

Coagulation (凝集)

* colloid stability

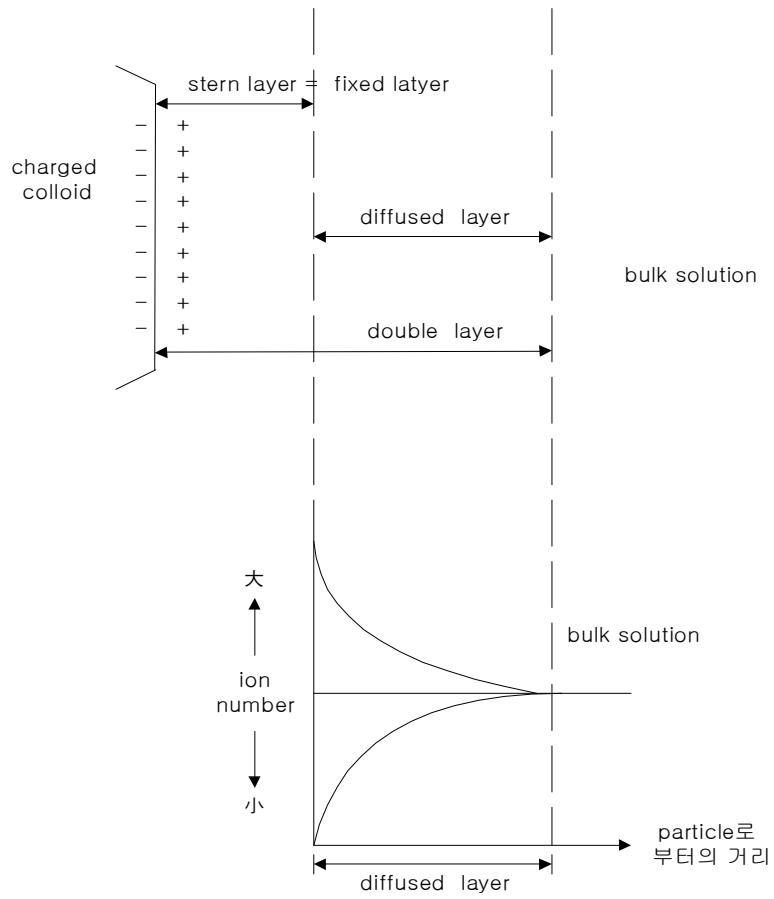
i) $1\text{nm} < \text{colloid} < 1\mu\text{m}$

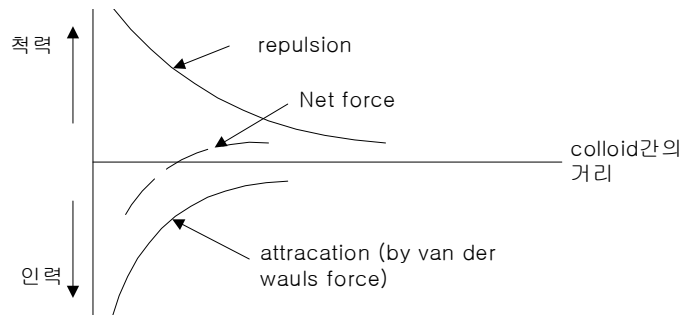
ii) surface phenomena $>$ mass phenomena

iii) electric charge를 띠고 대부분의 surface는 '-' charge ~ repulsion에 의해 coagulation과 precipitation을 방해한다.

→ colloid 안정성을 electrostatic repulsion에 기인

→ colloid charge를 중화시켜 침전

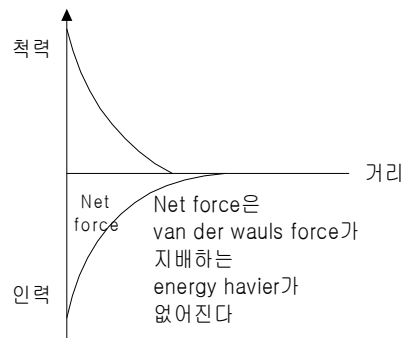
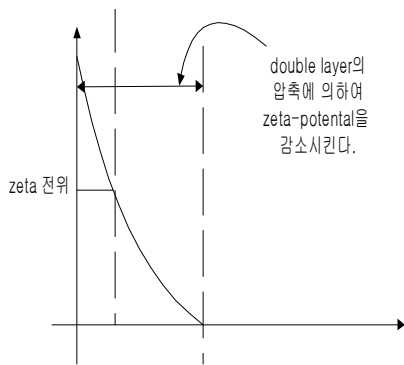
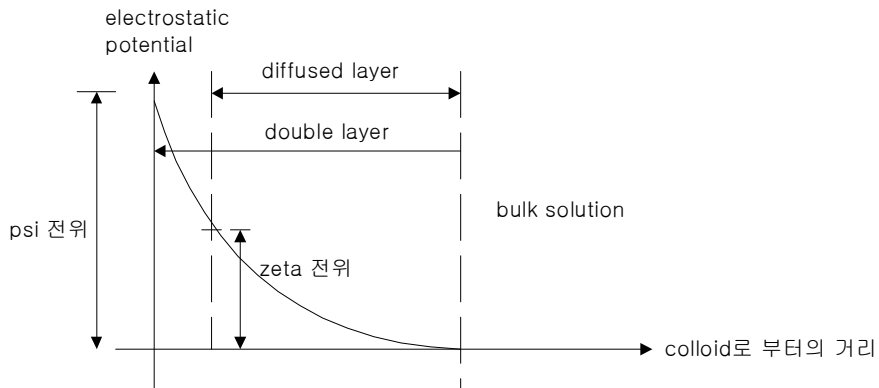




<Force field between colloid of like charge>

* coagulation theory

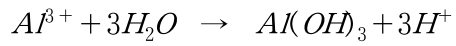
i) ionic layer compression ~ colloid 주위의 ion들이 electrostatic potential을 감소시킨다.



ii) adsorption and charge neutralization

- 응집제의 금속이온들이 colloid surface에 흡착되어 solution charge를 중화시킨다.

ex) $Al_2(SO_4)_3 \rightarrow$ 수중에서 Al^{+3} , SO_4^{-2}



iii) entrapment in a flocculent mass

iv) interparticle bridging (with polymer)

* Jar test for optimum coagulant dosage

i) 응집제와 보조 응집제 선정

ii) optimum dosage 결정

iii) operating variable

① pH

② Alkalinity

③ pollutant concentration (SS, COD, turbidity, color)

④ 온도

⑤ mixing intensity

⑥ mixing time

iv) experimental method

① rapid mixing for 1 ~ 3 min (coagulation step)

② slow mixing for 15 ~ 20 min (flocculation step)

③ precipitation for 30 min (precipitation step)

* Alkalinity - coagulation relationships

theoretical reaction equation

i) aluminium sulfate



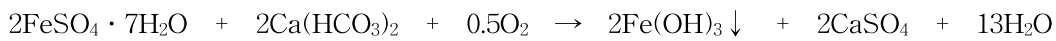
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Natural alkalinity

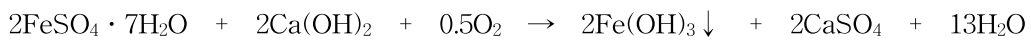
ii) Ferric chloride (염화철)



iii) Ferrous sulfate (황산 제1철)



if alkalinity가 부족하면 'Line'을 주입



* 화학 응집조에 있어서의 mixing

i) 혼합정도를 'velocity gradient'(G)로 나타낸다.

$$\hookrightarrow \frac{\text{relative velocity of two particles of fluid}}{\text{distance between}} \quad [\text{sec}^{-1}]$$

ii) experimental eq.

$$G = \left(\frac{P}{V\mu} \right)^{\frac{1}{2}} \quad \text{-----} \quad \textcircled{1} \quad G = \text{velocity gradient } [S^{-1}]$$

P = power input {N · m/s}

V = volume of mixing basin [m³]

μ = viscosity [kg/m · s]

iii) rapid mixing (coagulation) G = 700 ~ 1000 [sec⁻¹]

slow mixing (flocculation) G = 30 ~ 80 [sec⁻¹]

iv) flocculation tank에서의 input power calculation

$$P = Dv_P \quad \text{-----} \quad \textcircled{2}$$

P : power input [N × m/s]

D : drag force on paddles [N]

v_P : paddle velocity [m/s]

$$D = C_D A_P \rho \frac{v_P^2}{2} \quad \text{-----} \quad \textcircled{3}$$

C_D : drag coefficient, 1.8, for flat blades [-]

A_P : area of paddle blades [m²]

ρ : water density [kg/m³]

$$\text{from } \textcircled{2} \textcircled{3} \quad P = \frac{C_D A_P \rho v_P^3}{2} \quad \text{-----} \quad \textcircled{4}$$

$$\text{form } \textcircled{3} \textcircled{4} \quad G = \left(\frac{C_D A_P \rho v_P^3}{2 V \mu} \right)^{\frac{1}{2}}$$

4 - 7

* stabilization

i) Complete removal of hardness cannot be accomplished by chemical precipitation.

ii) after water treatment

CaCO₃ 40 mg/ℓ

Mg(OH)₂ 10 mg/ℓ

$$10 \text{ ppm Mg(OH)}_2 \left[\frac{\text{Mg(OH)}_2 \text{ 1g당량}}{29g \text{ Mg(OH)}_2} \right] \parallel \left[\frac{\text{CaCO}_3 \text{ 1g당량}}{\text{Mg(OH)}_2 \text{ 1g당량}} \right] \parallel \left[\frac{\text{CaCO}_3 \text{ 50g}}{\text{CaCO}_3 \text{ 1g당량}} \right]$$

=17 mg/ℓ (as CaCO₃)

iii) 과포화 CaCO₃, Mg(OH)₂가 침전하여 관에 쌓인다.

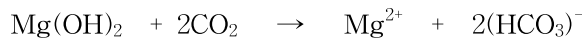
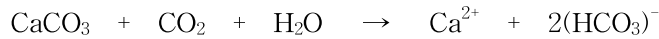
iv) 이온化시켜 stabilization이 필요하다

~연수에서 Ca⁺⁺, Mg⁺⁺ 허용기준이 있기에 가능하다.

㉠ H₂SO₄

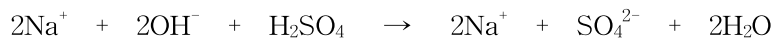
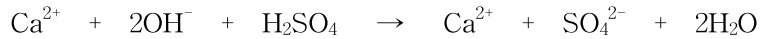


㉡ CO₂ (this process is 'recarbonation')

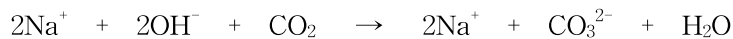
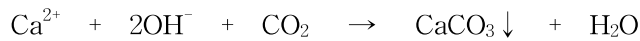


v) 높은 pH (pH 10.5 ~ 11)에서 Mg⁺⁺ 까지 제거 한 다음 stabilization 시키기 전에 과잉의 OH⁻를 중화시킬 필요가 있다. → pH 8.5 까지

㉠ H₂SO₄ (중화)



㉡ CO₂ (중화)



ex) 4-7 Lime - soda ash process에 의한 Ca^{++} hardness 제거
 (CaO) (Na_2CO_3) (Mg^{++} 무시)

	1.0	5.0	6.0	8.0
meq/L	Ca^{2+}		Mg^{2+}	Na^+
	CO_2	HCO_3^-	SO_4^{2-}	
		3.5		8.0

<assumption>

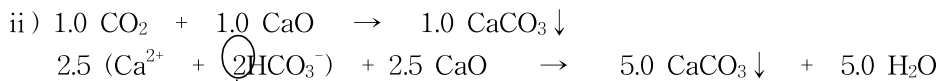
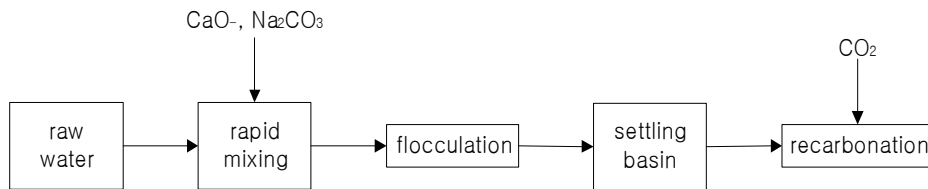
i) Mg^{++} 정도 negligible

ii) 처리후 40 mg/ℓ CaCO_3 가 용해되어 있다.

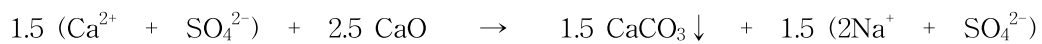
iii) CaCO_3 의 solubility는 15 mg/ℓ CaCO_3

① chemical requirement in milli equivalent/ℓ

i)



↓
 당량 농도를 mol 농도로 환산



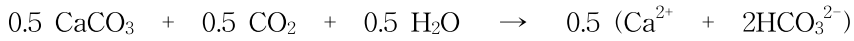
⊕ Lime = 1.0 + 2.5 = 3.5 m equivalent/ℓ

⊖ Soda ash = 1.5 m eq/ℓ

iii) recarbonation ~ supersaturated CaCO₃를 CO₂를 利用하여 ion化

$$40 - 15 = 25 \text{ mg/}\ell \text{ CaCO}_3 \left[\frac{\text{CaCO}_3 \text{ milliequivalent}}{\text{CaCO}_3 \text{ 50mg}} \right]$$

$$= 0.5 \text{ mg/}\ell \text{ CaCO}_3$$



$$\ominus \text{ CO}_2 = 0.5 \text{ meq/}\ell$$

② produced solid (meq/ℓ)

$$\text{CaCO}_3 = (1.0 + 5.0 + 1.5) \text{ meq/}\ell - 40 \text{ mg/}\ell \left[\frac{\text{CaCO}_3 \text{ meq}}{\text{CaCO}_3 \text{ 50mg}} \right]$$

$$= 7.5 - 0.8$$

$$= 6.7 \text{ (meq/}\ell \text{)}$$

③ bar diagram for 처리수

i) 용해되어 있는 CaCO₃ ; Ca²⁺, CO₃²⁻ = 15mg/ℓ = 0.3meq/ℓ

ii) recarbonation으로 생성 : Ca²⁺, HCO₃⁻ = 0.5meq/ℓ

iii) Mg⁺⁺, SO₄⁻² 불변

iv) Na⁺ = 2.0 + 1.5 = 3.5 meq/ℓ

		0.8		1.8	5.3
Ca ²⁺		Mg ²⁺		Na ⁺	
CO ₃ ⁻	HCO ₃ ⁻		SO ₄ ²⁻		
0.3	0.8		5.3		

④ 폐수 유량 = 25,000 m³/d 일 때 약품사용량 & 생성 고형물량
(단 CaO의 순도 90%, Na₂CO₃의 순도 85%)

$$\text{CaO} = \frac{\text{원자량}}{\text{원자가}} = \frac{40 + 16}{2} = 28 \text{ mg/meq}$$

$$\text{Na}_2\text{CO}_3 = \frac{2(23) + 12 + 3(16)}{2} = 53 \text{ mg/meq}$$

$$\text{CO}_2 = \frac{12 + 2(16)}{2} = 22 \text{ mg/meq}$$

약품사용량

$$\textcircled{1} \text{ CaO} = \left(\frac{1}{0.9}\right) 28 \left[\frac{\text{mg}}{\text{meq}}\right] (3.5\text{meq}/\ell) \times 25,000\text{m}^3/d = 2722\text{kg}/d$$

$$\textcircled{2} \text{ Na}_2\text{CO}_3 = \left(\frac{1}{0.85}\right)(3.5\text{meq}/\ell) \times 25,000\text{m}^3/d = 2338\text{kg}/d$$

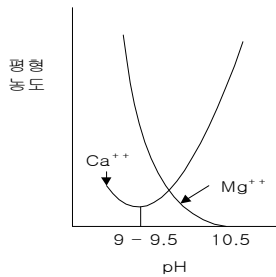
$$\textcircled{3} \text{ CO}_2 = (22\text{mg}/\text{meq})(0.5\text{meq}/\ell) \times 25,000\text{m}^3/d = 275\text{kg}/d$$

생성 고형물량

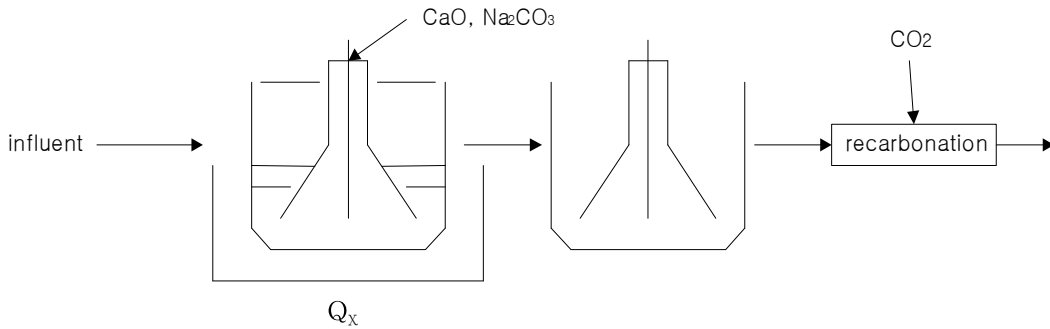
$$\text{CaCO}_3 = (50\text{mg}/\text{meq})(6.7\text{meq}/\ell) \times 25,000\text{m}^3/d = 8375\text{kg}/d$$

* Softening operation

split treatment ... Mg^{++} 경도가 높을 경우



- i) Mg^{++} 경도가 높을 경우 influent 일부분을 bypass
- ii) excess Lime으로 1차에서 Mg^{++} 제거
- iii) 중화시키는 대신에 2차에서 Ca^{++} 제거
- iv) bypass 中の Mg^{++} 는 미처리
→ bypass fraction은 raw water의 initial Mg^{++} (Mg_r) 농도와 허용 Mg^{++} (Mg_f) 농도에 의한다.



$$Q_x = \frac{Mg_f - Mg_1}{Mg_r - Mg_1}$$

Q_x : bypass fraction

Mg_f : 허용농도 40~50 mg/l (as $CaCO_3$)

Mg_r : raw water의 농도

Mg_1 : 1차 처리후의 농도 10 mg/l $Mg(OH)_2$ (as $CaCO_3$)

ex) 4-9 split treatment 時 chemical 요구량 求? (meq/l)

	0.6	4.0	7.0	8.0
meq/L	Ca^{2+}		Mg^{2+}	Na^+
	HCO_3^-	SO_4^{2-}		
	5.5		8.0	

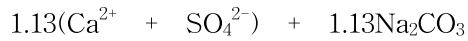
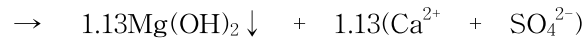
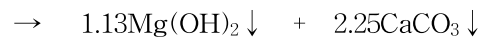
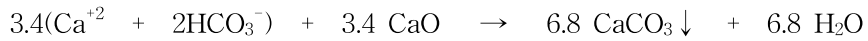
i) Mg_f : 40~50 mg/l (as $CaCO_3$) = 0.8~1 meq/l = 0.9 meq/l

Mg_1 : 10 mg/l (as $CaCO_3$) = 0.2 meq/l

Mg_r : 3.0 meq/l

$$\rightarrow Q_x = \frac{Mg_f - Mg_1}{Mg_r - Mg_1} = \frac{0.9 - 0.2}{3.0 - 0.2} = 0.25$$

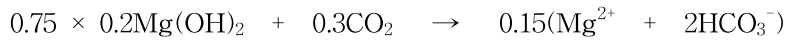
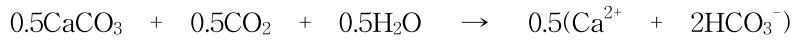
ii) 1st stage에서의 chemical 量



$$\textcircled{+} \text{ Lime} = 0.6+3.4+(1-0.25)(3.0+1.5) = 7.38 \text{ meq}/\ell$$

$$\textcircled{-} \text{ Soda ash} = 1.13 \text{ meq}/\ell$$

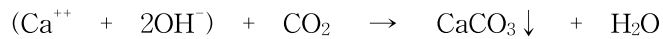
iii) 2nd stage recarbonation



$$\textcircled{+} \text{ CO}_2 = 0.5 + 0.3 = 0.8 \text{ meq}/\ell$$

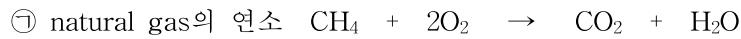
* Recarbonation by CO₂

i) pH reduction

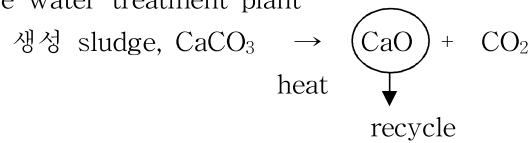


ii) stabilization ~ pipe 내부의 침전을 막기 위하여 과포화 상태의 CaCO₃, Mg(OH)₂를 ion化

iii) CO₂ 공급



㉡ Large water-treatment plant



* Ion exchange

이온화 energy (E) ~ 원자 1mol에서 전자 1mol을 떼어 내는데 必要한 energy

i) E ↓ 할수록 전자를 잃어 양이온(cation)이 되기 쉽다.

ii) 같은 주기에서 원자번호 ↑ 할수록 E는 ↑ 한다.

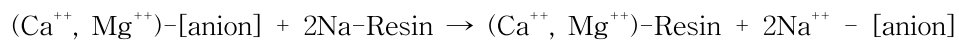
ex) 3주기 Na < Mg < Al < Si < P < S

iii) 같은 족에서 원자번호 ↑ 할수록 E는 ↓ 한다

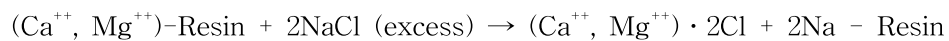
iv) 경도 ion (Ca⁺⁺, Mg⁺⁺)을 제거하기 위해 Na⁺-Resin을 사용

이온화 E : Na < Ca < Mg

v) ion exchange



vi) regeneration ~ strong NaCl overrides the selectivity of the adsorption site



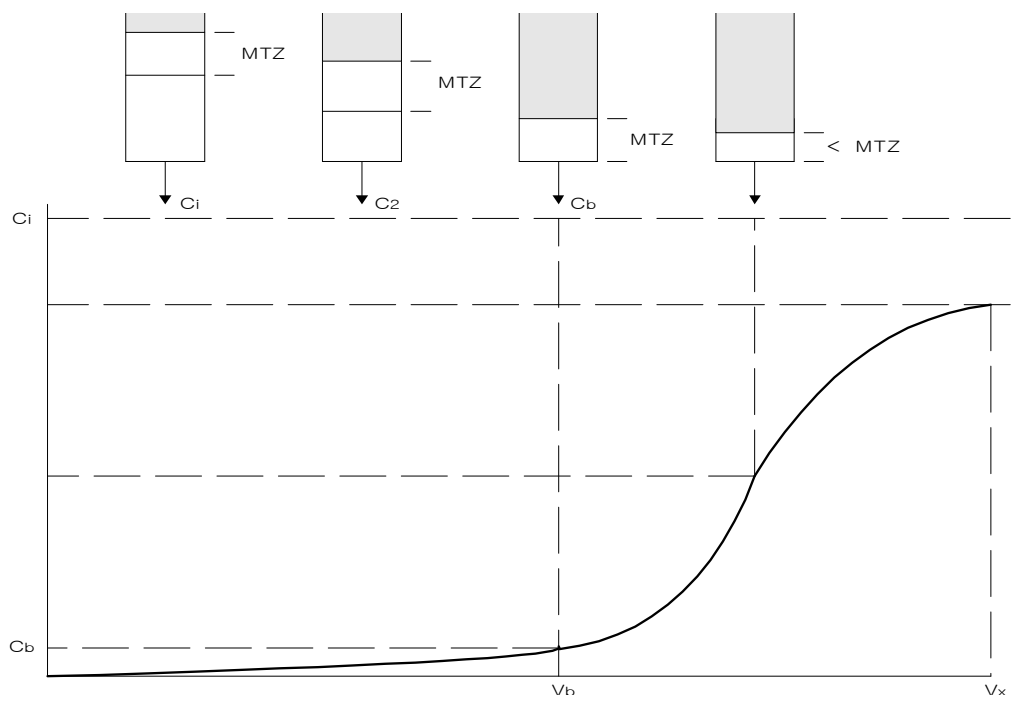
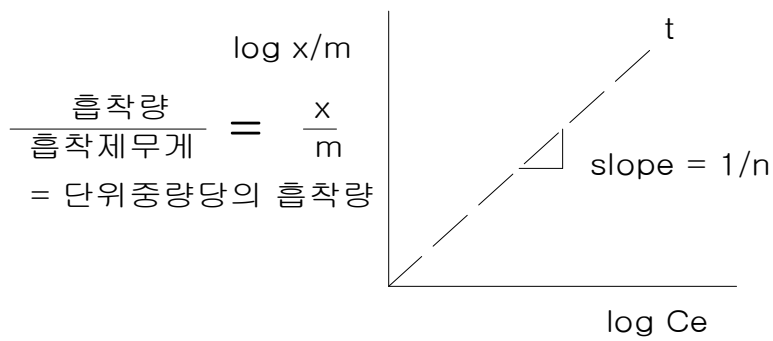
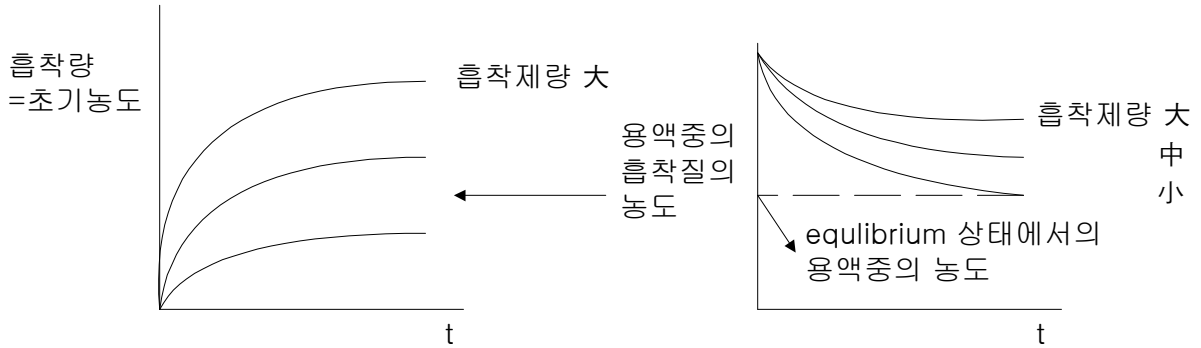


그림 7-8. 처리된 물의 부피에 따른 MTZ의 이동을 보여주는 활성탄의 일반적인 누출곡선

<batch system>



<Freundlich eq>

$$\frac{x}{m} = K_f C_e^{\frac{1}{n}} \quad \leftarrow \quad \log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} \log C_e$$

x/m : 단위 중량의 흡착제에 흡착된 물질량

C_e : 흡착이 일어난 후 용액중의 흡착질의 평형농도

K_f, n : 실험으로 구해지는 상수

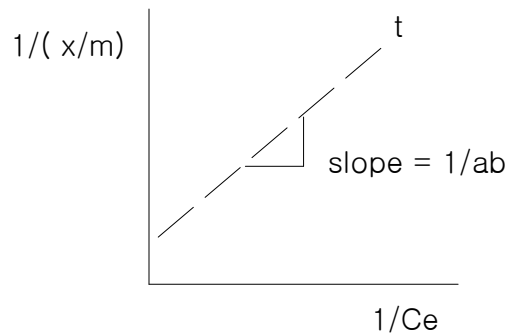
<Langmuin eq>

$$\frac{x}{m} = \frac{abC_e}{1+aC_e} \quad \rightarrow \quad \frac{1}{x/m} = \frac{1}{b} + \frac{1}{ab} \frac{1}{C_e}$$

a, b : 실험으로 구해지는 상수

a : 흡착평형상수

b : 최대흡착량



* Ion exchange (softening 用)

① capacity and efficiency of ion-exchange

- i) type of solid medium ex) resin, zeolite
- ii) type of exchange medium used for coating ex) H^+ , Na^+
- iii) quantity of regeneration material
- iv) regeneration contact time

② 성능

- i) 2~10 mequir/g 이온교환수지
- ii) regeneration 80~160 kg NaCl/m³ resin
→ 5~20% NaCl solution의 flow rate 40 ℓ/min · m²

③ 장 · 단점

가. 장점

- ㉠ chemical precipitation 보다 softening
- ㉡ lime-soda process 보다 적은 sludge
- ㉢ physical & mechanical 장치는 smaller and simpler

나. 단점

- ㉣ filter 작용으로 plugging 되므로 turbidity 사전 제거 필요
- ㉤ medium의 adsorbent 역할로 organic 물질에 의한 coating
- ㉥ oxidation이 일어나면 Fe, Mn 침전에 의해 medium 표면 fouling
 - 깨끗한 지하수는 aeration 전에 즉시 ion-exchange
 - surface water는 사전에 necessary treatment를 모두 행한다.

* 여과방법

(1) 규조토막 여과

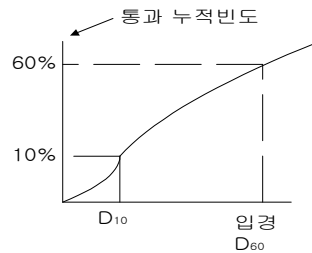
- precoat filtration
- 규조토의 얇은 막에 고형물이 결합하여 미세 스크린상에서 cake를 형성

(2) 미세여과 (microstrainer)

- 다공질 ceramic 沱材 또는 합성수지, 금속, 섬유류의 미세망
- 회전 드럼 형태로 연속 역세척 가능
- 여과막 간격 23~35 μ m

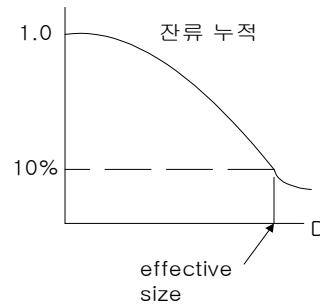
(3) 완속 모래여과 (slow sand filter)

- 유효 모래 크기 0.2mm
- biofilm이 물-모래 계면에 형성
- 0.12~0.32 m/h 낮은 여과 속도
- 넓은 부지가 필요



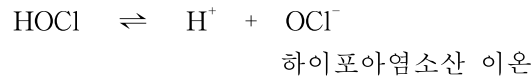
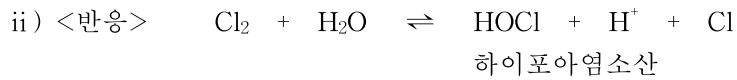
(4) 급속 모래여과 (Rapid sand filter)

- 0.6~0.75m 깊이의 규사토층
- 유효크기 0.45~0.55 mm
- 2.5~5.0 m/h의 빠른 여과 속도
- 역세척이 필수
- uniform coefficient $1.65 \left(\frac{D_{60}}{D_{10}} \right)$

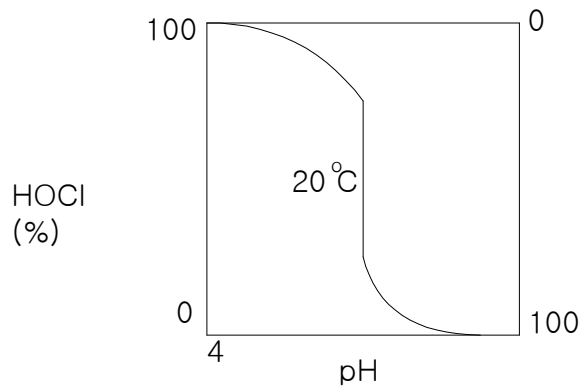


* 염소소독 (chlorine disinfection)

- i) 사용되는 염소의 형태 ; Cl_2 , $\text{Ca}(\text{OCl})_2$, $\text{Na}(\text{OCl})_4$, ClO_2
 염소가스 차아염소산칼슘 차아염소산나트륨 이산화염소
 ↓
 가장 대표적



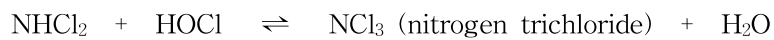
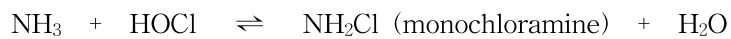
HOCl , OCl^- : 유리잔유염소 (free available chlorine)



HOCl 의 살균력이 OCl^- 보다 40~80배 크기 때문에 반응시킬 때 산성쪽이 효과가 있다.

iii) 염소는 수중의 무기물질과 반응하여 여러 생성물을 만든다.

특히 암모니아(NH_3)와 반응하여 → chloramine 생성



NH_2Cl , NHCl_2 , NCl_3 : 결합잔유염소 (combined chlorine residual)

iv) 이 밖에도 염소는 여러 물질과 반응한다. (→ chlorinated hydrocarbon compound)

① Fe^{+2} , Mn^{+2} , H_2S , 유기물 등과 같이 쉽게 산화되는 물질과 즉각적으로 반응한다.

② $phenol + Cl_2 \rightarrow chlorophenol$

C_6H_6O

③ humic acid (식물류 부패 추출물) + $Cl_2 \rightarrow$ Trihalomethane (THM)

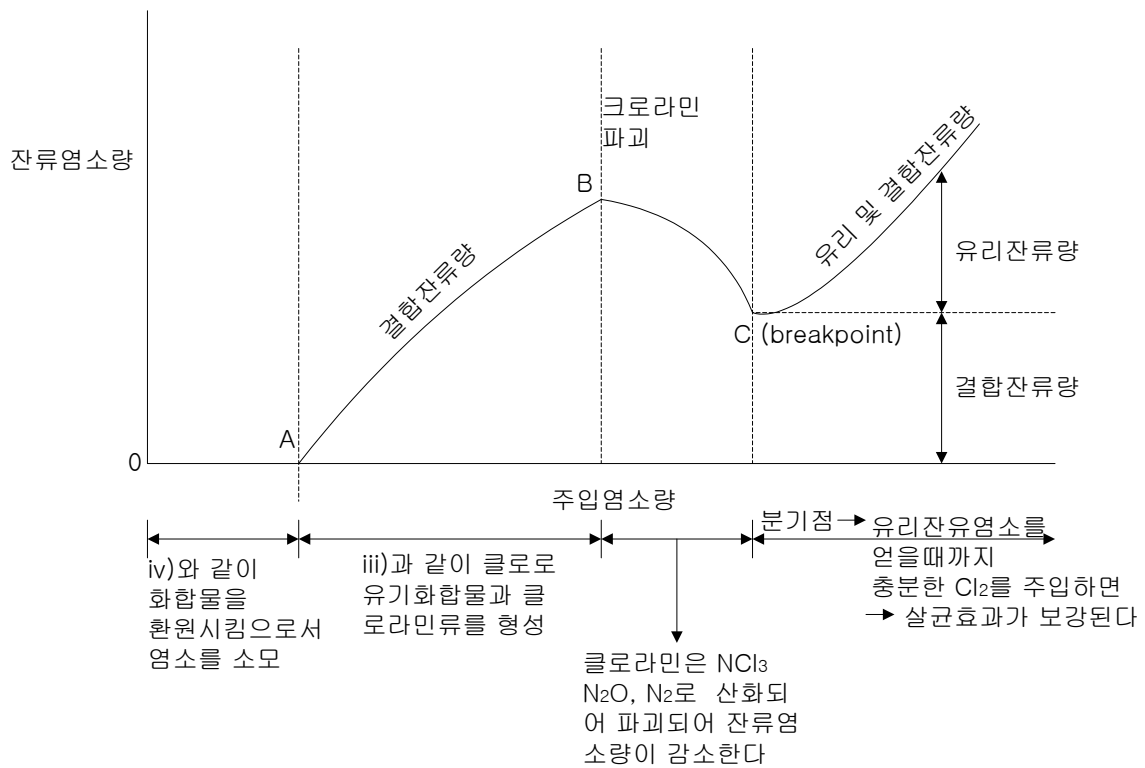
v) 잔류염소량 = 유리잔류염소량 + 결합잔류염소량

vi) 염소 요구량 (chlorine demand) = 주입한 염소량 - 잔류염소량

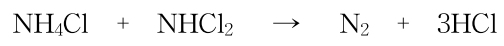
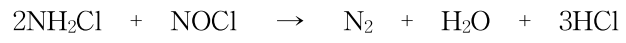
↑

수중에 있는 물질에 의하여 환원되거나 변화되는 염소량

vii) 분기점 염소화 (breakpoint chlorination)



* Chloramine이 감소하는 이유

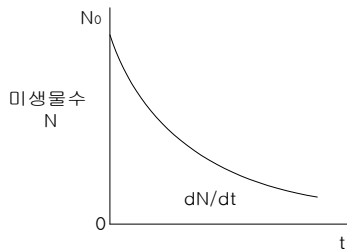


나. 살균과 관련된 이론

① 살균제와 접촉시간

<batch system>

i) "Chick eq" (살균에 의한 미생물 감소 속도가 1차)



$$\frac{dN}{dt} = -KN \quad (N : \text{미생물의 수})$$

$$t=0, N=N_0$$

$$t=t, N=N_t$$

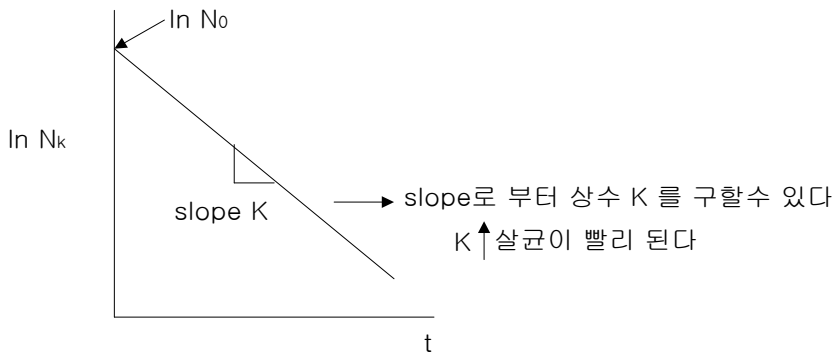
$$\int_{N_0}^{N_t} \frac{dN}{N} = - \int_0^t K dt$$

$$\text{at } t=0, N_0$$

$$t=t, N_t$$

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

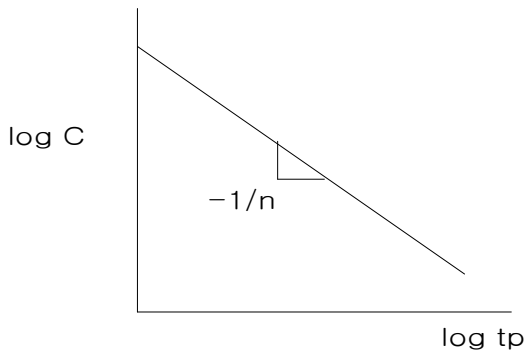
$$\ln N_t = \ln N_0 - Kt$$



* Chlorine concentration and contact time 관계

$$C^n t_p = k \quad t_p : \text{time required for given \% kill}$$

$$\log C = -\frac{1}{n} \log t_p$$

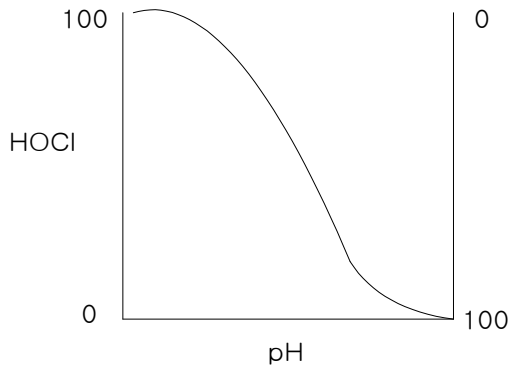


C ↑ 할수록 살균시간 ↓



$$K = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} \quad T \uparrow \text{ 할수록 } K \uparrow$$

i) pH 영향

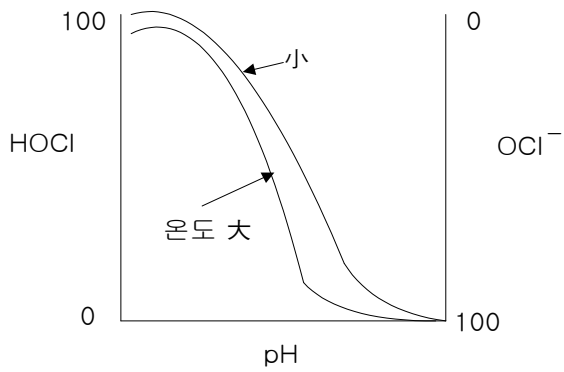


ii) 온도 영향 (pH const)

HOCl distribution

$$\frac{[\text{HOCl}]}{[\text{HOCl}] + [\text{OCl}^-]} = \frac{1}{1 + [\text{OCl}^-]/[\text{HOCl}]} = \frac{1}{K[\text{H}^+]}$$

T ↑ 할수록 K ↑ 하므로 HOCl 농도 ↓ [OCl⁻] ↑



4 - 10 DS removal

① Inorganic material

* Ion exchange

i) Na^+ - Resin

- no net decrease in DS

at softening에서 Na^+ 와 (Ca^{++} , Mg^{++})의 교환

- regeneration ... excess NaCl

ii) H^+ - Resin, OH^- - Re

- dissolved cation, anion 제거 (DS감소)

- pH 불변 (finally H_2O 생성)

- regeneration ... acid, base

㉔ Organic Material

* Adsorption

i) adsorbent 흡착제
adsorbate 흡착질

ii) GAC - PAC

granular powdered

iii) GAC column

fixed ... backwashing

moving system

㉠ spent carbon bottle에서 제거

㉡ new carbon top에서 보충

iv) PAC

㉠ head loss 때문에 fixed bed로 사용할 수 없다.

㉡ open vessel에서 suspension 상태로 작용

- contact time 필요

- solid removal process가 필요

㉢ regeneration이 어렵다

ex) solid waste의 Activated carbon으로 재활용 연구

* chemical oxidation

i) refractory organic component의 제거 ... 흡착법에 견줄 만하다.

ii) 강력한 oxidant에 의해 저분자화

(O₃, Cl₂)

iii) 부가적 Advantage

- ammonia removal
- inorganic 물질(ex> Fe, Mn)의 oxidation
- disinfection

iv) O₃

- Europe
- taste, odor, color-producing organics을 ozonation
- oxidation과 disinfection이 동시에 일어난다.

v) process 위치

- 2nd treatment 처리 추가 more cost-effective

* Zeta potential (ζ)

$$\zeta = \frac{4\pi\eta v}{\epsilon\chi} = \frac{4\pi\eta EM}{\epsilon} [\text{mV}]$$

$$\text{전기장}(E) = \frac{F}{q}$$

$$\text{Volt} = \frac{\text{Joule}}{\text{coul}}$$

v = particle velocity

ϵ = medium의 誘電定數 (dielectric constant) [$\text{coul}^2 / \text{N} \cdot \text{m}^2$]

η = viscosity [$\text{g} / \text{cm} \cdot \text{sec}$]

χ = potential / cell length [Volt / length]

EM = electrophoretic mobility ($= \frac{v}{E}$)
= 전기영동 [= $\frac{\text{속도}}{\text{단위거리전기장}}$]

i) 측정되는 zeta-potential은 ion들이 붙어있는 fixed layer의 potential

ii) solution component에 의해 zeta-potential은 변한다 \rightarrow not repeatable measurement

* Particle aggregation

i) diffuse electric layer 감소 \rightarrow zeta potential 감소

ii) surface charge neutralization

iii) Addition of long chained organic molecule \rightarrow bridging

< Experiment >

i) 조건 : Temperature에 따라 viscosity, 유전율

ii) Voltage / cell 길이

\rightarrow electrophoretic grid division 거리 측정(using microscope)