CIVE 3331 - ENVIRONMENTAL ENGINEERING
Spring 2003

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Purpose: Lecture #10 CIVE3331

Water Quality Control

Water quality control concerns the engineering strategies that are used to treat and/or prevent pollution. It encompasses (in principle) everything from stormwater management to drinking water treatment to wastewater treatment.

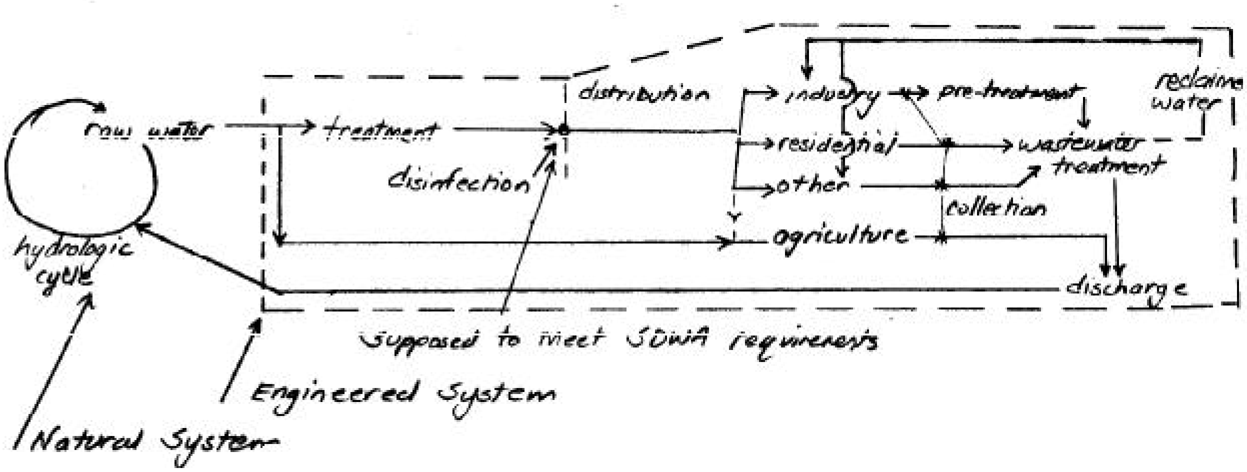


Figure 1. Schematic of Natural and Engineered Water System Orientation

Drinking water – SDWA requirements include various MCL standards for chemicals, radionuclides, microbiological indicators & “secondary standards” Very few, if any raw sources meet all these standards so some form of treatment is required.

<u>Typical Treatment Technologies</u>

1. Screening – to remove gross pollutants, trash, and flotables (see picture) - used in both drinking and wastewater industy.
2. Mixing coagulant chemicals (to improve settling rate) – uses a high-shear mixer and vigorous mixing.
3. Flocculation (low shear mixer) gentle mixing
4. Settling – the water rich slurry separates from the solids rich slurry. The solids rich slurry is sent to sludge handling facilities (later).
5. Filtration of the water rich slurry to further remove solids – usually uses a media (deep bed-type) filter.
6. Disinfection – inactivates pathogens.
7. Distribution (send water to customers).

Figure 2. Bar Screen

Figure 3. Mixing Vessel

Figure 4. Circular clarifier

Figure 5. Typical Media Filter Vessel

Screening

Coagulation/Flocculation

Natural solids have a negative surface charge. Coauglaunts nuteralize this surface charge so that particles can come together to form “flocs” that settle because of density differences (relative to the water). Common inorganic chemicals used are:

Alum

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

Ferric Chloride ($FeCl_3$)

Also many organic polymers are available for the same application, and work on the same general principle (functional groups handle the charge neutralization). Polymer dosage is still an area of serious vendor-user contention. Some polymers may not suitable for drinking water applications.

These chemicals “work” by binding ions so that particles no-longer repel each other – as in the drawing below.

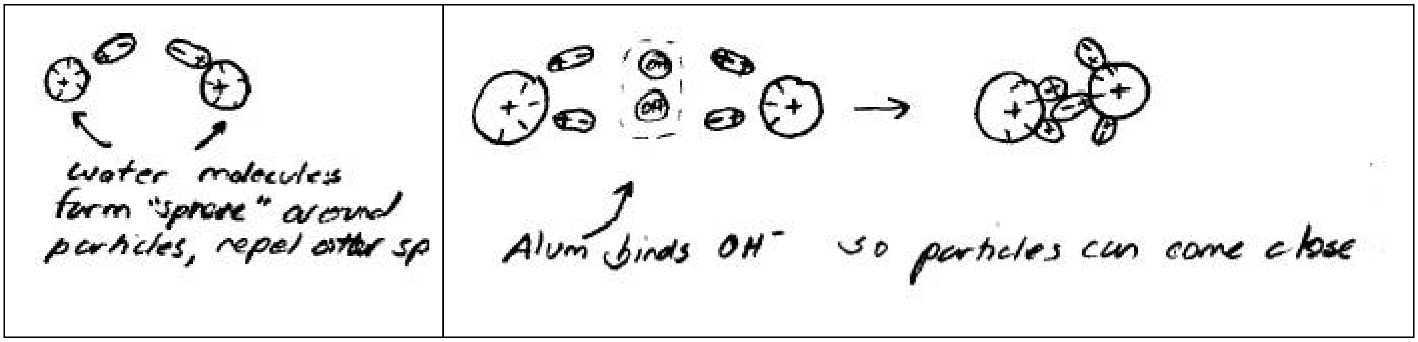


Figure 6. Coagulation process

Sedimentation

Once the flocs are created, particle size is increased and gravity forces overcomes the hydration effect and the flocs settle. Settling basins are designed so that the floc settles to the basin bottom before the water exits the basin (clarifier). The hydraulic retention time (V/Q) and the basin geometry are the basic design parameters controlling the size of particles removed and the overall efficiency of the clarification step.

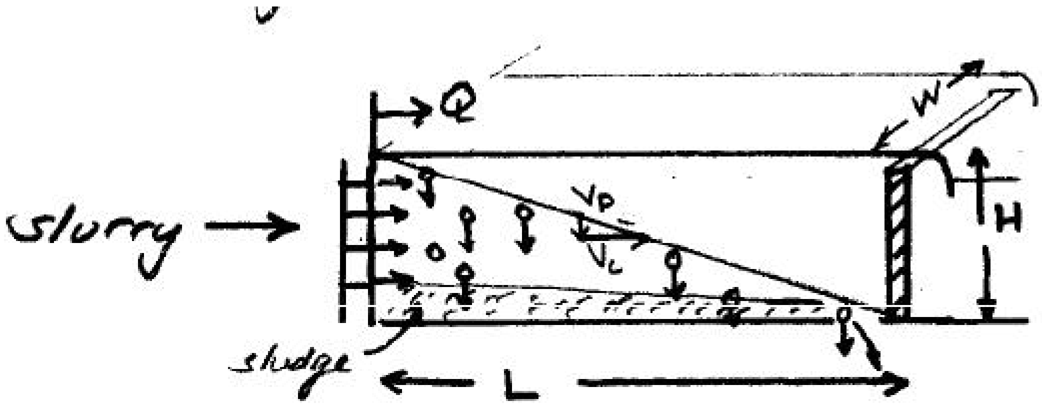


Figure 7. Generic clarifier concepts

Settling concepts – ideal basin.

Particle size determines Vp. Flow rate and geometry (Q,H,L,W) establish Vc, and the relationship of Vp and Vc determines the particle sizes that will be removed. The goal of sedimentation is not to remove all particles, but to remove particles of a certain size (and larger) then filter the rest. Complete particle removal by sedimentation is impractical if not impossible. The ideal basin assumes continuous particle removal from the bottom of the basin. In addition it assumes horizontal flow in the settling zone, uniform concentration of particles at the inlet. Particles are assumed to be removed from the basin, continuously, when they reach the bottom. Particles are assumed to settle discretely, without interference from other particles.

Vc is the “critical” velocity and is based on the surface loading rate, Vc = Q/Asurf. In the above sketch Asurf = L*W. Vp is the particle settling velocity, a function of the particle size. For particles with the property, Vp>Vc, the basin will remove all these particles. For particles with Vp<Vc only a fraction of these particles will be removed, Xr = Vp/Vc. As the particles get smaller, the fractional removal becomes negligible.

Example

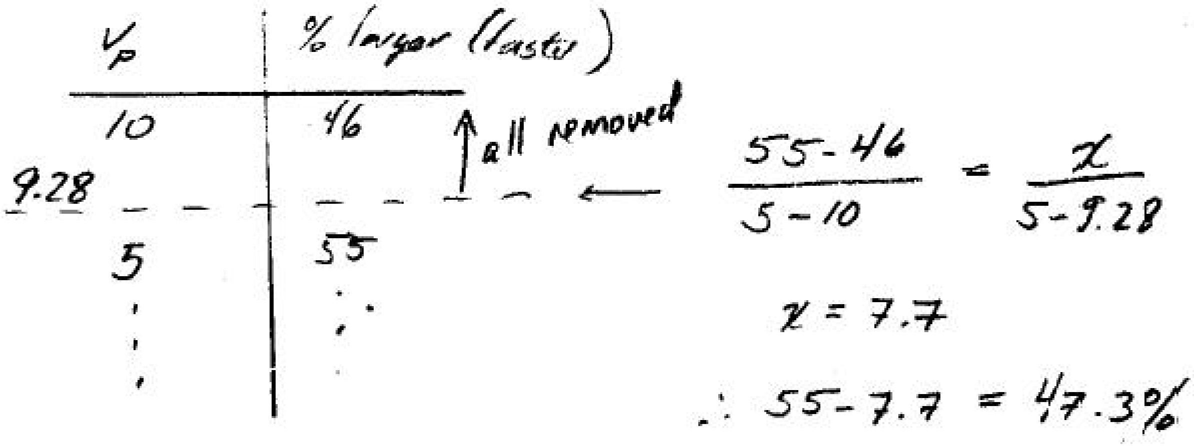
Suppose a settling tank is fed with a water with a slurry of grit sizes in the table below. The loading rate is 100,000 gal/sq.ft./day (Q/Asurf). Find the %-grit removal. Consider first, only particles with Xr =1 are removed, then consider fractional removal.

Vp(ft/min)	%-smaller	%-larger
10.0	54	46
5.0	45	55
2.0	35	65
1.0	20	80
0.75	10	90
0.50	3	97

Convert the surface loading rate into the cross flow (critical velocity) value:

Q/A = 100,000gal/sq.ft./day*1cu.ft./7.48gal*1day/1440min=9.28 ft/min

Thus the Vc=9.28 ft/min. So particles falling faster will be removed while those falling slower will not (remember first part is to ignore fractional removal). Now 9.28 falls between the 5.0 and 10.0 range of fall velocities so the fraction removed will be between the 46-55% lines (note, we need to look at %-larger because they fall faster).



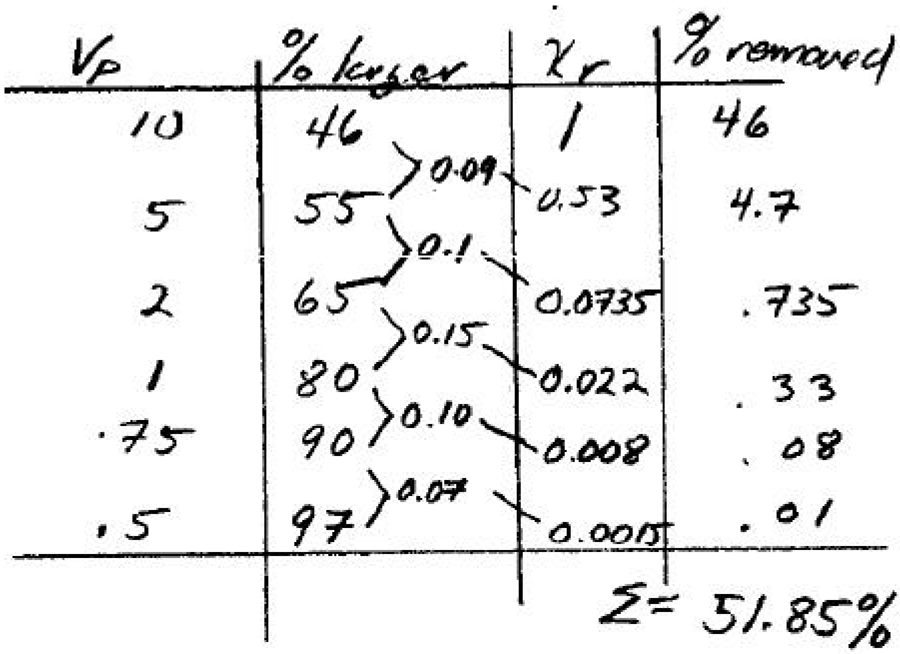
V_p	% larger (faster)
10	46
9.28	
5	55
⋮	⋮

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

$$x = 7.7$$

$$\therefore 55-7.7 = 47.3\%$$

Figure 8. %-removal calculation



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

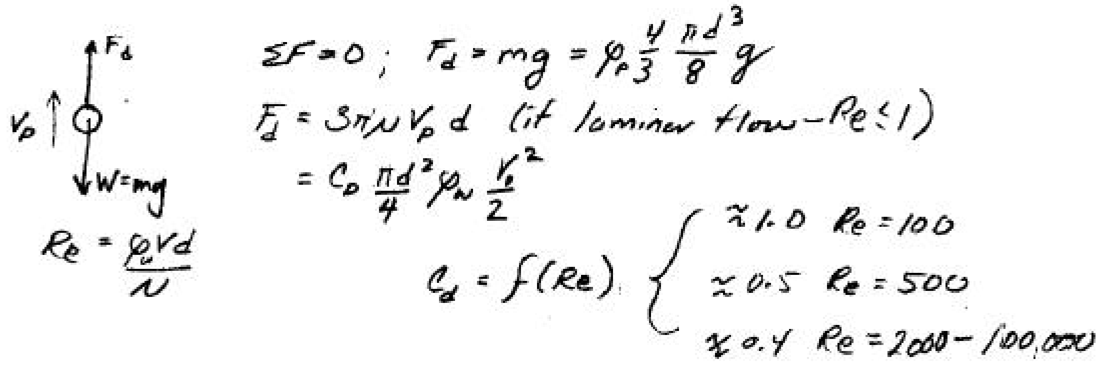
$$\Sigma = 51.85\%$$

Figure 9. Fractional removal calculations

Particle Fall Velocity

The next obvious question is how to determine fall velocity. Two considerations are used, the first is to assume Stokes Law is valid, calculate the vecloity and check the Reynolds number. If it is on the order of 1, then Stokes law is valid, of not then a more complicated model is used.

Figure # is a sketch of the force-balance concepts used.



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

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

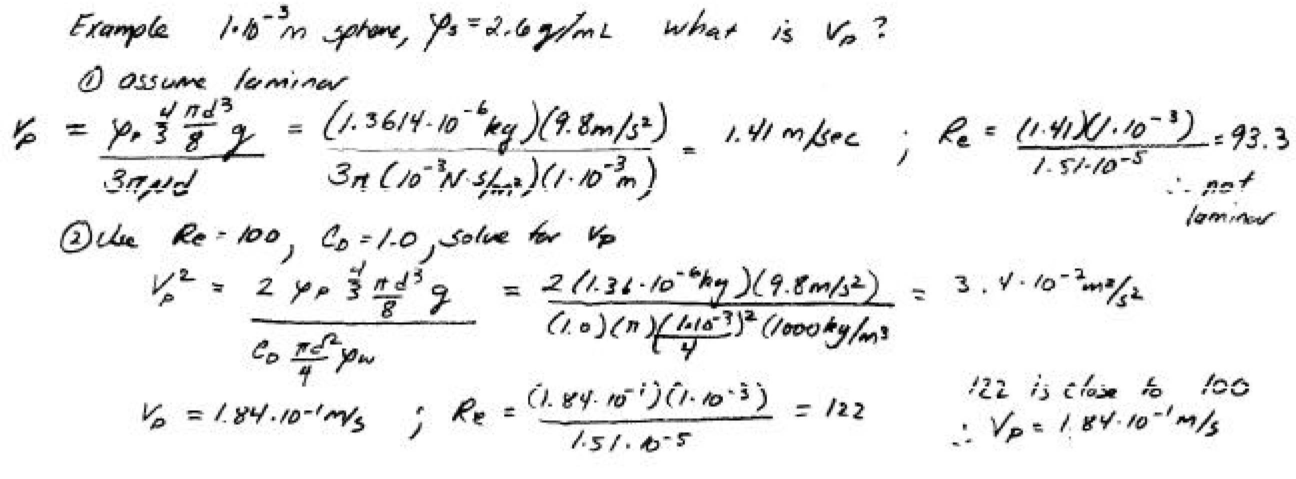
$F_d = 3\pi\mu V_p d$ (if laminar flow $- Re \le 1$)

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

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

Figure 10. Force-balance for particle settling

Once the settling velocities are established for different size ranges, then calculations like those above can be used to estimate clarifier performance.



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

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

$V_p = 1.84\cdot10^{-1}$ 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

Figure 11. Example fall velocity calculations

[Insert more particle theory and quadratic formulas from MWA Design manual in next update]

Disinfection

This process inactivates pathogens. The chemicals used are Cl_2(gas),NaOCl,$Ca(OCl)_2$. They are thought to work by denaturing proteins and enzymes in pathogens because of a strong oxidization action – but no-one really knows for sure. The principal disinfectant is hypochlorous acid.

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

$HOCl \Leftrightarrow H^+ + OCl^-$

The concentration [HOCl] and [OCl^-] is called the free available chlorine. The chemicals are added so that there is residual (excess) free chlorine in a water system. To increase duration of the residual ammonia is often added to create a chemicals called chloroamines (which are also disinfectants) that last longer is the distribution system. Residual chlorine bound to ammonia is called combined available chlorine.

Chlorination produces harmful by-products (suspected carcinogens) called tri-halomethanes (THM) and other disinfection by-products (DBP). Current strategy to limit these chemicals is to disinfect just before release of the water into the distribution system. On a side note, the number of people spared from disease by chlorination is millions of times larger than the number of people who might experience an adverse reaction to DBPs – on a risk weighted basis chlorine is the single most important contribution to public health ever. (DDT might be a close second).

Alternatives to chlorine are O_3 (ozone), ClO_2. Both are powerful disinfectants but O_3 has no residual and ClO_2 may produce toxic by-products. Iodine is also a legitimate disinfectant, but a significant number of the population is allergic to iodine, and it is rarely used for non-emergency disinfection.

Hardness and Alkalinity

[Typeset next revision – use scanned notes for time being]

Carbonate and Non-Carbonate Hardness

Softening

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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

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

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

[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.

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

Calculations made using equivalent weights

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

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

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

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

Eq. weight of Ca^{2+}

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

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

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

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

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

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

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

Fe^{3+} mg/L 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 io

Carbonate & Non-carbonate hardness

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

Alkalinity

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

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

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

TH = $Ca^{2+} + Mg^{2+}$

= $\frac{80 \cdot 50 \cdot 2}{40} + \frac{30 \cdot 50 \cdot 2}{24}$ = 200mg/L as $CaCO_3$ + 123mg/L as $CaCO_3$ = 323mg/L as Ca

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

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

∴ CH = 135.24 mg/L

NCH = TH − CH

= 323 − 135.24 = 188 mg/L as $CaCO_3$

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

$= 135.24\,mg/L + 0 + \underbrace{5\cdot 10^{-4.5} + 5\cdot 10^{-3.5}}_{negligible}$

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

pH = 7.5

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

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

$= \frac{10^{-4.5}\cdot 50\cdot 1}{1} = 5\cdot 10^{-3.5}$

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

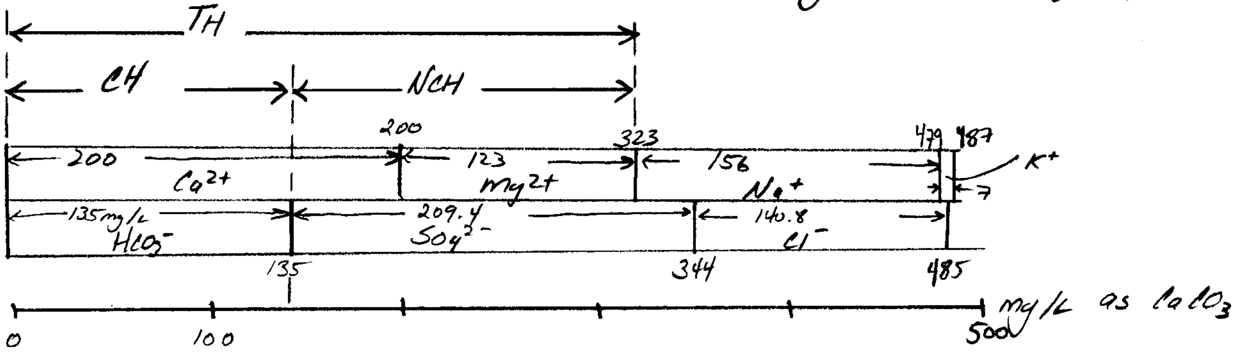
$OH^- = 10^{-6.5} \cdot \frac{1700mg}{1mol}$

$\approx 10^{-5.5}$

$\frac{10^{-5.5}\cdot 50\cdot 1}{17} = 5\cdot 10^{-4.5}$

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

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

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

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<u>Example</u> Water

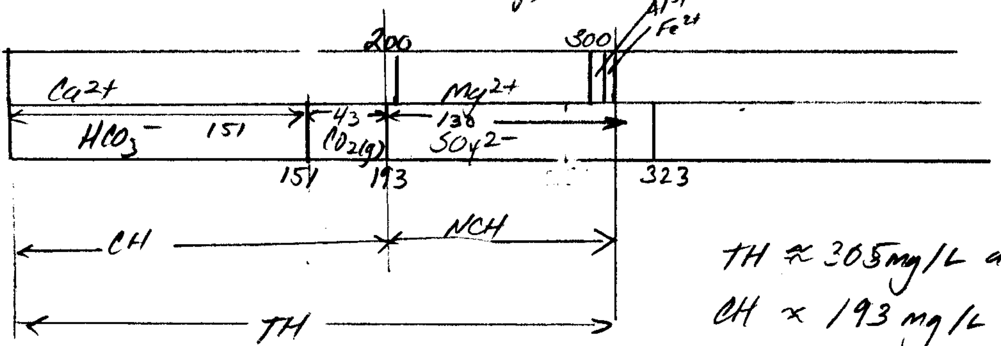
Ca^{2+}	80.2 mg/L	CO_3^{2-}	0 mg/L
Al^{3+}	0.5	HCO_3^-	185
Fe^{2+}	1.0	SO_4^{2-}	125
Mg^{2+}	24.3	CO_2	19
Na^+	46.0		

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

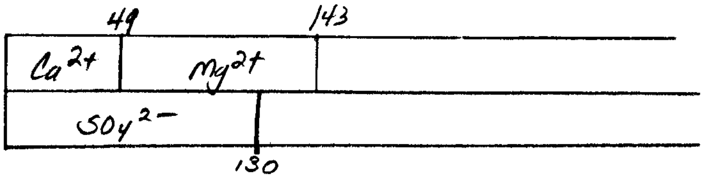
Need 43 mg/L lime as $CaCO_3$.

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



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

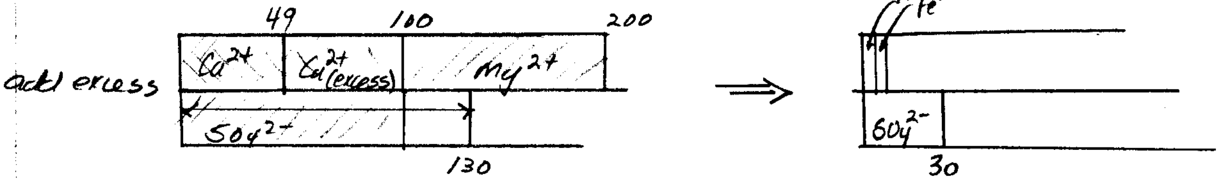
$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_{3(s)} + 2NaOH$

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

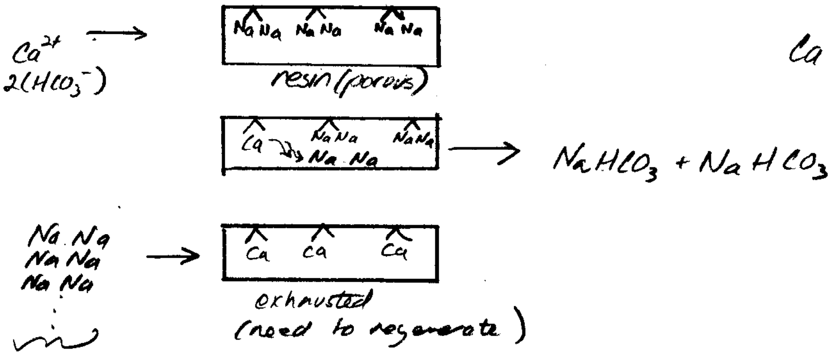
After excess lime and Na_2CO_3



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

<u>Ion exchange</u>

Produces very high quality water



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

Very concentrated brine, will displace Ca^{2+}

Example — how many pounds of salt required

$Ca(HCO_3)_2$ 137 mg/L as $CaCO_3$ to regenerate ion exchange resis

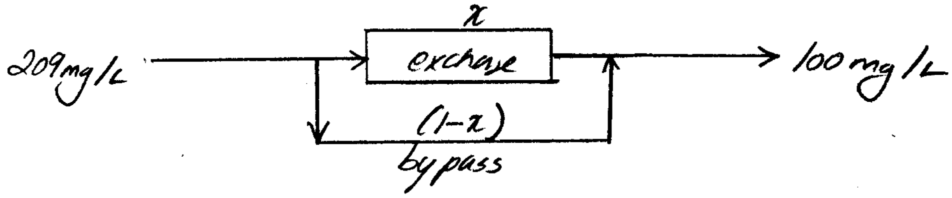
CO_2 0 if exchange capacity 10,000 grain hardness/

$MgSO_4$ 72 salt req. .5 lbs/1000 grains removed

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

Want to treat 10^6 gal/d

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



$$\therefore\quad 209(1-x) + 0(x) = 100$$
$$1-x = 0.45$$
$$x = 0.52$$

$$Q_x = 10^6\,gal\,(0.52) = 0.52\cdot10^6\,gal/day = 1.52\,MGD$$
$$Q_{by} = 10^6\,(.45) = 0.45\cdot10^6\,gpd = 0.45\,MGD$$

Convert exchange capacity to mg/ft^3 of resin

$1\,oz = 437.5\,grain = 28.35\,grams$

$$\frac{10000\,\text{grain}}{ft^3}\cdot\frac{1\,oz}{437.5\,\text{grain}}\cdot\frac{28.35\,\text{gram}}{1\,oz}\cdot\frac{1000\,mg}{\text{gram}} = 6.48\cdot10^5\,mg/ft^3 \text{ of bed}$$

to treat $1\cdot10^6\,gal$ need to handle $0.52\cdot10^6\,gal$ through resin bed

$\therefore$ Need resin volume to treat $(0.52\cdot10^6\,gal)\left(\frac{209\,mg}{L}\right)\left(\frac{3.785\,L}{gal}\right) = 4.11\cdot10^8\,mg$

$$4.11\cdot10^8\,mg\ \frac{1\,ft^3}{6.48\cdot10^5\,mg} = 634.8\,ft^3 \text{ of resin}$$

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

Summary: Need resin bed of $635\,ft^3$ to deliver 1MGD water

Need 3175 lbs NaCl/day to regenerate bed

Other methods

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.