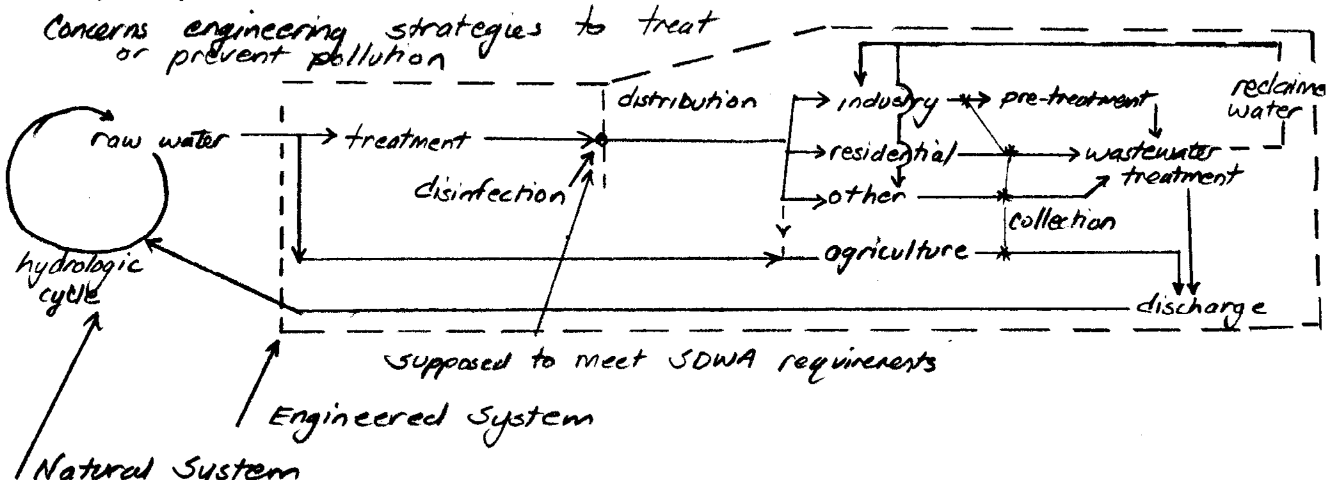
Water quality control

Concerns engineering strategies to treat or prevent pollution



SDWA requirements include various MCL standards for chemicals, radionuclides microbiological indicators & "secondary standards"

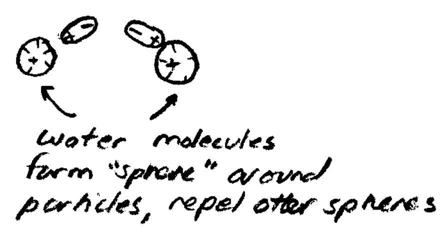
Typical Water treatment methods

- screening – remove gross particulates and flotables
- mixing coagulant chemicals (high shear mixing) (vigorous)
- flocculation (low shear mixing) (gentle)
- settling – water rich slurry separates from solids rich slurry → sludge handling
- filtration (removes more solids)
- disinfection (inactivates pathogens)
- distribution

Coagulation & flocculation

Natural solids have ⊖ surface charge

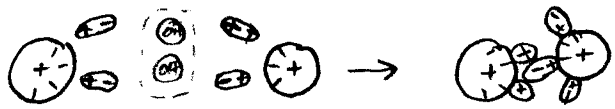
Coagulants neutralize charge so particles can come together to form large flocs that settle because of density difference.



Common inorganic flocculants

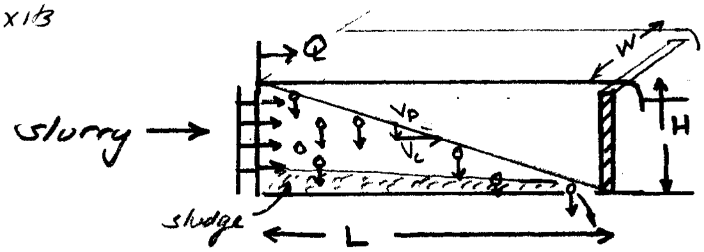
Alum ($Al_2(SO_4)_3 \cdot 18H_2O$) and Ferric Chloride $FeCl_3$ are most common chemicals in use

$$Al_2(SO_4)_3 \cdot 18H_2O + 6HCO_3^- \rightleftharpoons 2Al(OH_3)_{solid} + 6CO_2 + 18H_2O + 3SO_4^{2-}$$



Alum binds OH^- so particles can come close

Sedimentation - once flocs are created, particle size increased gravity force overcomes hydration effect & flocs settle. Settling basins designed so floc settles to basin bottom before water exits



Particle size determines V_p which determines V_c, H & L & W. Sedimentation is not to remove all particles, but does remove all particles of some size. Then filter remainder.

Settling Concepts - Ideal Basin Assumptions

Horizontal flow in settling zone, uniform flow velocity, uniform concentration of particles (all sizes) at inlet. Particles removed once reach bottom of settling zone. Particles settle discretely without interference from other particles

V_c is critical velocity (U above) and is based on surface loading rate $V_c = \frac{Q}{A_{surface}}$ $A_{surface} = L \cdot W$

V_p is particle settling velocity, function of particle size

For particles whose $V_p > V_c$, basin will remove all particles

For particles $V_p < V_c$ fraction removed is $X_R = \frac{V_p}{V_c}$

<u>Example</u> Settling tank $\frac{Q}{A} = 100{,}000 \frac{gal}{ft^2\,day}$. Slurry with grit of sizes is introd

Find % of grit removed

V_p (ft/hr)	% smaller	% larger
10.	54	46
5.	45	55
2.	35	65
1.	20	80
.75	10	90
.50	3	[illegible]

$$Q/A = \frac{100{,}000\,g}{ft^2\cdot day}\cdot\frac{ft^3}{7.48\,gal}\cdot\frac{1\,day}{24\,hr}\cdot\frac{1\,hr}{60\,min} = 9.28\,ft/min$$

$\therefore V_c = 9.28\ ft/min$

V_p	% larger (faster)	
10	46	↑ all removed
9.28		←
5	55	
⋮	⋮	

$$\frac{55-46}{5-10} = \frac{x}{5-9.28}$$

$x = 7.7$

$\therefore 55 - 7.7 = 47.3\%$ removed (completely)

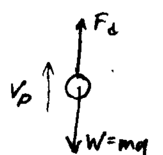
Now if we consider fractional removal

V_p	% larger		x_r	% removed
10	46		1	46
5	55	0.09	0.53	4.7
2	65	0.1	0.0735	.735
1	80	0.15	0.022	.33
.75	90	0.10	0.008	.08
.5	97	0.07	0.0015	.01

$\Sigma = 51.85\%$ removed.

Summary 47.3% of particles have $V_p > V_c$, all these particles are removed
51.85% of all particles entering are removed.

How to determine V_p?



$\Sigma F = 0$; $F_d = mg = \rho_p \frac{4}{3}\frac{\pi d^3}{8} g$

$F_d = 3\pi\mu V_p d$ (if laminar flow – $Re \le 1$)

$= C_D \frac{\pi d^2}{4}\rho_w \frac{V_t^2}{2}$

$C_d = f(Re)$ $\begin{cases} \approx 1.0 & Re = 100 \\ \approx 0.5 & Re = 500 \\ \approx 0.4 & Re = 2000 - 100{,}000 \end{cases}$

$Re = \frac{\rho_w V d}{\mu}$

Example $1\cdot10^{-3}$ m sphere, $\rho_s = 2.6\ g/mL$ what is V_p?

① assume laminar

$$V_p = \frac{\rho_p \frac{4}{3}\frac{\pi d^3}{8} g}{3\pi\mu d} = \frac{(1.3614\cdot10^{-6}\,kg)(9.8\,m/s^2)}{3\pi(10^{-3}\,N\cdot s/m^2)(1\cdot10^{-3}\,m)} = 1.41\ m/sec\ ;\quad Re = \frac{(1.41)(1\cdot10^{-3})}{1.51\cdot10^{-5}} = 93.3$$

$\therefore$ not laminar

② Use $Re = 100$, $C_D = 1.0$, solve for V_p

$$V_p^2 = \frac{2\rho_p \frac{4}{3}\frac{\pi d^3}{8} g}{C_D \frac{\pi d^2}{4}\rho_w} = \frac{2(1.36\cdot10^{-6}\,kg)(9.8\,m/s^2)}{(1.0)(\pi)\left(\frac{(1\cdot10^{-3})^2}{4}\right)(1000\,kg/m^3)} = 3.4\cdot10^{-2}\,m^2/s^2$$

$$V_p = 1.84\cdot10^{-1}\,m/s\ ;\quad Re = \frac{(1.84\cdot10^{-1})(1\cdot10^{-3})}{1.51\cdot10^{-5}} = 122$$

122 is close to 100
$\therefore V_p = 1.84\cdot10^{-1}\,m/s$

Disinfection

Inactivate pathogens. Chemicals used: Cl_2 (gas); $NaOCl$, $Ca(OCl)_2$
Thought to work by denaturing proteins & enzymes in pathogens because of strong oxidization properties. Principal disinfectant is hypochlorous acid

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

$$HOCl \rightarrow H^+ + \underline{\underline{OCl^-}}$$

$[HOCl]$ & $[OCl^-]$ free available chlorine. Added so there is residual (excess) free chlorine. To increase duration of residual ammonia is often added to create chloramines (another disinfectant) that last longer. Residual chlorine bound to ammonia is called <u>combined</u> available chlorine.

Chlorination produces harmful by-products (THM). Current strategy is to chlorinate just before distribution

Alternatives to chlorine are O_3 (ozone), ClO_2. Both powerful disinfectants - O_3 - no residual; ClO_2 may have toxic by-products

Hardness & Alkalinity

Hardness is caused by the presence of Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+} ... in water. Ca & Mg are largest proportion. Causes "boiler scale" and "soap curd". Scale because $CaCO_3$ & $Mg(OH)_2$ have reduced solubility at high temp.

$$\text{Hardness} = [Ca^{2+}] + [Mg^{2+}] + [Al^{3+}] + [Fe^{2+}] + \cdots \quad (\text{multi-valent} \oplus \text{ion})$$

Calculations made using equivalent weights

$1eq = \frac{MW}{n}$ n = valence number of compound involved

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$

$$MW = 40 + 12 + 3(16) = 100$$

$$\therefore 1eq = \frac{100g}{2} = 50g \quad \therefore \quad CaCO_3 \Rightarrow \frac{50g}{1eq.}$$

Eq. weight of Ca^{2+}

$$MW = 40, \quad 1eq = \frac{40g}{2} = 20g \quad \therefore \quad Ca^{2+} \Rightarrow \frac{20g}{1eq.}$$

In hardness & water softening calculations one converts from mg/L to mg/L as Ca

$$Y mg/L \text{ as } CaCO_3 = \frac{X mg/L \cdot 50 \, mg\, CaCO_3/meq \cdot n_x}{MW_x}$$

$$\text{Total hardness} = Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+} \quad (\text{as equivalents})$$

Fe^{2+} & Fe^{3+} are small but sometimes important components of water

$$Fe^{2+}\,mg/L \text{ as } CaCO_3 = \frac{Fe^{2+}\,mg/L \cdot 50\,mg\,CaCO_3/meq \cdot 2}{55.85} = 1.79\,Fe^{2+}\,mg/L$$

$\therefore$ To convert Fe^{2+} mg/L into Fe^{2+} mg/L as $CaCO_3$ multiply mg/L by 1.79

$$Fe^{3+}\,mg/L \text{ as } CaCO_3 = \frac{Fe^{3+}\,mg/L \cdot 50 \cdot 3}{55.85} = 2.69\,Fe^{3+}\,mg/L$$

In many references these conversions are tabulated for most important ion

<u>Carbonate & Non-carbonate hardness</u>

Carbonate hardness is that associated with HCO_3^- & CO_3^{2-}. It is removed by heating

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

In other words, carbonate hardness is that fraction of hardness (Ca^{2+}) that can combine with HCO_3^- & CO_3^{2-} in water to remove CO_3 species from water. Non carbonate is the remainder

<u>Alkalinity</u>

$$\begin{aligned} Alk. &= [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (\text{Molarity}) \\ &= HCO_3^- + CO_3^{2-} + OH^- - H^+ \quad (\text{Equivalents}) \end{aligned}$$

Example – find TH, Carbonate H, & Alk of:, TDS

Ca^{2+}	80 mg/L	Cl^-	100 mg/L	pH = 7.5
Mg^{2+}	30	SO_4^{2-}	201	
Na^+	72	HCO_3^-	165	
K^+	6			

$$\begin{aligned} TH &= Ca^{2+} + Mg^{2+} \\ &= \frac{80 \cdot 50 \cdot 2}{40} + \frac{30 \cdot 50 \cdot 2}{24} = 200\,mg/L \text{ as } CaCO_3 + 123\,mg/L \text{ as } CaCO_3 = 323\,mg/L \text{ as } CaCO_3 \end{aligned}$$

CH = amount of hardness that can precip. as $CaCO_3$

$$HCO_3^- = \frac{165 \cdot 50 \cdot 1}{61} = 135.24\,mg/L \text{ as } CaCO_3\ ;\ Ca^{2+} = 200\,mg/L \quad \therefore \text{ all } HCO_3^- \text{ can be used}$$

$$\therefore CH = 135.24\,mg/L$$

$$\begin{aligned} NCH &= TH - CH \\ &= 323 - 135.24 = 188\,mg/L \text{ as } CaCO_3 \end{aligned}$$

$Alk = HCO_3^- + CO_3^{2-} + OH^- - H^+$

$= 135.24\,mg/L + 0 + \underbrace{5\cdot10^{-4.5} + 5\cdot10^{-3.5}}_{negligible}$

$= 135.24\,mg/L$ as $CaCO_3$

$pH = 7.5$

$H^+ = 10^{-7.5}\,mol/L \cdot \frac{1000mg}{1mol}$

$= 10^{-4.5}\,mg/L$

$= \frac{10^{-4.5}\cdot 50.1}{1} = 5\cdot10^{-3.5}$

or

$= [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$

$= \frac{165}{61}\,mol/L + 0 + \underbrace{10^{-6.5} - 10^{-7.5}}_{negligible}$

$= \frac{165}{61}\,mol/L$

$pOH = 6.5$

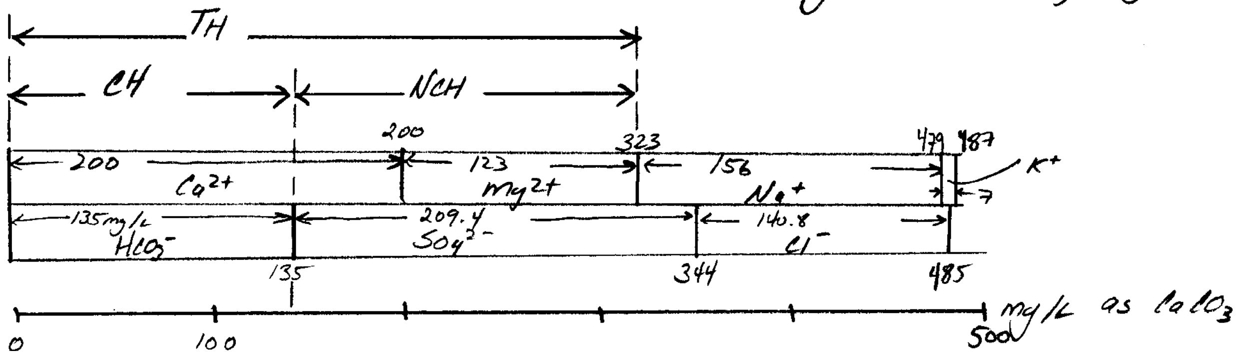
$OH^- = 10^{-6.5} \cdot \frac{1700mg}{1mol}$

$\approx 10^{-5.5}$

$\frac{10^{-5.5}\cdot 50.1}{17} = 5\cdot10^{-4.5}$

TDS sum of all dissolved compounds in mol/L

TDS = 80 + 30 + 72 + 6 + 100 + 201 + 165 = 654 mg/L (relatively high)



Softening

A water treatment process to reduce hardness.

lime-soda & ion exchange

lime-soda

add CaO (lime) or $Ca(OH)_2$ (hydrated lime) to remove bicarbonate

carbonate hardness

$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_{3(s)} + 2H_2O$ ppt

lime

Non carbonate hardness

$Ca(OH)_2 + Mg(HCO_3)_2 \rightarrow 2CaCO_{3(s)} + Mg(OH)_{2(s)} + 2H_2O$ ppt ppt

Usually use excess lime, then add soda ash Na_2CO_3 to remove excess lime

$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_{3(s)} + 2NaOH$

$2NaOH + MgSO_4 \rightarrow MgOH_{(2)} + Na_2SO_4$

Example Water

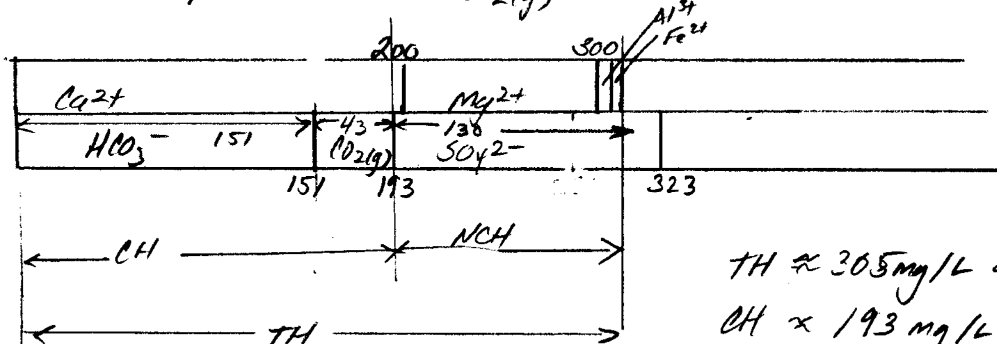
Ca^{2+}	80.2 mg/L	CO_3^{2-}	0 mg/L
Al^{3+}	0.5	HCO_3^-	185
Fe^{2+}	1.0	SO_4^{2-}	125
Mg^{2+}	24.3	CO_2	19
Na^+	46.0		

Find TH, CH, NCH, how much lime to remove CH., Soda Ash to remove NCH

- Express as mg/L $CaCO_3$

Ca^{2+}	200.25	HCO_3^-	151.7
Mg^{2+}	100.08	SO_4^{2-}	130
Al^{3+}	2.78	CO_3^{2-}	0
Fe^{2+}	1.79	$CO_{2(g)}$	43

$$\begin{array}{r} 151 \\ +\ 43 \\ \hline 193 \\ 130 \\ \hline 323 \end{array}$$



TH ≈ 305 mg/L as $CaCO_3$

CH ≈ 193 mg/L as $CaCO_3$

NCH ≈ 112 mg/L as $CaCO_3$

Add $Ca(OH)_2$ to remove CH.

① $CO_{2(aq)} + Ca(OH_2) \rightarrow CaCO_{3(s)} + H_2O$

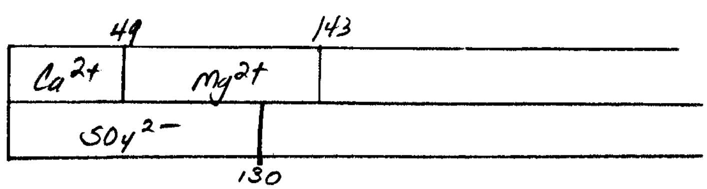
Need 43 mg/L lime as $CaCO_3$.

② $Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_{3(s)} + 2H_2O$

Need 151 mg/L lime as $CaCO_3$

∴ Add 194.8 mg/L lime as $CaCO_3$

After lime addition water is



Now add soda ash to use remaining Ca^{2+}

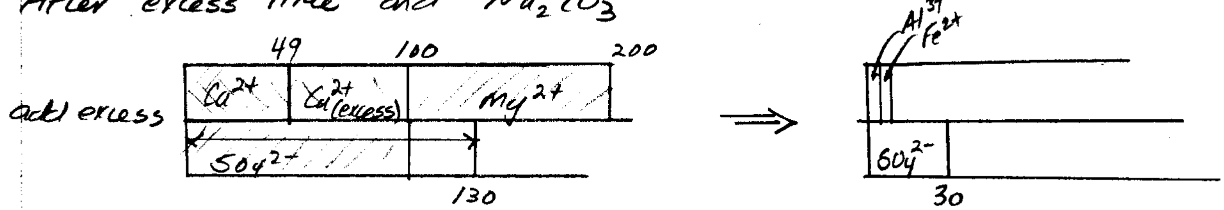
$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_{3(s)} + 2NaOH$

Need 49 mg/L Na_2CO_3 as $CaCO_3$, to use remaining Ca^{2+}

This will also remove 49 mg/L of $MgSO_4$ but need to remove 100 mg/L.

∴ Add 51 mg/L excess lime and 100 mg/L Na_2CO_3

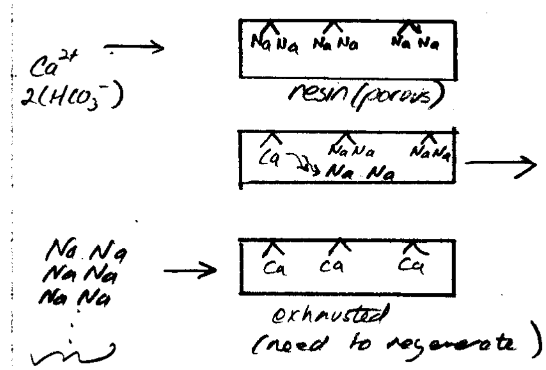
After excess lime and Na_2CO_3



Soda ash: precipitates 100 mg/L $CaCO_3$ and 100 mg/L $MgOH_{(s)}$

<u>Ion exchange</u>

Produces very high quality water



$Ca(HCO_3)_2 + Na_2R \rightarrow CaR + 2NaHCO_3$

Example

$Ca(HCO_3)_2$	137 mg/L as $CaCO_3$	
CO_2	0	
$MgSO_4$	72	

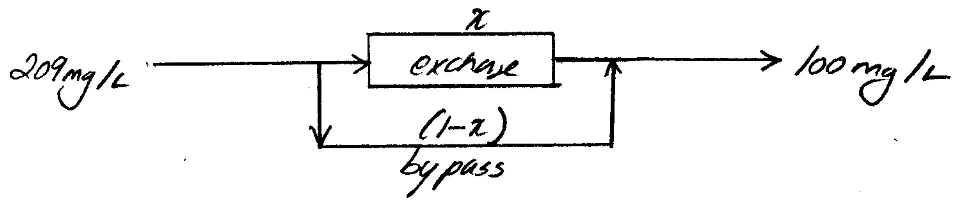
— how many pounds of salt required to regenerate ion exchange resin if exchange capacity 10,000 grain hardness/ft³

salt req. .5 lbs/1000 grains removed

W.Q. should be 100 mg/L hardness to dist.

Want to treat 10^6 gal/d

$\frac{10000 \text{ grains}}{ft^3} \cdot \frac{0.5 \text{ lb}}{1000 \text{ grain}} = \frac{5 \text{ lb salt}}{ft^3 \text{ resin}}.$



$\therefore \quad 209(1-x) + 0(x) = 100$

$1-x = 0.45$

$x = 0.52$

$Q_x = 10^6 \text{ gal}(0.52) = 0.52 \cdot 10^6 \text{ gal/day} = 0.52 \text{ MGD}$

$Q_{by} = 10^6 \; (.45) = 0.45 \cdot 10^6 \text{ gpd} = 0.45 \text{ MGD}$

Convert exchange capacity to mg/ft^3 of resin

$1 oz = 437.5 \text{ grain} = 28.35 \text{ grams}$

$\frac{10000 \text{ grain}}{ft^3} \cdot \frac{1 oz}{437.5 \text{ grain}} \cdot \frac{28.35 \text{ gram}}{1 oz} \cdot \frac{1000 mg}{gram} = 6.48 \cdot 10^5 mg/ft^3$ of bed

to treat $1 \cdot 10^6$ gal need to handle $0.52 \cdot 10^6$ gal through resin bed

$\therefore$ Need resin volume to treat $(0.52 \cdot 10^6 \text{gal})\left(\frac{209 mg}{L}\right)\left(\frac{3.785 L}{gal}\right) = 4.11 \cdot 10^8 mg$

$4.11 \cdot 10^8 mg \; \frac{1 ft^3}{6.48 \cdot 10^5 mg} = 634.8 ft^3$ of resin

Regeneration salt is $\frac{5 lbs}{ft^3 \text{ resin}} \cdot 634.8 ft^3 = 3174$ lbs salt / day

Summary : Need resin bed of $635 ft^3$ to deliver 1 MGD water
Need 3175 lbs NaCl/day to regenerate bed

<u>Other methods</u>

Distillation (use heat & vaccum) — phase change H_2O then recondense
— can produce extremely pure water. Uses lots of Btu's.

RO / UF Reverse osmosis, Ultrafiltration
Use a membrane as filter - designed to only pass H_2O and reject pollutants. Energy intensive; but rapidly developing. Expect to see large scale in USA in next decade.