Chlorination

WAT-E2120 Physical and Chemical Treatment of Water and Waste

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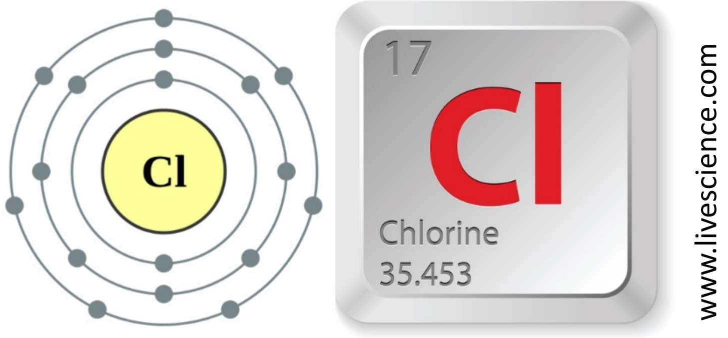
Pre-reading assignment

- AWWA Staff, 2006. Water Chlorination/Chloramination Practices and Principles. AWWA Manual Series M20. American Water Works Assoc. 2nd ed. eBook ISBN 9781613000267
  - Pages 19-29

Contents

- Mechanisms of chlorination
- Disinfection kinetics
- Chemistry of chlorine



Uses of chlorination

- Disinfection of drinking water at treatment plants (primary disinfection)
- Secondary disinfection in distribution networks
- Treated wastewater chlorination
- Shock chlorination of contaminated:
  - Distribution networks
  - Storage tanks
  - Private wells...
- Swimming pools
- Domestic cleaning

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Chlorination chemicals

- Chlorine gas
- Chlorine dioxide
- Hypochlorites
  - Sodium hypochlorite ($NaOCl$)
  - Calcium hypochlorite ($Ca(OCl)_2$
- Chloramine
  - Hypochlorite + ammonium = NH_2Cl (monochloramine)

Chlorine reactions in water

Chlorine gas hydrolyzation reaction results as hypochlorous acid:

$$\underset{\text{Chlorine Gas}}{Cl_2 + H_2O} \leftrightarrow \underset{\text{Hypochlorous Acid}}{HOCl + H^+} + Cl^-$$

Hypochlorous acid dissociates to hypochlorite ion according to pH:

$$\underset{\text{Hypochlorous Acid}}{HOCl} \leftrightarrow H^+ + \underset{\text{Hypochlorite Ion}}{OCl^-}$$

Both hypochlorous acid and hypochlorite are regarded as free chlorine, though hypochlorous acid is more effective disinfectant. In fact, it is the most effective chlorine form.

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]}$$

pKa = 7,6, 20 °C
Means that below this pH hypochlorous acid is the predominant form.

pH and hypochlorate/hypochloric acid ratio

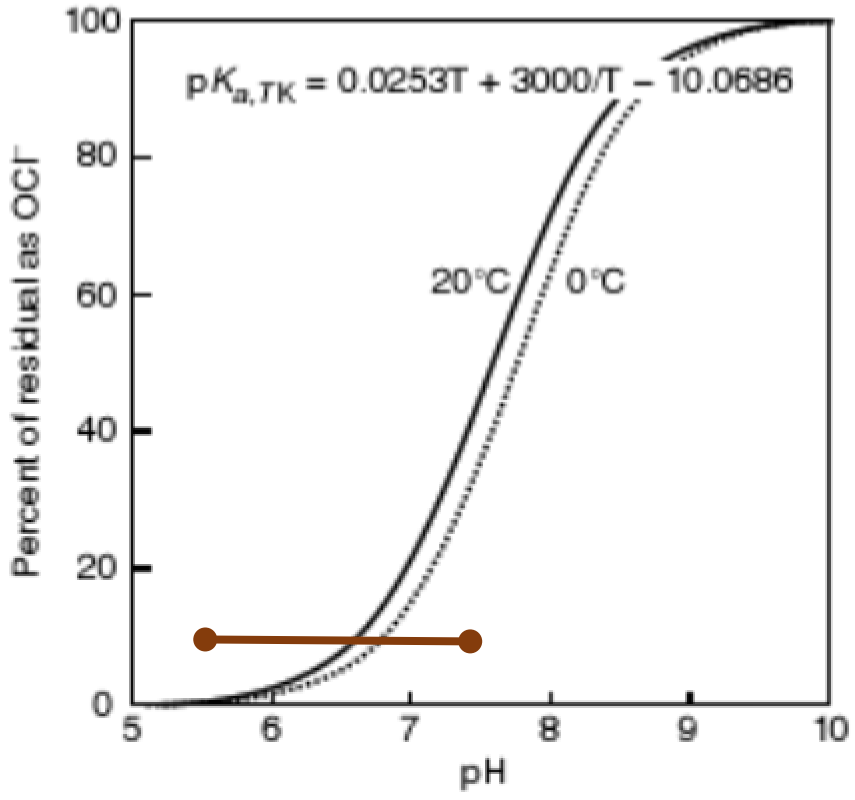


Figure 13-9
Effect of temperature and pH on fraction of free chlorine present as hypochlorous acid. (Adapted from Morris, 1966.)

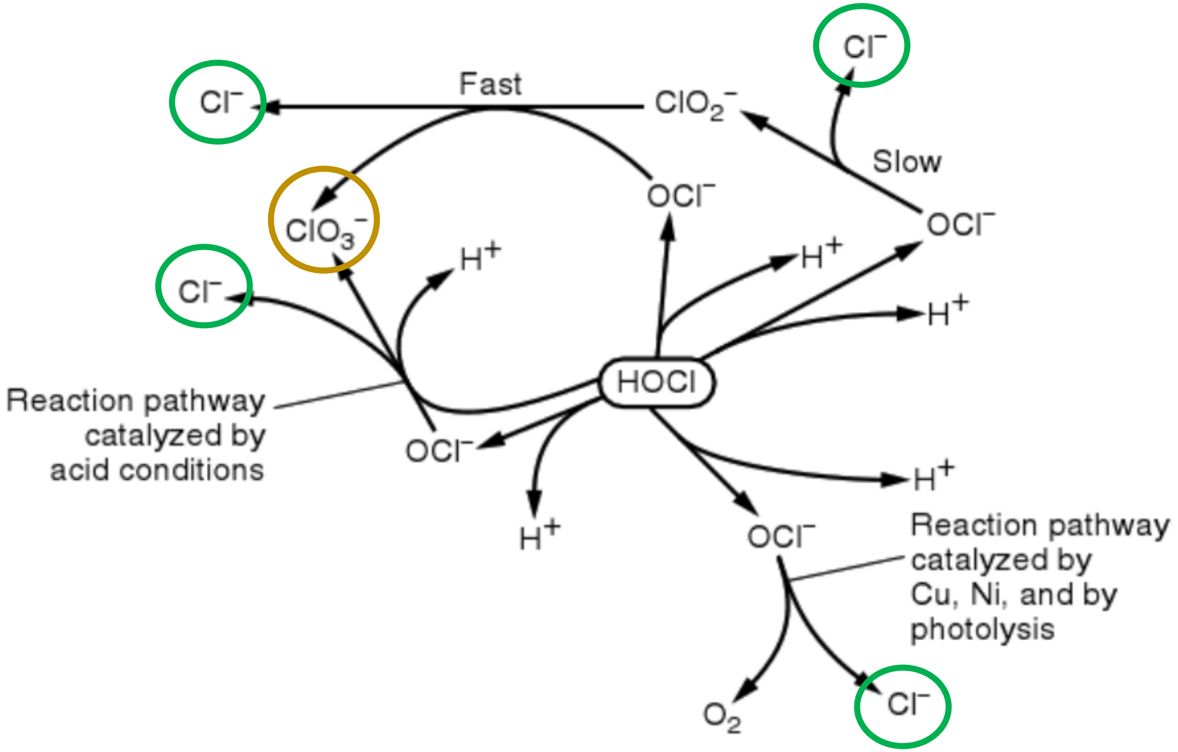
Calculated similarly as the example with NH_3/NH_4^+ on the second lecture

Chlorination is most effective in pH 5.5-7.5

Hypochlorite chlorination practices

- Liquid solution
  - Typical concentration 10 or 15% as Cl_2
  - Storage time in a cooled tank should not exceed 3- 5 months
- Typical feed 0.5 –1.0 g/m^3
  - Added dose of solution 0.5 –1 l/100 m^3
- If needed, the solution is diluted for dosing
- Chemical tanks need safety basins

Hypochlorite solution decay reactions



Decay is modeled with second order kinetics

$$\frac{C}{C_0} = \frac{1}{1 - k_d C_0 t}$$

C = bleach concentration after time t, mol/L

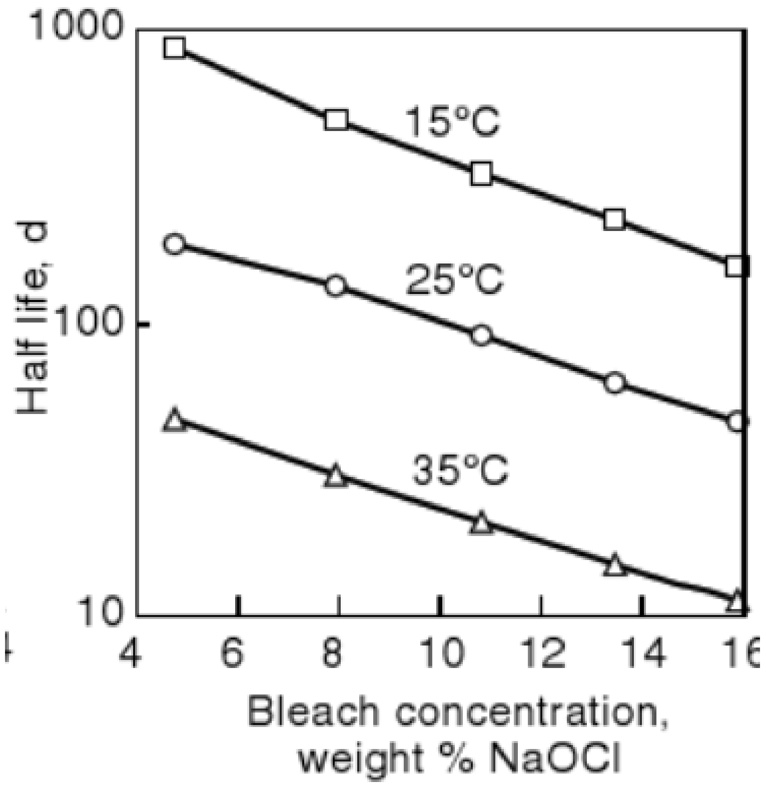
C_0 = bleach concentration at time 0, mol/L

k_d = second-order decay coefficient, L/mol · s

t = time, s

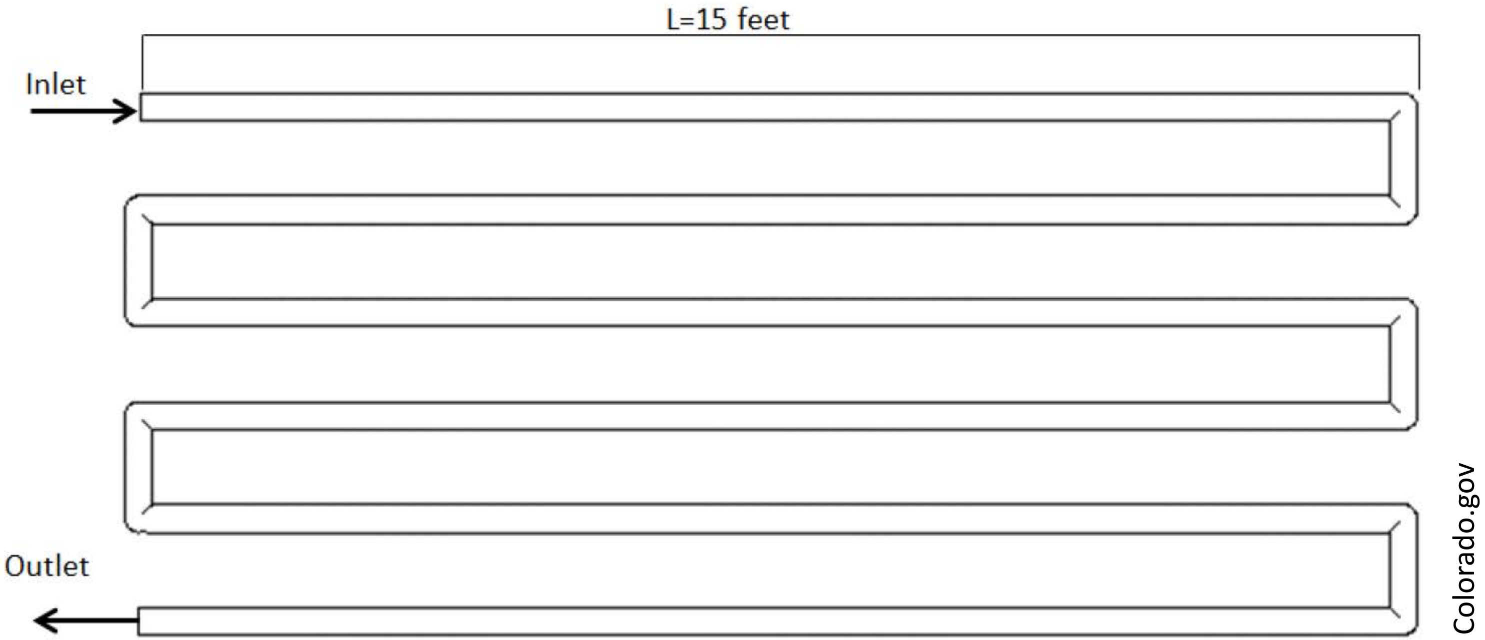
Hypochlorite solution decay

- Half-life of hypochlorite solution in storage depends on temperature
- Has to be taken into account in designing storage tanks and dosing.



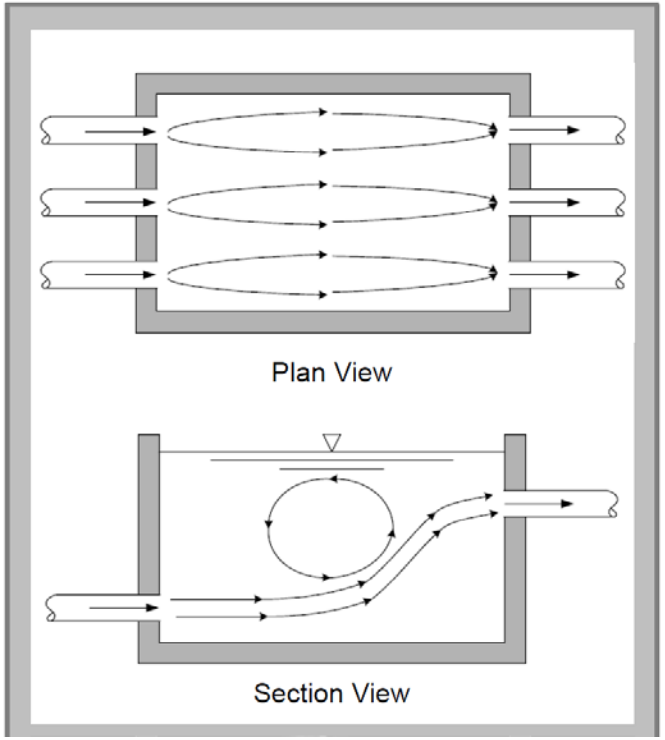
Chlorine contact chambers

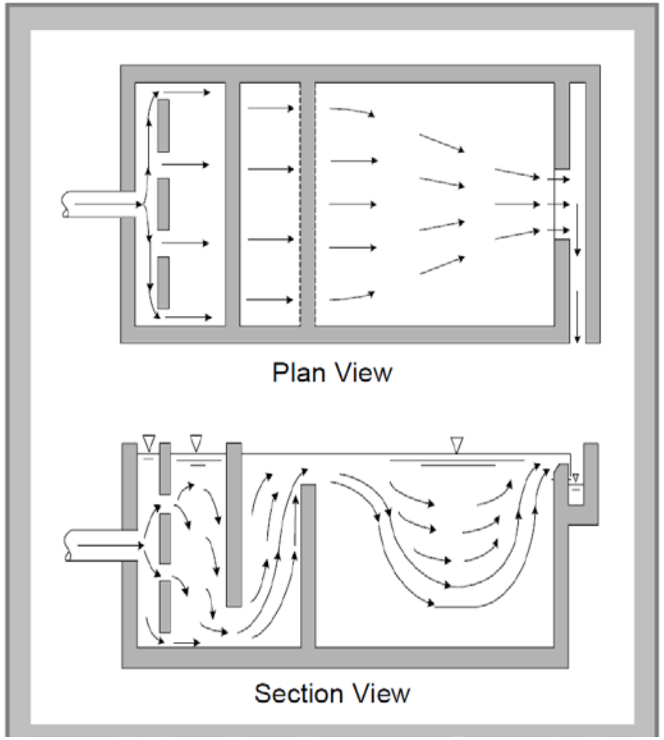
- It's important thet the whole volume of water in contacted with the disinfectant
- Pipe loop contactor
- Plug flow reactor

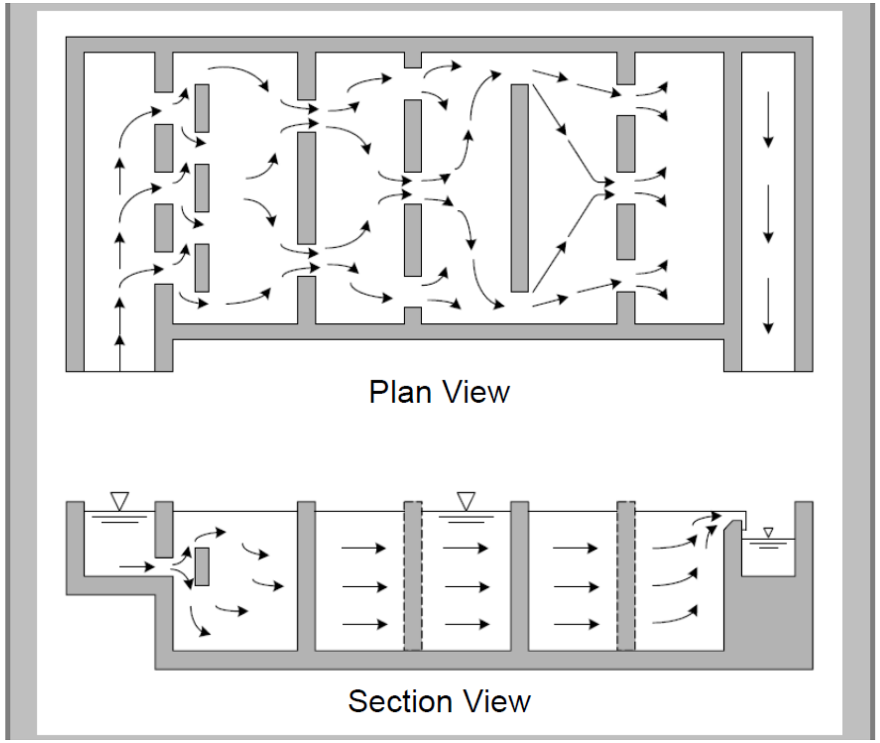


Baffled contact chambers

Properly placed baffles in the chlorien contact chambers prevent <u>short circuits</u> and <u>dead spaces</u>
Baffles are walls with openings



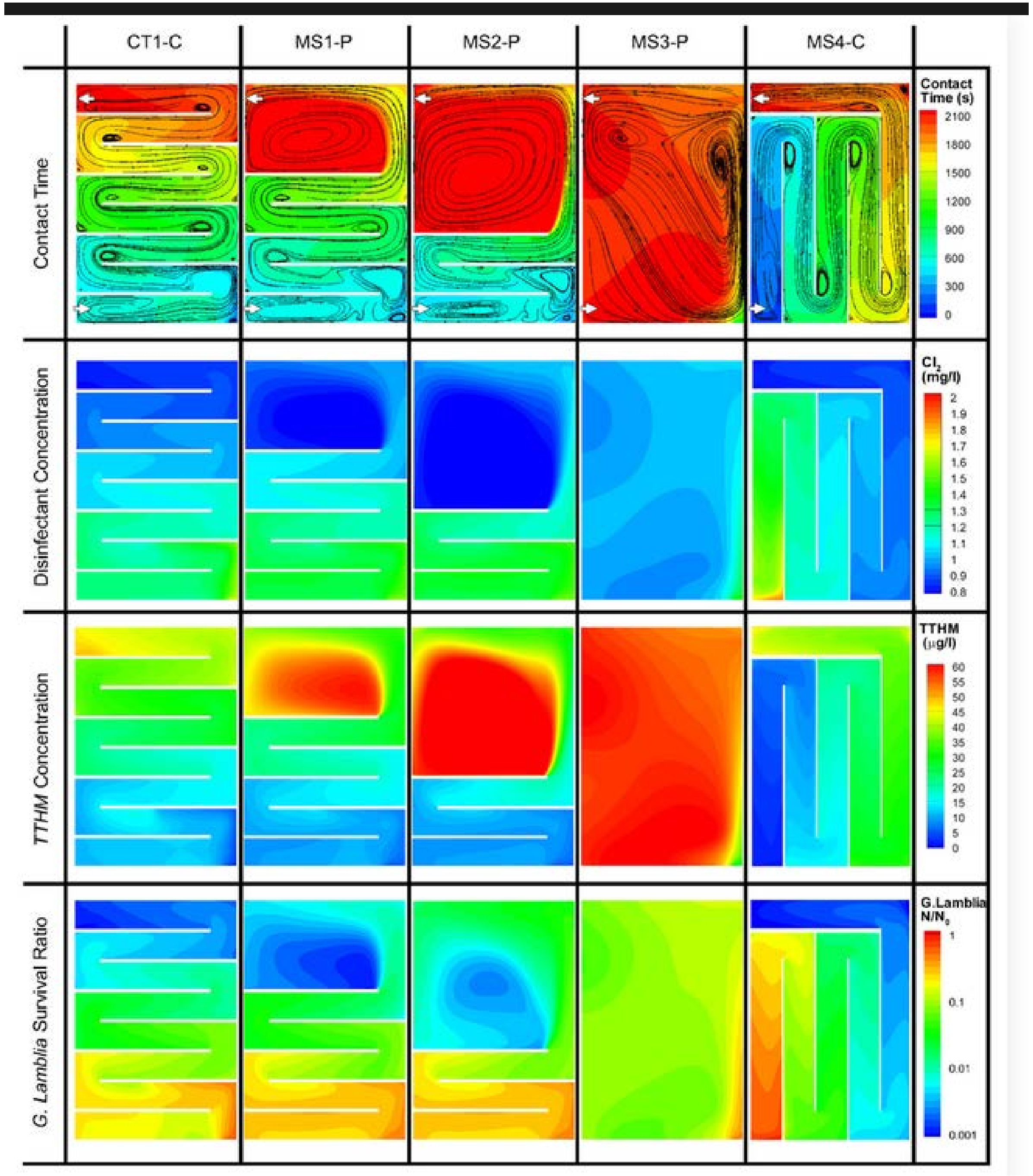




Poor baffling

Average baffling

Good baffling



https://www.researchgate.net/publication/262386893

CFD modeling of baffled basins

Modeling of flow conditions, contact time profiles and concentration profiles of disinfectant, disinfection by-products, and surviving pathogens in different types of baffled contact chambers

Controlling chlorine feed

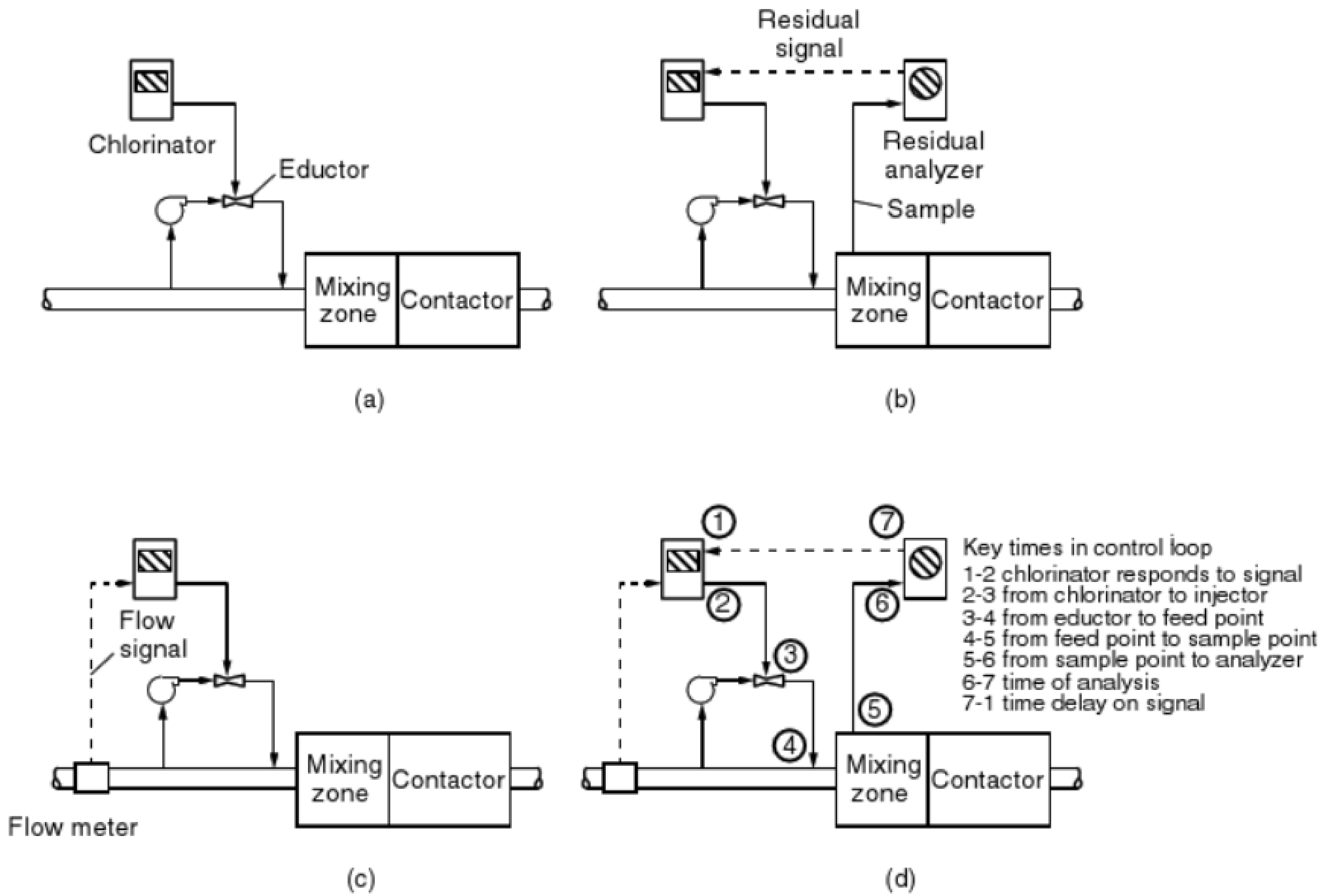
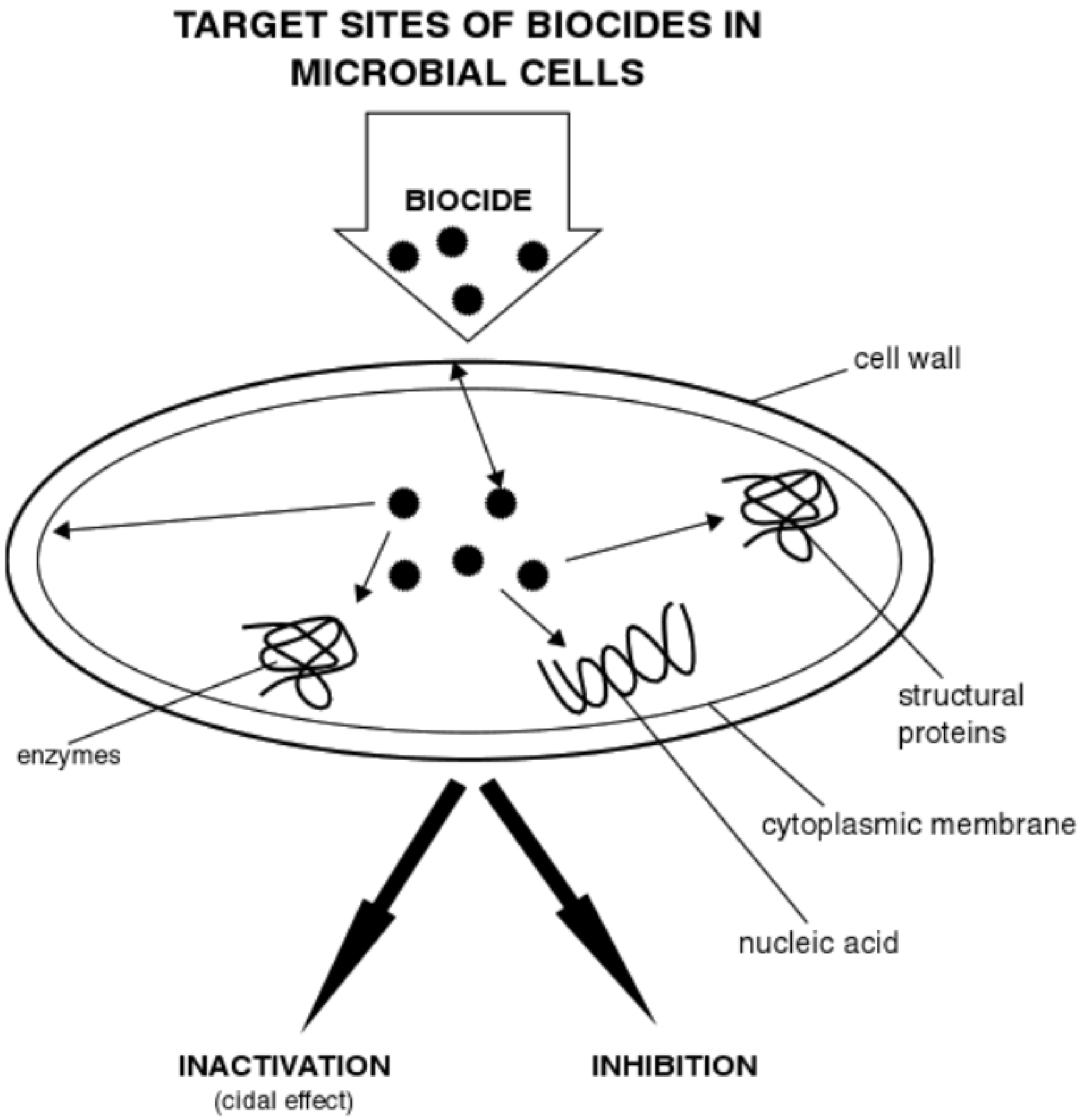


Figure 13-13
Control of chlorine gas feed rate: (a) manual control, (b) feedback or residual control, (c) feed forward control, and (d) compound loop control.

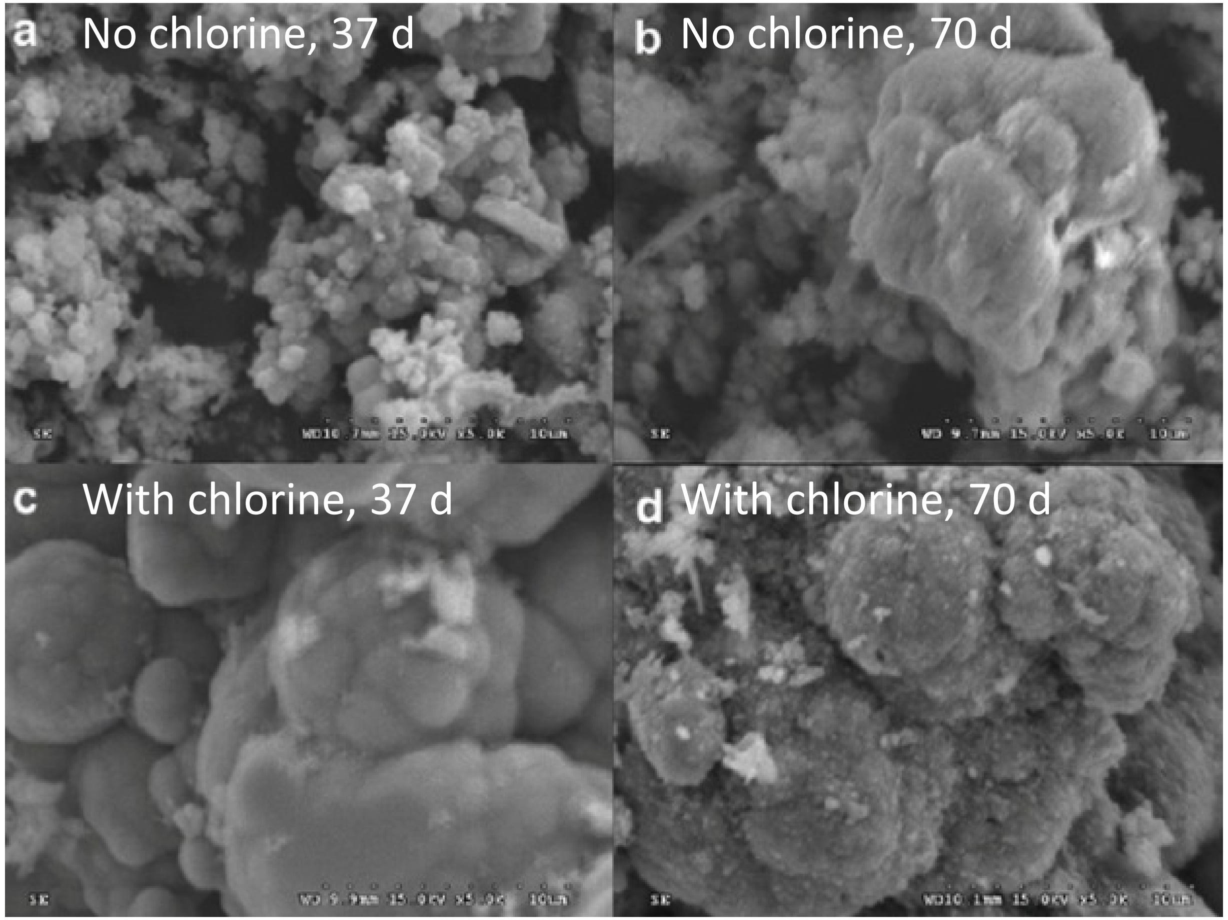
Disinfection mechanisms

- Disrupting cell permeability lead to cell death
  - Leakage of proteins, RNA, DNA
  - Decrease in potassium uptake and in protein and DNA synthesis
- Damage to nucleic acids and enzymes
- Repression of gene transcription
  - E.g. in staphylococcus aureus hypochlorous acid repressed genes controlling cell wall synthesis, protein synthesis, membrane transport and primary metabolism
- Other mechanisms



Target sites of biocides in microbial cells. Adapted from Russel et al. (1997). Amer. Soc. Microbiol. News 63: 481–487.

Biofilm growth with chlorine and without



- A biofilm protects the bacteria against chlorine.
- Notice the extra-cellular polymeric substance (EPS) in pictures c and d. Apparently bacteria have grown more EPS with chlorine.

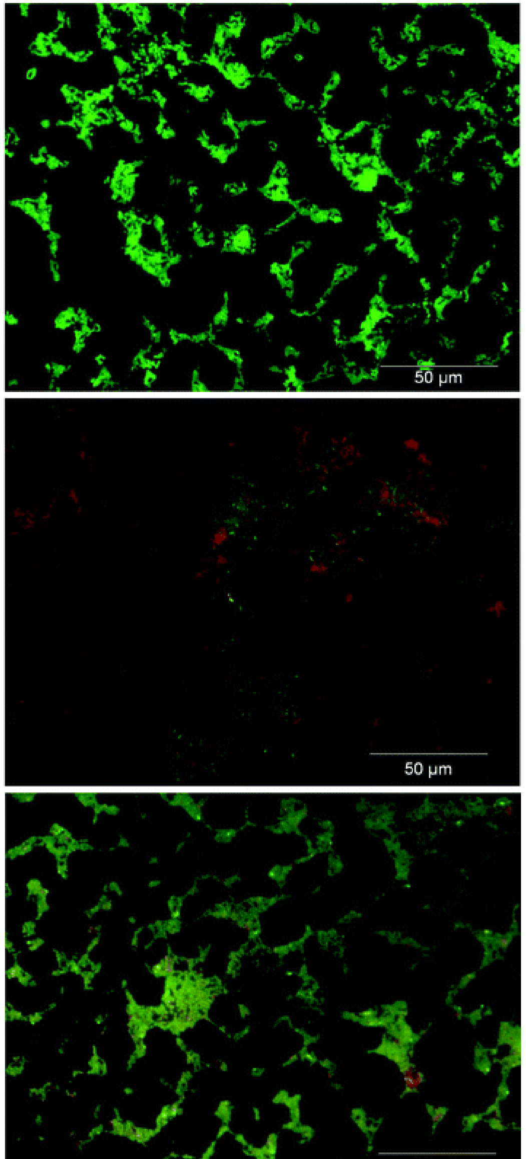
Scanning electron microscopy (SEM) micrographs of the biofilm formed on cast iron coupons

Bacteria can stay viable after chlorination

a

b

c



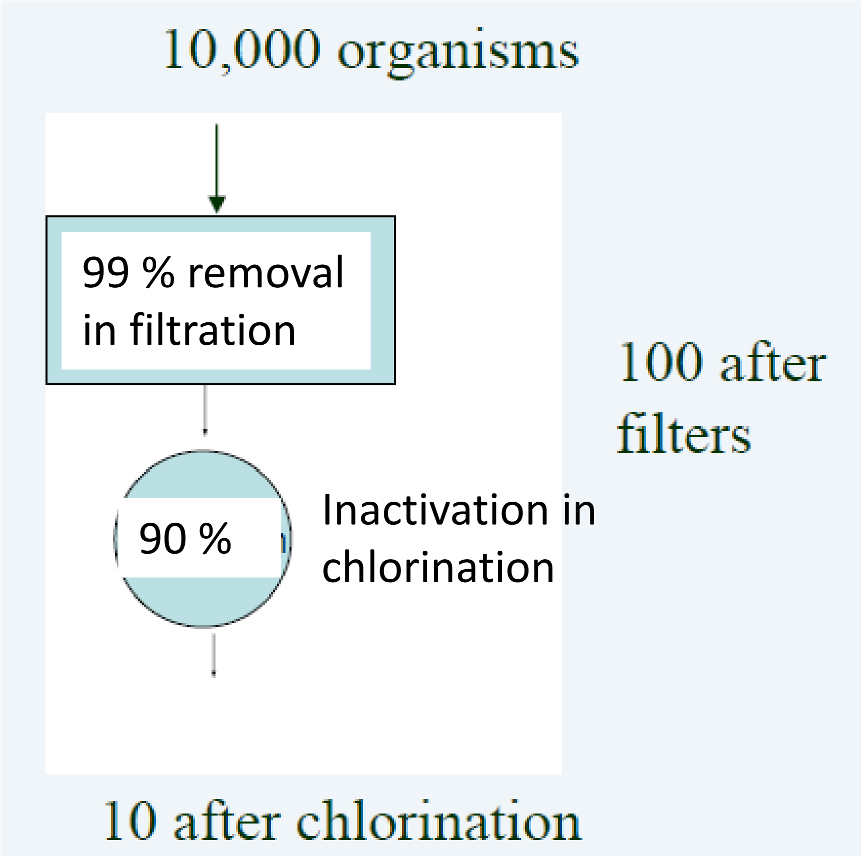
- Effects of chlorine disinfection on the viability of drinking water multispecies biofilms and their ability to recover after treatment
- The epifluorescence photomicrographs show the biofilms (a) before treatment with 10 mg l^{-1} sodium hypochlorite; (b) immediately after and (c) 24 h later
  - Magnification, ×400; bar = 50 µm
  - Viable cells are green and non-viable cells are red
  - The drinking water biofilm was composed of A. calcoaceticus, B. cepacia, Methylobacterium spp., M. mucogenicum, S. capsulata and Staphylococcus spp.

Log removal

"x" LOG	% Removal
0.5	68
1	90
2	99
3	99.9
4	99.99

Roughly: "Number of nines in the reduction percentage"

- Log-reductions can be summed with sequencing process units
- Example:
- 2-log removal of pathogens in filtration AND
- 1-log inactivation of pathogens in chlorination
- Results as 3-log total reduction (99.9 %)



Ct

- Ct = chlorine concentration as mg/l multiplied by inactivation time as minutes
  - 2-log removal efficiency
  - Sometimes expressed without units (=> extra carefulness needed!)
- The higher Ct the more resistant micro-organism
- Resistance to disinfection increases in the following order:
  - Non-spore forming bacteria < enteric viruses < spore-forming bacteria < protozoan cysts
- E.g. in pH 6 with hypochlorous acid:
  - E. coli, Ct = 0.04
  - Poliovirus type 1, Ct = 1.05
  - Giardia lamblia cysts, Ct = 80

Ct, cont'd

Microbial inactivation by chlorine: some *Ct* values reported in the literature

Microorganism	Chlorine Concentration, mg/L	Inactivation Time, min	*Ct*
Escherichia coli[a]	0.1	0.4	0.04
Adenovirus type 2[b]			0.023–0.027
Adenovirus type 3[b]			0.027–0.067
Poliovirus 1[a]	1.0	1.7	1.7
Human rotaviruses[e]			5.55–5.59
Entamoeba histolytica cysts[a]	5.0	18	90
Giardia lamblia cysts[a]	1.0	50	50
	2.0	40	80
	2.5	100	250
G. muris cysts[a]	2.5	100	250
Cryptosporidium parvum[c]			3700
Cladosporium tenuissimum[d]			71
Aspergillus terreus[d]			1404

[a]Conditions: 5°C; pH = 6.0 (Hoff and Akin (1986); *Environ. Health Perspect.* 69:7–13).
[b]Conditions: 4°C; pH = 7 (Page et al. (2009). *Water Res.* 43:2916–2926).
[c]Conditions: 20°C; pH = 6 (Driedger et al. (2000). *Water Res.* 34:3591–3597).
[d]Conditions: 25°C; pH = 7 (Pereira et al. (2013). *Water Res.* 47:517–523).
[e]Conditions: 20°C; pH = 7.2 (Xue et al. (2013a). *Water Res.* 47:3329–3338).

- Ct values of selected pathogens
- E.g. C. Parvum requires high chlorine concentrations and/or long HRT

Effectiveness of different chlorine products

Comparative efficiency of disinfectants for the production of 99% bacterial inactivation

Disinfectant	*Escherichia coli*			Heterotrophic bacteria		
	pH	Temp (°C)	CT mg/min l^{-1}	pH	Temp (°C)	CT mg/min l^{-1}
Hypochlorous acid	6.0	5	0.04	7.0	1–2	0.08 ± 0.02
Hypochlorite ion	10.0	5	0.92	8.5	1–2	3.3 ± 1.0
Chlorine dioxide	6.5	20	0.18	7.0	1–2	0.13 ± 0.02
	6.5	15	0.38	8.5	1–2	0.19 ± 0.06
	7.0	25	0.28			
Monochloramine	9.0	15	64	7.0	1–2	94.0 ± 7.0
				8.5	1–2	278 ± 46.0

Source: Adapted from LeChevallier, Cawthon & Lee (1988)

- Hypochlorous acid is the most effective
- Chlorine dioxide is next effective
- After that comes hypochlorite ion
- Notice the difference of hypochlorous acid and hypochlorite ion. They are present in the same solution depending on pH
- Monochloramine is the weakest disinfectant of all the shown (least reactive)

Chlorine dioxide

- Becoming more popular because
  - ClO_2 produces less THMs and HAAs than free chlorine
  - Does not react with ammonia to form chloramines
- ClO_2 must be generated at the site:

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

- ClO_2 is effective against bacterial and viral pathogens and protozoan parasites

Chloramine chlorination

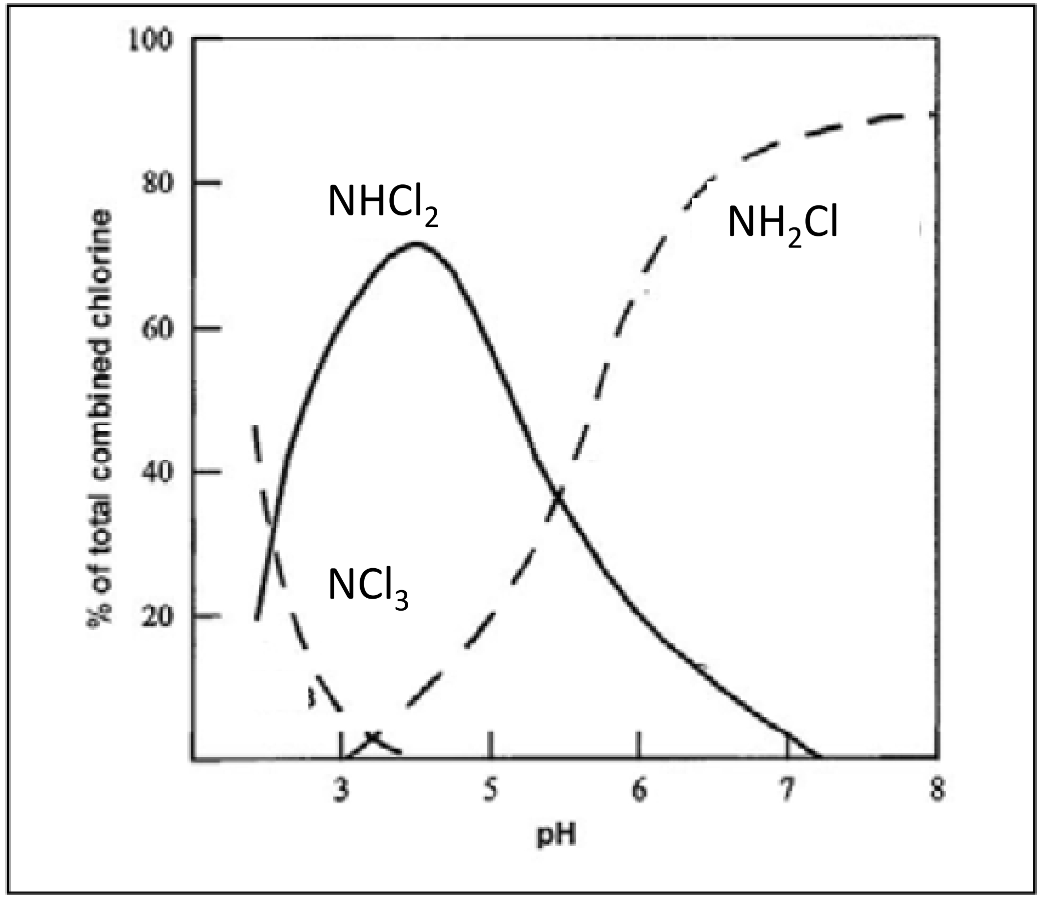
Chloramine formation reactions with ammonia and hypochlorite:

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad \text{(monochloramine formation)}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad \text{(dichloramine formation)}$$

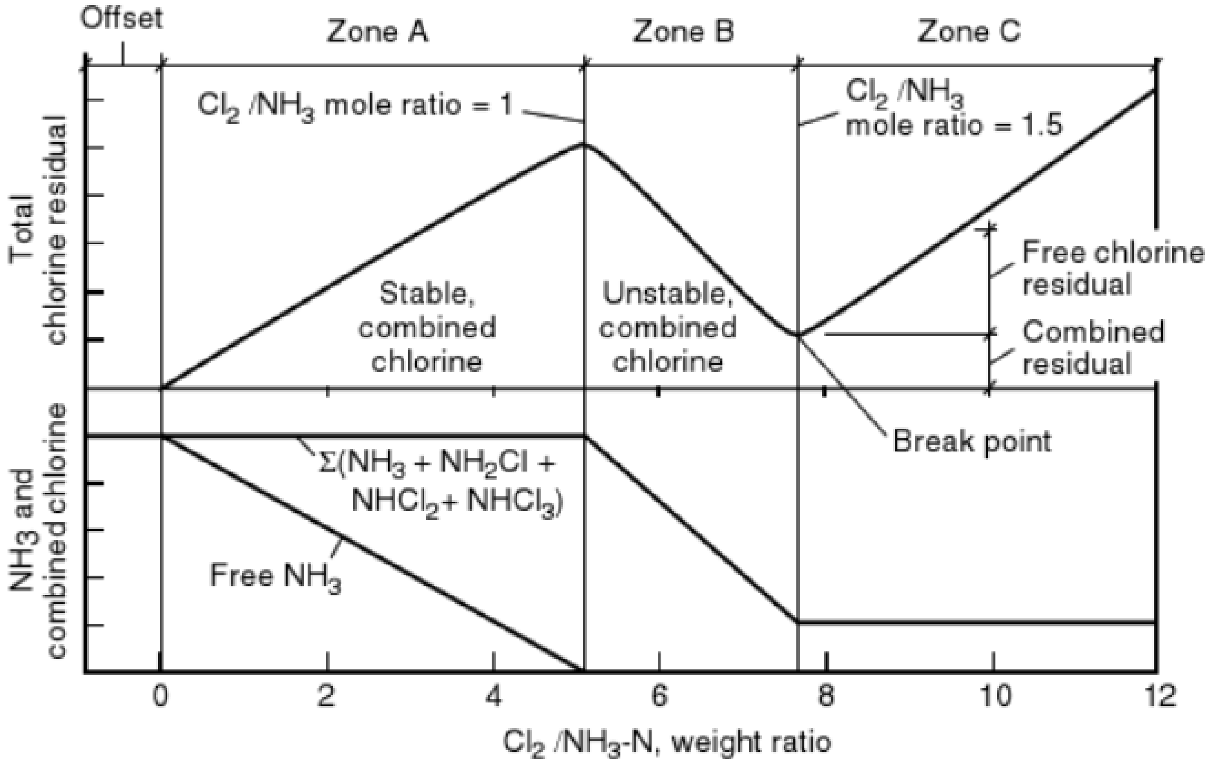
$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O \quad \text{(trichloramine formation)}$$

- Monochloramine is the desired product
- Used especially for secondary disinfection in distribution networks
  - Less reactive than chlorine => disinfection for longer HRTs in the network
- Cl_2:NH_4^+-N mass ratio (maximum) 4.5-5 to reduce the amount of free ammonia
- Monochloramine formation depends on pH
  - Optimum pH is 8.3
- With pH below 7.5 and Cl_2:NH_4^+-N mass ratio above 5
  - Dichloramine and trichloramine formation increases
  - Both have strong chlorinous taste



Distribution of chloramine formation with varying pH

Breakpoint chlorination



- If water contains ammonia, it has to be removed before chlorination (otherwise it's chloramination)
- In breakpoint chlorination chlorine is added to remove first ammonia
- The breakpoint occurs at mole ratio $Cl_2:NH_3 = 1.5$
- Above the mole ratio ammonium is oxidized into nitrogen gas or nitrate ion and free chlorine concentration increases

Infobox

Free chlorine = $HOCl + OCl^-$

Combined chlorine = $NH_2Cl + NHCl_2 + NCl_3$

Total chlorine = free chlorine + combined chlorine

Modeling bacteria inactivation: Chick’s law (1908)

Wellcome Images

Harriette Chick
6.1.1875 – 9.7.1977

$$r = -k_c N$$

r = reaction rate for the decrease in viable organisms with time, org/L·min
k_c = Chick’s law rate constant, min^{-1}
N = concentration of organisms, org/L

- First order kinetics of the micro-organism concentration
- Temperature dependence of reaction rate coefficient (k) is calculated with Arrhenius equation (2nd lecture)
- Chlorine contact chamber volume is calculated similarly as dimensioning a reactor (2nd lecture)
  - Rate equation
  - Required removal
  - Reactor type

=> Hydraulic retention time

Modeling bacteria inactivation: Chick-Watson’s law

Watson’s law (1908)
(Incl. disinfectant concentration)

$$K = C^n t$$

where

K = constant for a given microorganism exposed to a disinfectant under specific conditions,
C = disinfectant concentration (mg/L),
t = time required to kill a certain percentage of the population (min), and
n = constant also called the “coefficient of dilution.”

Chick-Watson model (Haas & Karra, 1984)
(both disinfectant and pathogen concentrations)

$$r = -\Lambda_{CW} CN$$

where Λ_{CW} = coefficient of specific lethality (disinfection rate constant), L/mg·min
C = concentration of disinfectant, mg/L

Integrated form:

$$\ln\left(\frac{N}{N_0}\right) = -\Lambda_{CW} Ct$$

N_0 = concentration of organisms at time = 0, org/L
t = time, min

Modeling bacteria inactivation: Example of Rennecker-Mariñas kinetics

Task: Apply the Rennecker-Mariñas model evaluate the inactivation of C. parvum by chlorine dioxide. Assume that N_0 was underestimated ($\ln(N/N_0)= \log(S_0) < 0$). Use Excel spreadsheet and Solver function to determine the model parameters.

Rennecker-Mariñas model:

$$\ln\left(\frac{N}{N_0}\right) = \begin{cases} 0 & \text{for } Ct < b \\ -\Lambda_{CW}(Ct - b) & \text{for } Ct \geq b \end{cases}$$

N = Concentration of microbes at time t
N_0 = Concentration of microbes at time 0
b = Lag coefficient (mg*min/l)
Λ_{CW} = Chick-Watson coefficient of specific lethality (l/mg*min)
C = Disinfectant concentration (mg/l)
t= Time (min)

R-M model is used when there is lag in the effect of the disinfectant to the specific organism. Without lag R-M model reduces to Chick-Watson model.

Data:

C	t	$\log(N/N_0)$
mg/l	min	data
0,96	0	-0,21
0,96	15,5	-0,25
0,96	30,8	-0,38
0,96	46,1	-0,55
0,96	61,2	-1,04
0,96	76,2	-1,66
0,96	91,1	-2,03
0,48	0	-0,17
0,48	32	-0,12
0,48	61,6	-0,31
0,48	92	-0,6
0,48	122	-1,08
0,48	152	-1,68
4,64	0	-0,15
4,64	2,1	0,02
4,64	4,2	-0,11
4,64	6,2	-0,19
4,64	8,2	-0,29
4,64	10	-0,56
4,64	12	-0,79
4,64	13,9	-1,19
4,64	15,8	-1,47

Solution

Excel table

C	t	Ct	$\log(N/N_0)$	$\log(N/N_0)$	(Data-Model)^2	(Data-avg(Data))^2
mg/l	min	mg*min/l	data	Model		
0,96	0	0	-0,21	-0,19	0,00	0,21
0,96	15,5	14,88	-0,25	-0,19	0,00	0,18
0,96	30,8	29,568	-0,38	-0,19	0,04	0,09
0,96	46,1	44,256	-0,55	-0,52	0,00	0,02
0,96	61,2	58,752	-1,04	-1,04	0,00	0,13
0,96	76,2	73,152	-1,66	-1,56	0,01	0,97
0,96	91,1	87,456	-2,03	-2,07	0,00	1,84
0,48	0	0	-0,17	-0,19	0,00	0,25
0,48	32	15,36	-0,12	-0,19	0,00	0,31

The model function: =IF(Ct>b; $\log(S_0)$; $\log(S_0)+\Lambda_{CW}$*(b-Ct))

... 22 rows of data ...

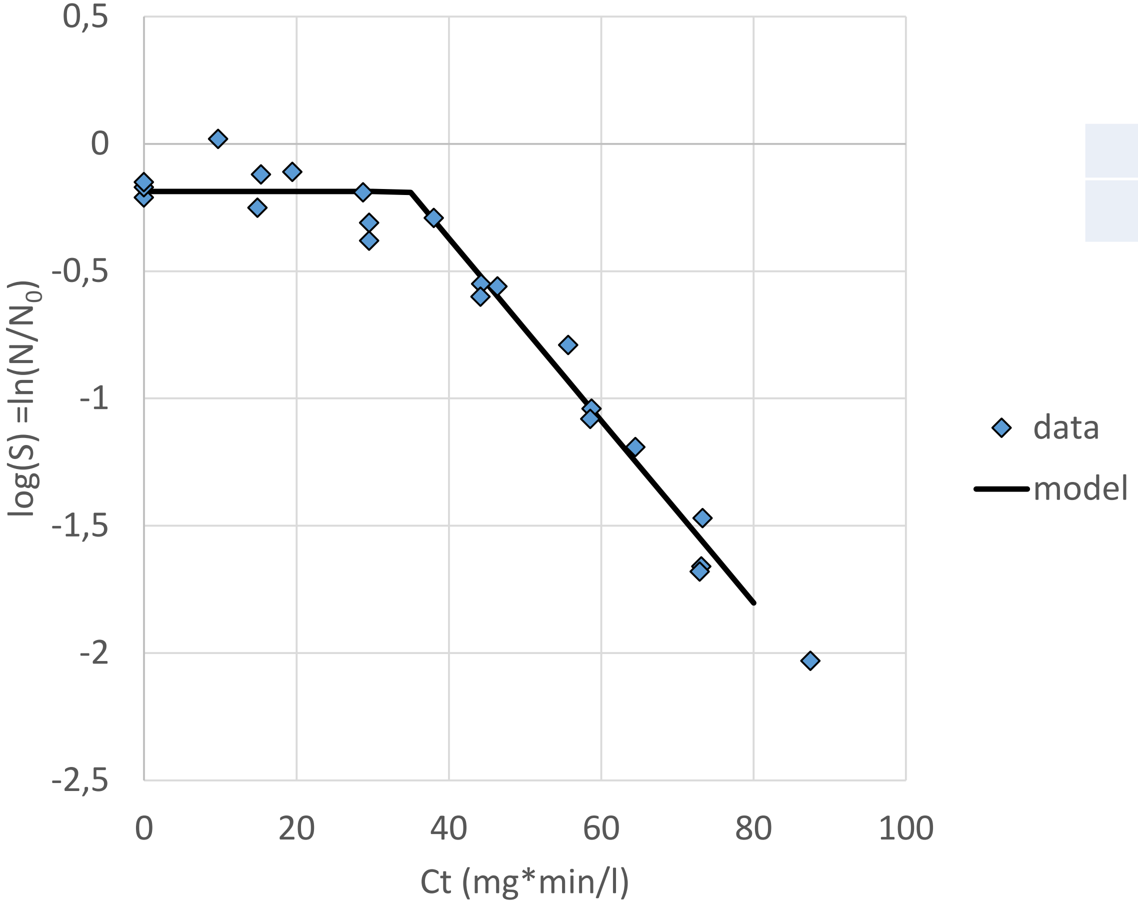
avg(Data)				-0,67			
sum(Data-model)^2						0,184	
sum(Data-avg(Data))^2							7,70
b	35						
Λ_{CW}	0,036						
$\log(S_0)$	-0,19						
Λ_{CW}(base e)	0,083						
r^2	0,98						

The sum of squares of errors is minimized with Solver

These are changed in Solver

Constraint in Solver: $\log(S_0) < 0$

Data and modeled values



	$\ln(N/N_0)$=	-0,19	When Ct<35	
		-0,083*(Ct-35) when Ct>=35		

Note: Exercise

Disinfection by-products

- Formed in chlorination with organic compounds
- Trihalomethanes (THMs)
  - Carcinogenic in animal tests
  - Possible reproductive and developmental toxicity in animal tests
- Haloacetic acids (HAAs)
  - Carcinogenic in animal tests
  - Neurotoxin in higher doses in animal tests

DBPs, cont'd

DBPs formed with chlorine

Trihalomethanes	Chloroform	$CHCl_3$
	Bromodichloromethane	$CHBrCl_2$
	Dibromochloromethane	$CHBr_2Cl$
	Bromoform	$CHBr_3$
	Dichloroiodomethane	$CHICl_2$
	Chlorodiiodomethane	CHI_2Cl
	Bromochloroiodomethane	$CHBrICl$
	Dibromoiodomethane	$CHBr_2I$
	Bromodiiodomethane	$CHBrI_2$
	Triiodomethane	CHI_3
Haloacetic acids	Monochloroacetic acid	$CH_2ClCOOH$
	Dichloroacetic acid	$CHCl_2COOH$
	Trichloroacetic acid	CCl3COOH
	Bromochloroacetic acid	$CHBrClCOOH$
	Bromodichloroacetic acid	$CBrCl_2COOH$
	Dibromochloroacetic acid	$CBr_2ClCOOH$
	Monobromoacetic acid	$CH_2BrCOOH$
	Dibromoacetic acid	$CHBr_2COOH$
	Tribromoacetic acid	CBr_3COOH
Haloacetonitriles	Trichloroacetonitrile	$CCl_3C{\equiv}N$
	Dichloroacetonitrile	$CHCl_2C{\equiv}N$
	Bromochloroacetonitrile	$CHBrClC{\equiv}N$
	Dibromoacetonitrile	$CHBr_2C{\equiv}N$
Haloketones	1,1-Dichloroacetone	$CHCl_2COCH_3$
	1,1,1-Trichloroacetone	CCl_3COCH_3

More DBPs formed with chlorine

Miscellaneous	Chloral hydrate	$CCl_3CH(OH)_2$
Trihalonitromethanes	Trichloronitromethane (Chloropicrin)	CCl_3NO_2
	Bromodichloronitromethane	$CBrCl_2NO_2$
	Dibromochloronitromethane	CBr_2ClNO_2
	Tribromonitromethane	CBr_3NO_2

DBPs formed with chlorine dioxide

Oxyhalides	Chlorite	ClO_2^-
	Chlorate	ClO_3^-

DBPs formed with chloramine

Nitrosamines	N-Nitrosodimethylamine	$(CH_3)_2NNO$

Cyanogen halides	Cyanogen chloride	ClCN
	Cyanogen bromide	BrCN

Approaches for reducing and controlling DBPs in drinking water

- Removal of DBP precursors (NOM, extra-cellular products of micro-organims) before disinfection
  - Removal methods: enhanced coagulation, granular activated carbon (GAC), membrane filtration
  - Some DBPs can be removed with biodegradation in GAC or sand filters
- Preozonation reduces formation of THMs, HAAs and total organic halogens (TOX)
- If THMs are formed, they can be removed with post-aeration after drinking water treatment.
- Using alternative disinfectants: E.g. Chloramine use reduces THMs.
  - Risk for other DBPs

Chlorine residual modeling

- This was topic covered in the course WAT-E2110 - Design and Management of Water and Wastewater Networks
- If you did not go to that course, the slides are included as material on the current course

Shock chlorination

- Shock chlorination is needed in contamination cases
- Pathogens can be protected by biofilms
  - High chlorine concentrations and long HRT
- Example:
  - 10 mg/l Cl_2
  - 180-240 min
  - => Inactivated Yersinia pseudotuberculosis from biofilm (Räsänen et al. 2013)
- Flushing after shcok chlorination to get rid of the chlorine and possible DBPs

Most recent topics in chlorination research

1. DBPs
2. Chlorine-resistant pathogens

Digestion task

- Recognize the disinfection units of Vanhakaupunki WTP
- Why are the treatment units in this order?
  - How is the formation of DBPs taken into account?
  - Why is coagulation-flocculation in the beginning of the process train?
  - Why is chlorine added after GAC filtration?
  - Why is chloramine used for secondary disinfection?
  - Why is the pH of distributed water rather high (8.6)?

Digest with your favourite method (discussion, self-talking, walking, drinking coffee etc.)

Literature

- Available at Ebook Central:
  - AWWA Staff, 2006. Water Chlorination/Chloramination Practices and Principles. AWWA Manual Series M20. American Water Works Assoc. 2nd ed. eBook ISBN 9781613000267
  - LeChevallier, MW, Au, KK, 2004. Water treatment and pathogen control. WHO, IWA Publishing. 116 p. ISBN 92 4 1562255 2
  - Bitton, G, 2014. Microbiology of Drinking Water Production and Distribution. Wiley. 316 p. eBook ISBN 9781118744017 (Chapter 3, Chlorination, p. 65)
- Others:
  - Shock chlorination of private wells http://www.water-research.net/index.php/shock-well-disinfection
  - Inactivation of bacteria at epa.gov: https://www.epa.gov/sites/production/files/documents/giardiaandvirusCTcalculation.pdf