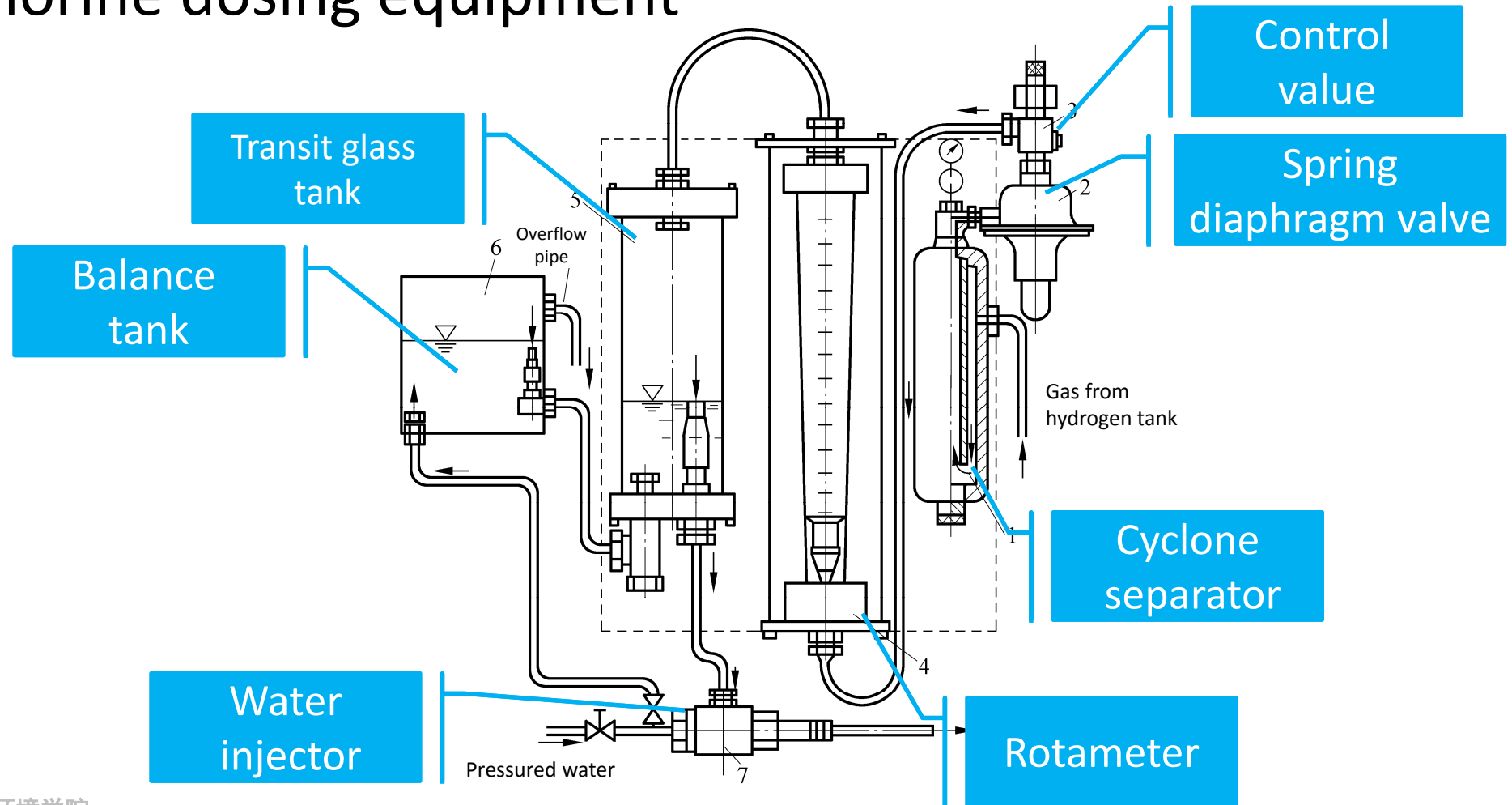
4. Chlorine dosing equipment



Equipment of disinfection by liquid chlorine



4. Chlorine dosing equipment



Rota-chlorine dosing equipment



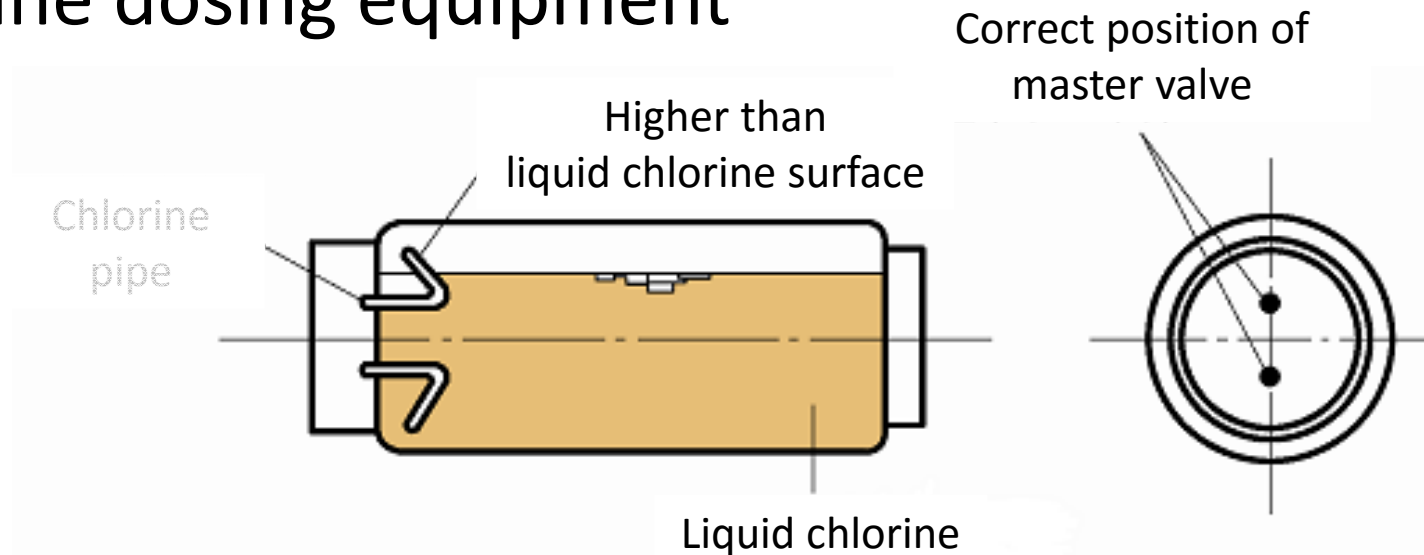
4. Chlorine dosing equipment



Liquid chlorine tank: Dry chlorine gas and liquid chlorine have no damage to the steel tanks, but once they get wet, chlorine will severely corrode the metal.



4. Chlorine dosing equipment



- Chlorine gas turns to liquid chlorine under 6~8 atm. The tank should be 80% full and lay down steadily;
- The evaporation of liquid chlorine is endothermic, so extra heat should be supplied;
- Usually 15-25 °C water is showered on the chlorine tank as a heat supply.



Section 5.4

Disinfection with Chlorine Dioxide



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1. Characters of chlorine dioxide

- ClO_2 is a **yellowish-green** gas with acrid odor under room temperature.
- Extremely unstable, both gas and liquid chlorine dioxide are explosive. Thus it should be prepared on site and used as aqueous solution.
- Soluble in water with a solubility 5 times of the chlorine's; and It exists in water as dissolved gas, without any hydrolysis.



2. Characters of disinfection with chlorine dioxide

- Very effective disinfectant, has good inactivation on bacteria and viruses.
in pH 6-9, its disinfection efficiency is weaker than ozone, but better than free chlorine.
- Disinfection is not affected by pH, and does not react with ammonia.
- Stability in water is worse than chloramines, but better than free chlorine.
- No formation of disinfection byproducts such as trihalomethanes.
- However, chlorine dioxide disinfection costs more than chlorine one.



3. Preparation of chlorine dioxide

(1) Sodium chlorite-acid method:

- $5\text{NaClO}_2 + 4\text{HCl} = 4\text{ClO}_2 + 5\text{NaCl} + 2\text{H}_2\text{O}$
- $5\text{NaClO}_2 + 2\text{H}_2\text{SO}_4 = 4\text{ClO}_2 + 2\text{Na}_2\text{SO}_4 + \text{NaCl} + 2\text{H}_2\text{O}$



3. Preparation of chlorine dioxide

(2) Sodium chlorite-hypochlorite method:

- $\text{Cl}_2 + \text{H}_2\text{O} = \text{HClO} + \text{HCl}$
- $2\text{NaClO}_2 + \text{HClO} + \text{HCl} = 2 \text{ClO}_2 + 2\text{NaCl} + \text{H}_2\text{O}$



3. Preparation of chlorine dioxide

(3) Sodium chlorate-hydrochloric acid method



(4) Electrolysis method

- From sodium hypochlorite generator.
- By electrolysis of sodium chlorate solution, the solution containing ClO_2 (10%-20%) and NaClO (dominant) would be obtained on site.



4. Dosage of chlorine dioxide

- Disinfection in water treatment
 - Dosage between 0.2 to 0.5 mg/L
 - Contact time: no less than 30 min
 - Residual $\text{ClO}_2 \geq 0.1 \text{ mg/L}$ in effluent; $\geq 0.02 \text{ mg/L}$ at the end of pipelines.
- Disinfection in wastewater treatment
 - Secondary effluent, dosage between 6-15 mg/L



5. Disinfection byproducts

- The intermediate product is chlorite (ClO_2^-), which is harmful to human health.
- “*Standards for drinking water quality*” rules that the highest permit concentrations of chlorite and chlorate are both 0.7 mg/L.



Section 5.5

Disinfection with Ultraviolet Light



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1. Characters of ultraviolet

Ultraviolet (UV) is invisible light with wavelength of 100-400nm.

Band A: long-wave ultraviolet
UV-A, 320~400 nm

It produces melanin or a “tan” in human skin; but has poor disinfection ability.

Band B: middle-wave ultraviolet
UV-B, 275~320 nm

Has disinfection ability

Band C: short-wave ultraviolet
UV-C, 200~275 nm

Band D: vacuum ultraviolet
UV-D, 100~200 nm

It can generate ozone in air

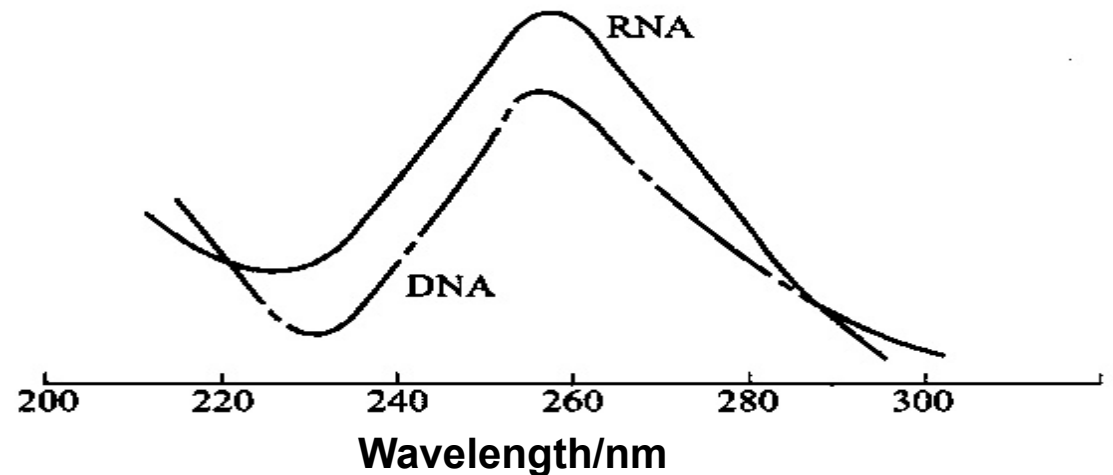


2. Mechanism of disinfection with ultraviolet light

UV with wavelength of 240~280 nm has a strong disinfection ability.

Ultraviolet of 250 ~ 260 nm can be absorbed by DNA and RNA. Other structure of protein, such as phenylalanine, tryptophan, tyrosine aromatic ring have the absorption peak at around 280 nm.

UV can alter and damage the structure of DNA or RNA, change the nucleic acid structure, and make the organisms lose the ability of reproduction, and thus achieve the inactivation of organisms.



3. Equipment for disinfection with ultraviolet light

Artificial UV light is usually applied in water disinfection.

Main types of UV light :

Low pressure low intensity UV lamp

Low pressure high intensity UV lamp

Medium pressure high intensity UV lamp

Most widely used



3. Equipment for disinfection with ultraviolet light

Tubular disinfection equipment and canal disinfection equipment



Tubular disinfection equipment
(Mostly in water disinfection)



Canal
disinfection equipment
(Mostly in wastewater disinfection)

Multiple UV lights are set inside either equipment.
Disinfection is finished within seconds as water flows
across the UV lights.

4. Dosage of ultraviolet light

$$D = It$$

D : Dosage of UV, mJ/cm^2

I : Intensity, mW/cm^2

T : Irradiation time, s

- Inactivation performance is related to the dosage of UV.
- Similar to chemical disinfection's CT values.

Under the same condition, once the dosage of UV is the same, the disinfection result is the same as well.



4. Dosage of ultraviolet light

UV disinfection for drinking water:

Mandatory minimum dosage of UV disinfection:

45mJ/cm² (Australia) , 40mJ/cm² (USA)

In China: 40 mJ/cm²

UV disinfection for wastewater :

“Code for design of outdoor wastewater engineering” in China rules the UV dosage should be determined based on reference practical experiences or experiment data.

Reference number: Secondary effluent: 15-22 mJ/cm²

Reclaimed water: 24-30 mJ/cm²

UV disinfection technology for large-scale applications in water treatment began in the late 1990s.

