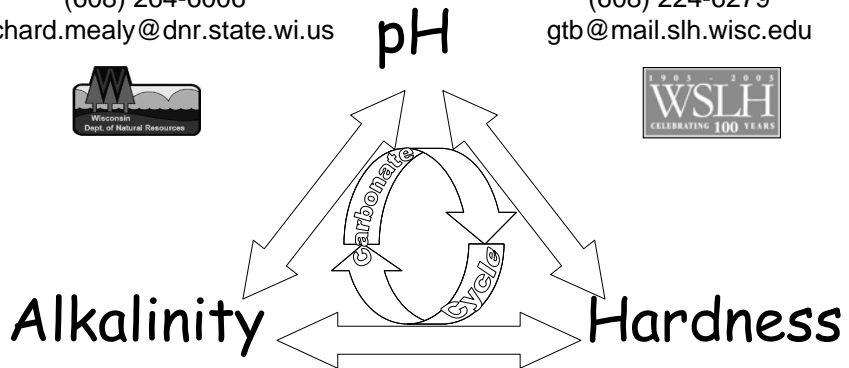


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Importance of
General Chemistry Relationships
in Water Treatment

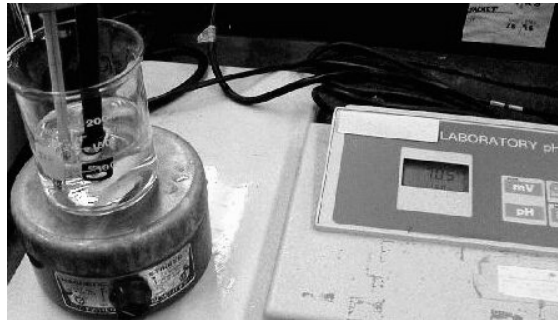
pH
Carbonate Chemistry
Alkalinity
Hardness
Effective Disinfection
 Basic chlorine systems
 Alternative disinfection
Arsenic
 Chemistry
 Treatment

Session Discussion Topics



pH

What is it
pH and temperature
How is it measured
Not as simple as you might think

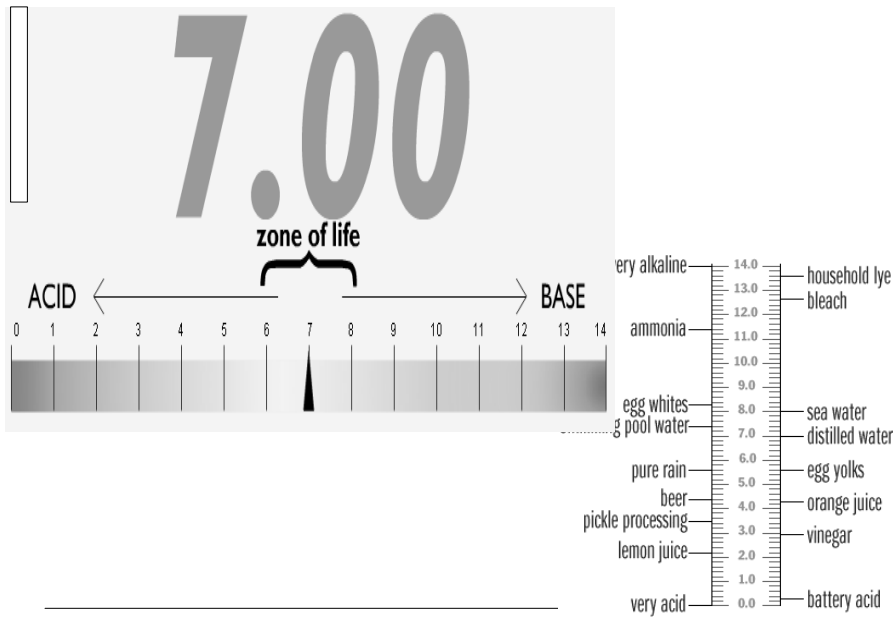


- pH is the term used universally to express the intensity of the acidity of a solution.
- More precisely, acids are defined as those compounds that release a proton (H^+ , hydrogen ion) whereas bases are those compounds that accept protons. Thus, pH is the measurement of hydrogen ion (H^+) activity.
- Pure water dissociates to yield equivalent concentrations of hydrogen [H^+] and hydroxide [OH^-] ions:



- The equilibrium for pure water is $[H^+] \times [OH^-] = K_w = 10^{-14}$
 $= 10^{-7} \times 10^{-7}$
- Therefore at equilibrium, $[H^+] = [OH^-] = 10^{-7}$ = **pH of 7**
- The scale ranges from 0 to 14 $[H^+] = 10^0$ to 10^{-14}

What is pH?



pH scale

- pH = "potential Hydrogen" ion concentration
- pH is usually expressed as $\log 1 / [H^+]$ or $-\log [H^+]$
- pH tells us whether a solution is acid, alkaline or neutral and relative acidity. It does not tell us how much acid or alkali is present.
- pH is a critical measurement. Life depends upon it. For instance, human blood is basic with a pH between 7.3 and 7.5.
 - If the blood pH drops < 7.3 , acidosis occurs (diabetes).
 - If blood pH rises > 7.5 , alkalosis occurs (Tums OD).
 - Below 7.0 and above 7.8, death occurs
- One unit in pH equals a 10x change in acidity.
 - Two units means 100 times change,
 - 3 units is 1000 times and so on.

pH

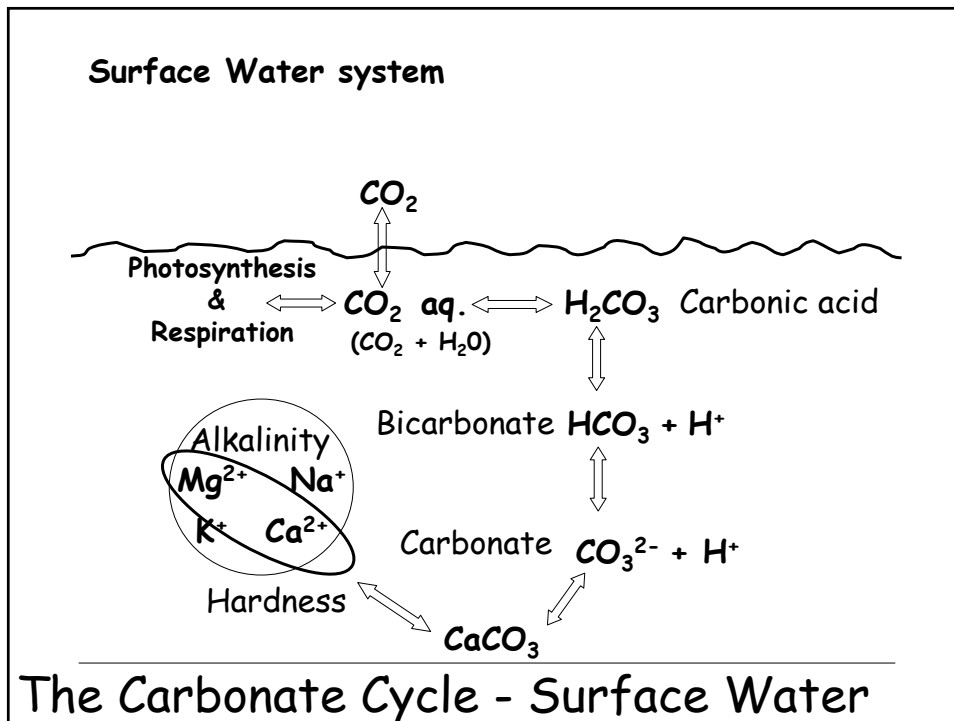
*** [OH ⁻] concentration ***		pH	*** [H ⁺] concentration ***	
(mol/L)	(mg/L)		(mg/L)	(mol/L)
1 x 10 ⁻¹⁴	0.0000000001	0	10000	1 x 10 ⁰
1 x 10 ⁻¹³	0.000000001	1	1000	1 x 10 ⁻¹
1 x 10 ⁻¹²	0.00000001	2	100	1 x 10 ⁻²
1 x 10 ⁻¹¹	0.0000001	3	10	1 x 10 ⁻³
1 x 10 ⁻¹⁰	0.000001	4	1.0	1 x 10 ⁻⁴
1 x 10 ⁻⁹	0.00001	5	0.1	1 x 10 ⁻⁵
1 x 10 ⁻⁸	0.0001	6	0.01	1 x 10 ⁻⁶
1 x 10 ⁻⁷	0.001	7	0.001	1 x 10 ⁻⁷
1 x 10 ⁻⁶	0.01	8	0.0001	1 x 10 ⁻⁸
1 x 10 ⁻⁵	0.1	9	0.00001	1 x 10 ⁻⁹
1 x 10 ⁻⁴	1.0	10	0.000001	1 x 10 ⁻¹⁰
1 x 10 ⁻³	10	11	0.0000001	1 x 10 ⁻¹¹
1 x 10 ⁻²	100	12	0.00000001	1 x 10 ⁻¹²
1 x 10 ⁻¹	1000	13	0.000000001	1 x 10 ⁻¹³
1 x 10 ⁰	10000	14	0.0000000001	1 x 10 ⁻¹⁴

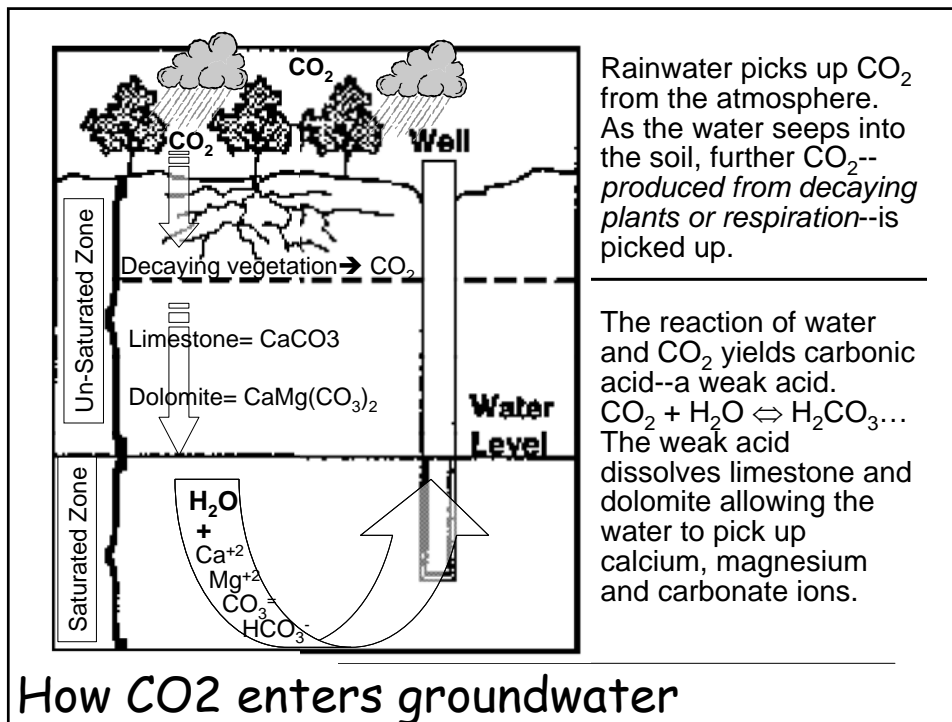
H⁺ concentration table another view

- pH is a measure of the available hydrogen ions (H⁺)
- pH is calculated as the negative log of the H⁺ concentration - log [H⁺]
- pH of n = a H⁺ concentration of 1 x 10⁻ⁿ
- pH describes a water's relative acidity, provides no measure of how the water will tolerate addition of acid or base to the system.
- pH is measured according to electrometric principles based on the Nernst equation. Temperature is the only variable.
- pH affects nearly every water and wastewater treatment function (wherever some chemistry is involved)

pH - what you need to know

Carbonate Chemistry





When carbon dioxide enters the water:

$$\text{CO}_2 \text{ (air, decaying OM)} \rightleftharpoons \text{CO}_2 \text{ (dissolved)} + \text{H}_2\text{O}$$

Some of the dissolved CO₂ hydrates (reacts with water) to form carbonic **acid** (H₂CO₃):

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$$

Carbonic acid will dissociate:

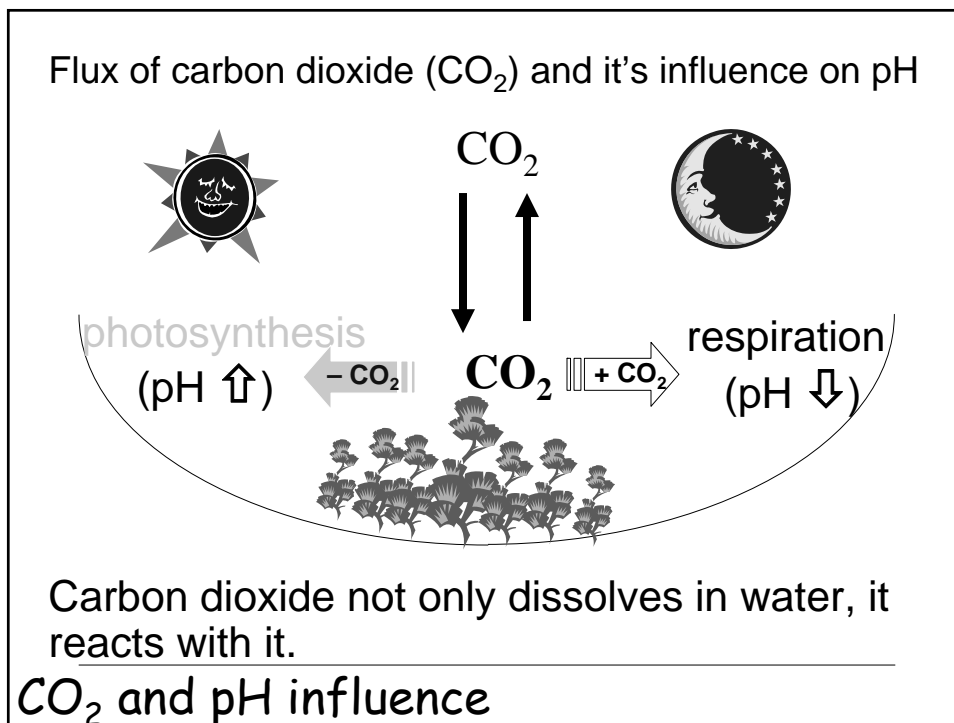
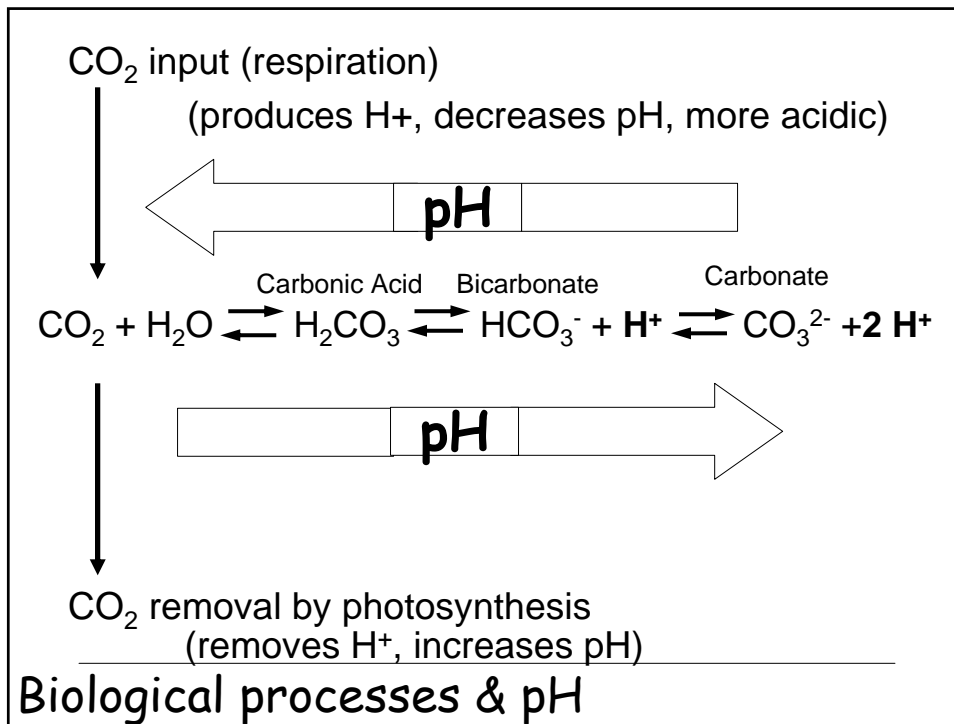
$$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$$

Forming bicarbonate and a free hydrogen ion

$$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$$

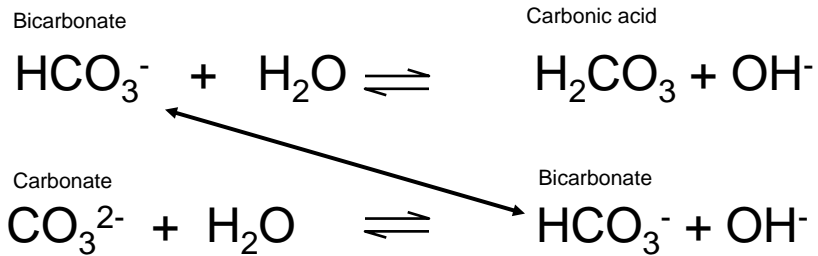
Bicarbonate further dissociates: to carbonate and a free hydrogen ion

CO₂ reactions



These reactions get a bit more complicated:

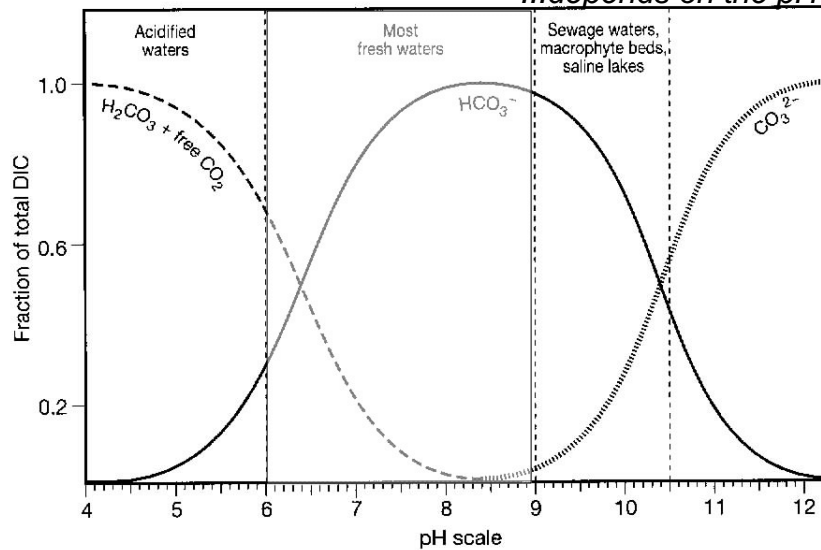
Also have reactions that result in the formation of the hydroxyl ion:



Further consideration: OH^-

Which form of carbon will dominate?

...depends on the pH



Carbon form vs. pH

Lakes/reservoirs (many western states) that have a lot of carbonate can resist changes in pH with the addition of acids

Ability to resist changes in pH with respect to the addition of acid is called

Alkalinity or
Acid neutralizing capacity (ANC)

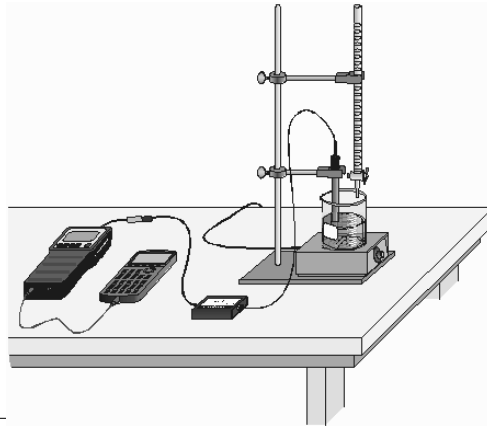
The Buffer System

- The carbonate system is dynamic
- The main formula is:
$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + 2 \text{H}^+$$
- Additions or reductions to any one side of the reaction will shift the reaction the opposite direction
- Respiration & photosynthesis affect this reaction by addition of or removal of CO_2
- Addition of CO_2 reduces the pH of a system
- Removal of CO_2 increases the pH of a system

Carbon Cycle - What you need to Know

ALKALINITY

- what is it?
- how is it measured?
- same as hardness?
- alkalinity affects on pH changes (treatment)
- acidity-alkalinity-pH chart



Alkalinity is a total measure of the substances in water that have "acid-neutralizing" ability. Alkalinity indicates a solution's power to react with acid and "buffer" its pH -- that is, the power to keep its pH from changing.

So... while pH measures the *strength* of an acid (base), alkalinity measures the ability to neutralize acid (base).

Mathematically, alkalinity can be determined by:

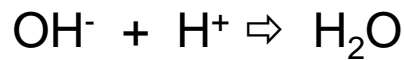
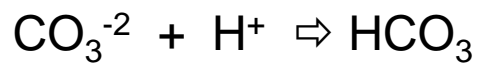
$$\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Alkalinity provides a buffering capacity to aqueous system. The higher the alkalinity is, the higher the buffering capacity against pH changes.

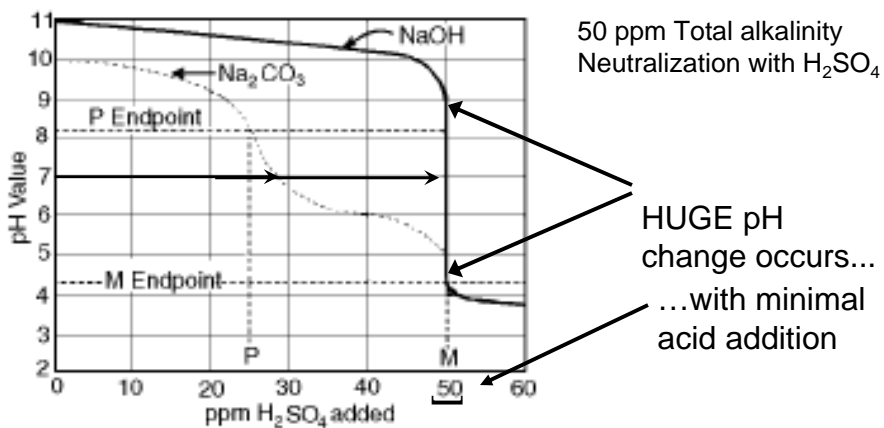
What is Alkalinity?

Alkalinity essentially becomes a measure of the buffering capacity of the Carbonate/Bicarbonate ions --- and to some extent---the hydroxide ions of water.

These 3 ions all react with H⁺ ions to reduce acidity, increasing alkalinity & pH



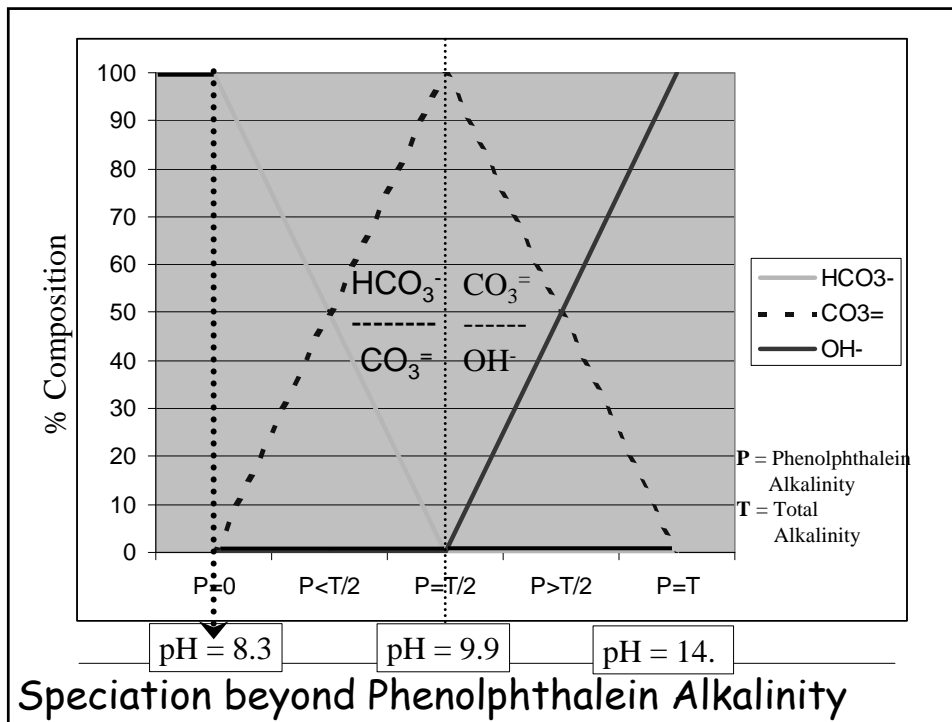
Alkalinity - closer look



Compare the neutralization of NaOH to that of Na₂CO₃

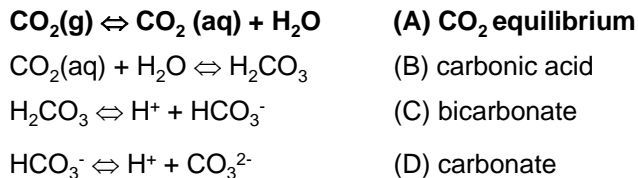
- If trying to control the pH of a process around pH=7
- Virtually impossible to use NaOH as the base
- SHARP inflection point (drop) of titration curve occurs pH 4.3 to 9

Alkalinity and NaOH neutralization



An aqueous solution that resists changes in pH when acid or base is added is known to have sufficient buffering capacity.

Atmospheric carbon dioxide produces a natural buffer and is the most important buffer system in water and wastewater treatment.



CO_2 in solution [$\text{CO}_2(\text{aq})$] is in equilibrium with atmospheric $\text{CO}_2(\text{g})$.

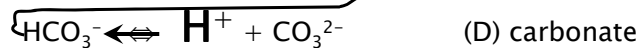
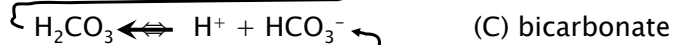
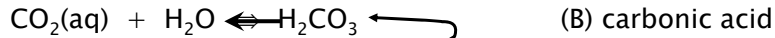
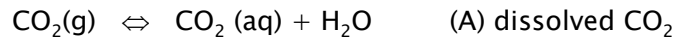
This is critical concept, because the change in any components in eqs. (B), (C), or (D) will disrupt that equilibrium causing CO_2 to either be released or to be dissolved into solution.

Buffering and the Carbonate System

If acid is added: H^+ increases in the system. This drives eq. (D) towards left thereby forming more bicarbonate.

The bicarbonate further combines with H^+ and forms carbonic acid [eq. (C)], which dissociates to CO_2 and water.

The excess carbon dioxide is then released to atmosphere.



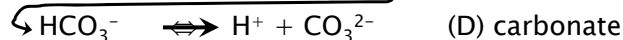
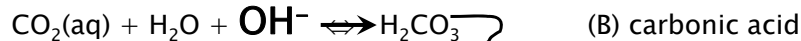
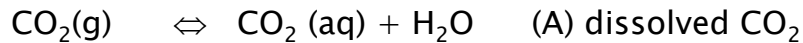
pH ↑

If CO_2 is stripped out from the system: The above reactions also shift towards left. CO_2 is removed from the solution.

The pH will increase

Buffering and Carbonate System

If base is added: H^+ is consumed in the system. This drives above eqs. towards right direction. This therefore converts the gaseous carbon dioxide to carbonate.



pH ↓

If CO_2 is bubbled into the system: The above reactions also shift towards right due to formation of carbonic acids. This is because CO_2 will combine with water. The pH will decrease.

Buffering and Carbonate System

<u>Chemical</u>	<u>Effect on pH</u>	<u>Effect on Alkalinity</u>
NaOH (caustic soda)	Increase	+1.55 mg/L as CaCO ₃ per mg/L
Ca(OH) ₂ (Lime)	Increase	+1.21 mg/L as CaCO ₃ per mg/L
NaHCO ₃ (sodium bicarbonate)	small increase	+0.60 mg/L as CaCO ₃ per mg/L
Na ₂ CO ₃ (soda ash)	moderate increase	+0.90 mg/L as CaCO ₃ per mg/L

Chemical Additions to Increase Alkalinity

- Alkalinity is a measure of a water's ability to resist pH changes
- Alkalinity is based on carbonate chemistry
- Alkalinity is expressed as mg/L as calcium carbonate (CaCO₃)

Alkalinity: What You Need to Know

HARDNESS

what is it?
how is it measured?
scale formation
preventing scale formation

Hardness is a chemical parameter of water that represents the total concentration of calcium and magnesium ions. Calcium typically represents 2/3 of total hardness; Mg typically about 1/3.

...is commonly confused with alkalinity. The confusion relates to the term used to report both measures, mg/L CaCO₃.

If limestone is primary source of both hardness and alkalinity, the concentrations will be similar if not identical.

Hardness is sometimes expressed in grains per gallon (water treatment industry), but **usually as parts per million (ppm) as calcium carbonate equivalent.**

The degree of hardness standard as developed by the Water Quality Association (WQA) is:

Term	Grains/gallon	mg/L or ppm
Soft	Less than 1.0	less than 17.1
Slightly Hard	1.0 to 3.5	17.1 to 60
Moderately Hard	3.5 to 7.0	60 to 120
Hard	7.0 to 10.5	120 to 180
Very Hard	10.5 and above	180 and above

NOTE: 1 grain/gal = 17.1 ppm or mg/L as CaCO₃

Hardness - What is it?

Hardness is reported in several ways, most typically:

As mg/L as calcium carbonate (CaCO₃)

Regardless of source, reported as equivalent weight of CaCO₃)

As grains per gallon (gpg)

1 grain = 0.06479891 gram (g) = 64.79891 milligrams (mg)

1 gallon = 3.7854 L

$$\frac{64.79891 \text{ mg}}{\text{grain}} \times \frac{1 \text{ gallon}}{3.7854 \text{ Liters}} = 17.1 \text{ mg/L as CaCO}_3$$

As German degrees of hardness (dGH)

1dGH (German scale) = 10 mg/liter CaO

Atomic Weight Ca = 40, O = 16, CaO = 56

So 10 mg/L CaO contains (40/56) * 10 = 7.143 mg/liter of Ca

Atomic weight CaCO₃ = 100

So 7.143 mg/liter of elemental Ca would be expressed as

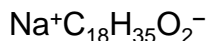
$$100/40 * 7.143 = 17.8575 \text{ mg/liter(ppm)CaCO}_3$$

Hardness and conversion factors

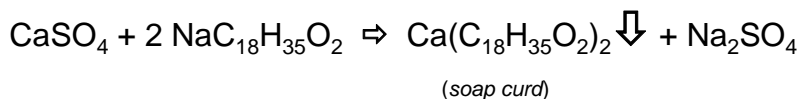
It is called hardness because if calcium and magnesium are present in your water, making a lather or suds for washing is "hard" (difficult) to do. Thus, cleaning with hard water is hard.

How do people decide when it's time to add salt to their water softener???

Common soap is a sodium salt of a fatty acid, stearic acid:

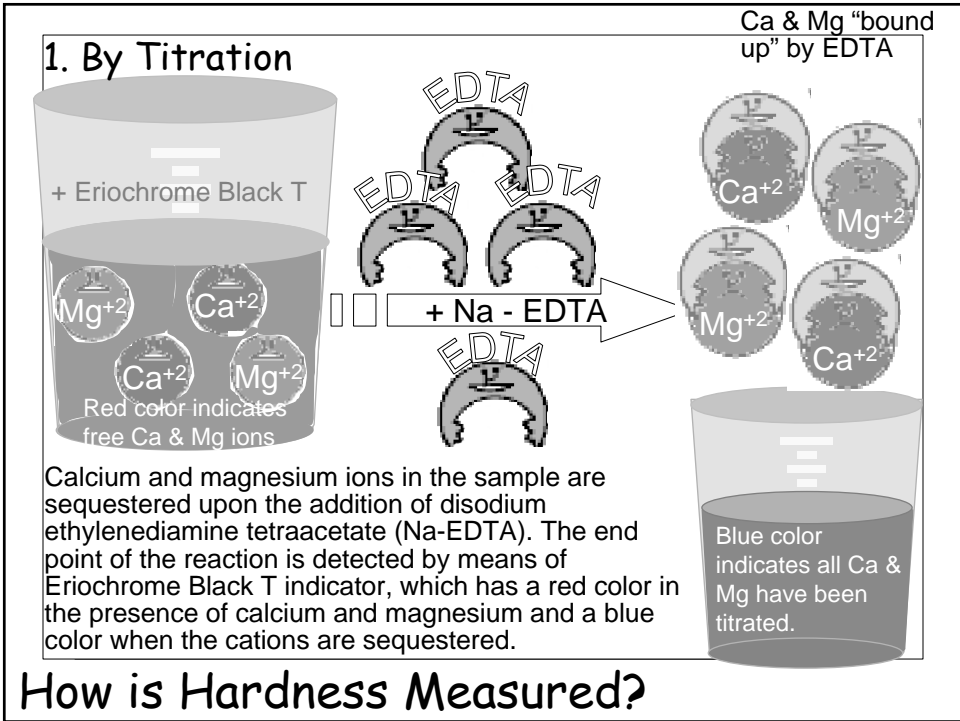
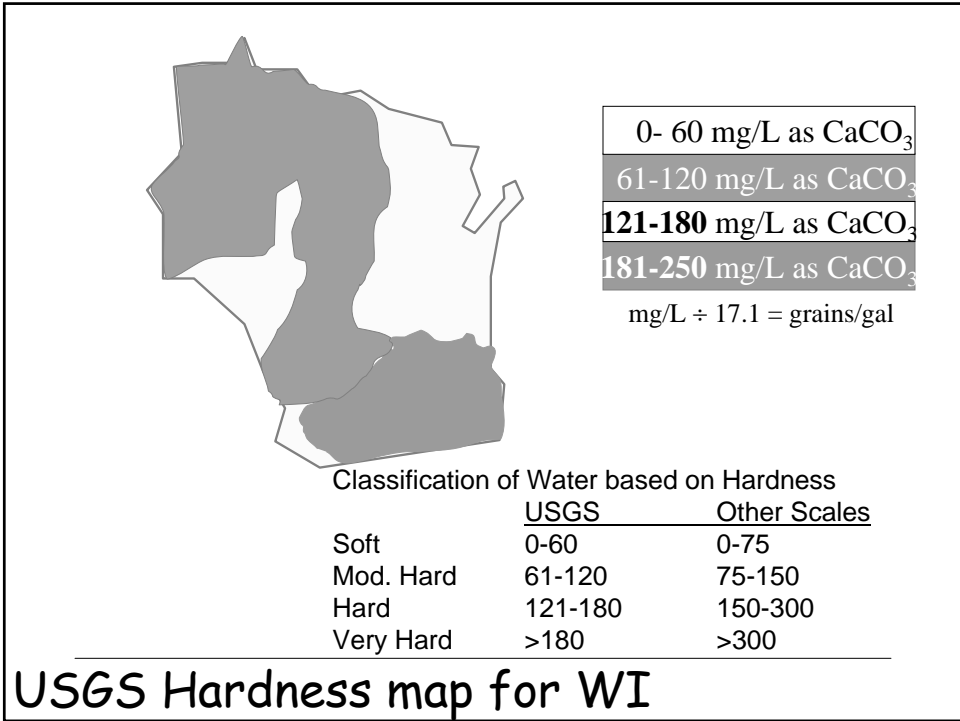


Soap reacts with Calcium (Magnesium) salts to form soap "curd"



Hard water is naturally likely to also have a high pH, because it is also high in carbonates that buffer the pH toward the alkaline side (due to carbonate hardness)

Why "hardness"?





- lowers toxicity of some metals (Pb, Cd, Cr, Zn)



- causes precipitation of other metals, thereby reducing their bioavailability



- hard water requires more soap and synthetic detergents for laundry and washing



- causes scaling in boilers and industrial equipment

Hardness - Impact

The white solid "scale" that can appear on plumbing components is calcium carbonate or CaCO_3 . If a water is supersaturated with calcium carbonate, then hardness scale can precipitate.

What problems can scale cause?

- Valves can leak if calcium carbonate salt crystals develop inside the valve, preventing it from sealing properly.
- Solenoid valves can leak when scale forms inside.
- Scale buildup inside flow switches makes them stick. This can cause actual leaks to go undetected or false alarms when there is no leak.
- Aesthetically, hard water deposits leave stains and build-up on the outside of valves and connections.

Hardness & Scale formation

Avoiding Scale Problems

If the Langelier Index calculation yields a positive index scaling problems can be avoided by:



- **Demineralization, Reverse Osmosis, distillation, or deionization.** Removing the dissolved minerals will lower the hardness.
- **Softening.** Water softening or cation exchange will reduce the calcium and magnesium concentrations in water.
- **Acidification.** Lowering the actual pH of the water to below the saturation pH_s will prevent scale deposits.
- **Low Temperature.** Avoiding high temperatures where scale formation is more likely will prevent scale deposits.



Hardness - Avoiding scale

- Has been used successfully by groundwater systems serving < 3,000
- Unlikely to be suitable for treating groundwater in systems serving fewer than 500 people unless those systems have a trained operator able to continually monitor the process.
- Add either hydrated lime [$Ca(OH)_2$] or quicklime [CaO]
- Goal: raise the pH of the water to about pH 10 to precipitate calcium carbonate ($CaCO_3$) and, if necessary, magnesium hydroxide [$Mg(OH)_2$] (requires raising pH to about 11).
- Need to pilot test each system on a small-scale
- Lime-softened water has high causticity and scale-formation potential;
- Re-carbonation is employed to reduce pH and mitigate scaling of downstream processes and pipelines.
- Onsite combustion generation of carbon dioxide (CO_2) or liquid CO_2 is the most common source of carbon dioxide for recarbonation.
- Best suited to groundwater sources with very stable water quality.

Lime Softening

Laundering --

- Fabrics washed in hard water wear out up to 15% quicker (Purdue, 1991)
- Colors fade & whites darken more quickly when cleaned with hard water.
- Laundry washed in hard water became re-soiled with greater ease.

Hard Water Scale --

- Can decrease the life of toilet flushing units by 70% (AWWA).
- Can decrease the life of water faucets by 40% (AWWA).
- Shortens life of dishwashers and clothes washers by as much as 30%.

Water Heater Efficiency --

- Can reduce a gas water heater's efficiency by as much as 29%,
- Can reduce an electric water heater's efficiency by as much as 21%.
- Water heater's useful life can be reduced by as much as 50 % . (USDI)

Cleaning Tasks --

- Time required for typical cleaning tasks was increased by almost 50%.
- Can result in streaks, spots and film on glass and dishware.
- Soap curd film on the body can leave skin dry and hair dull and limp.

Hardness - Facts and figures

- Due to natural geology, hardness is generally a problem in Wisconsin
- Scale formation can cause problems throughout a system
- It's the same CaCO_3 that causes scale that is also the source of most of a water's alkalinity.
- Hardness can result in precipitation of some toxic metals, lowering their bio-availability
(*Hardness is considered when establishing WPDES discharge permit limits for metals*)
- Any technique that will remove calcium and magnesium ions will reduce hardness

Hardness: What You Need to Know

- Langelier (Saturation) Index (LSI, LI) is most commonly used
- Aggressive Index is also used.
- These equations estimate the theoretical tendency [of a water] to precipitate a protective coating of calcium carbonate (CO_3^{-2}) on a pipe wall.
- Under-saturated water is corrosive (Negative LSI/ aggressive)
- Over-saturated water will deposit CaCO_3 (Positive LSI / Not aggressive)
- A thin layer (of CaCO_3) is desirable as it keeps water from contacting the pipe, thereby reducing chance for corrosion.

Corrosivity Indices

1. Determine the pH at which CaCO_3 is saturated

$$\text{pH}_{\text{S}=\text{CaCO}_3 \text{ saturation}} = (9.3 + \text{A} + \text{B}) - (\text{C} + \text{D})$$

$$\text{A} = \frac{(\log \text{TDS}) - 1}{10}$$

$$\text{B} = [-13.12 \times (\log \text{ } ^\circ\text{C} + 273)] + 34.55$$

$$\text{C} = (\log [\text{Ca}^{+2}] \text{ mg/L as } \text{CaCO}_3)] - 0.4$$

$$\text{D} = (\log [\text{Alkalinity}] \text{ mg/L as } \text{CaCO}_3)$$

2. Compare actual pH to pH at which CaCO_3 is saturated

$$\text{LSI} = \text{pH} - \text{pH}_{\text{s}=\text{CaCO}_3 \text{ saturation}}$$

3. Actual pH < saturation pH = increasing corrosivity
Actual pH > saturation pH = Tends to deposit CaCO_3

Langelier Index Explained

Factors Affecting LSI

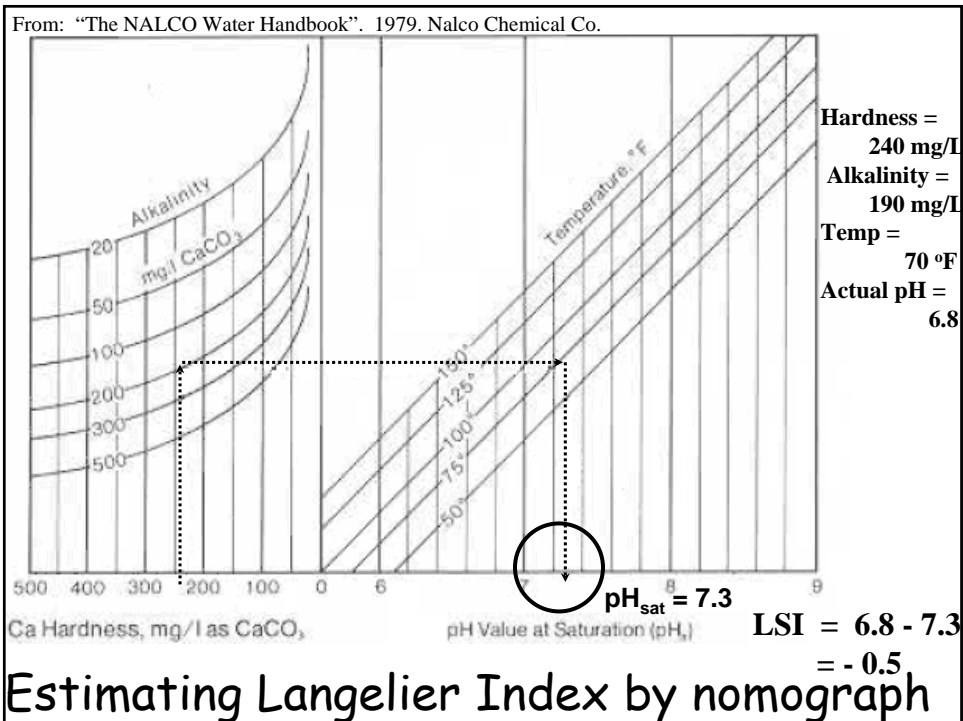
LSI will Increase (reduce corrosivity) in value if:

- Calcium hardness is increased
- pH is increased
- TDS is increased (if increase in TDS is due to Ca/Mg)
- Alkalinity is increased
- Temperature is increased

A change in pH has greatest impact on LSI

Ideal LSI = -0.50 to + 0.50

Langlier Index -Factors Affecting It



(Actual)pH=7.26
Temp=20°C
TDS=400

Hardness=310
Alkalinity= 130

1. Determine the pH of carbonate saturation (pH_{sat})

- Need actual pH, water temp, alkalinity, hardness
- convert data into the four variables: A,B,C,D

Temperature Variable
Water Temp
(° C/F) "A"

0 / 32	2.60
4 / 39	2.50
8 / 46	2.40
12 / 53	2.30
16 / 60	2.20
20 / 68	2.10
22 / 72	2.06
25 / 77	2.00
30 / 86	1.90
35 / 95	1.80
40 / 104	1.70
50 / 122	1.55

TDS Variable
TDS (mg/L) "B"

0	9.70
25	9.72
50	9.74
100	9.77
200	9.83
400	9.86
600	9.89
1000	9.90
≥ 1300	9.99

Hardness/ Alkalinity Variable

Hardness (mg/L)	"C"
Alkalinity (mg/L)	"D"
10	1.00
20	1.30
30	1.48
40	1.60
50	1.70
60	1.78
70	1.84
80	1.90
100	2.00
130	2.11
150	2.18
175	2.24
200	2.30
250	2.40
310	2.49
400	2.60
500	2.70
600	2.78
700	2.84
800	2.90
900	2.95
1000	3.00

$pH_{sat} = A + B - C - D$
 $pH_{sat} = 2.10 + 9.86 - 2.49 - 2.11 = 7.36$

Langlier Index = $pH_{actual} - pH_{sat}$
 Langlier Index = $7.26 - 7.36 = -0.10$

LSI Scale	Potential
- negative	No scale potential. Corrosive.
less than zero	Water will dissolve $CaCO_3$
+ positive	Scale can form
greater than zero	$CaCO_3$ precipitation may occur.
close to zero	Borderline scale potential. Water quality and temperature changes, or evaporation could change the index.

TDS can be estimated as 40% of EC

Langlier Index formula

Aggressive Index - Corrosion index calculated from pH, calcium hardness and total alkalinity.

$pH_{actual} + C + D = \text{Aggressive Index}$
 $7.26 + 2.49 + 2.11 = 11.86$

Characteristic	Aggressive Index
Non-Aggressive	> 12.0
Moderate Aggressive	10.0 to 11.9
Highly Aggressive	< 10.0

Since Hardness is typically gonna be ~ 150-250 ppm in WI, the "C" factor will range from 2.2 to 2.5

Alkalinities in WI typically range from 100-150 ppm, thus the "D" factor will range from 2.00 to 2.18.

Therefore, C + D ranges from 4.2 to 4.7
 This means that waters of pH 7.3 to 7.8 and above --or typical for most WI water sources-- will generally be NON-Aggressive. Instead of corrosion, scale formation is of concern.

Hardness/ Alkalinity Variable

Hardness (mg/L)	"C"
Alkalinity (mg/L)	"D"
10	1.00
20	1.30
30	1.48
40	1.60
50	1.70
60	1.78
70	1.84
80	1.90
100	2.00
130	2.11
150	2.18
175	2.24
200	2.30
250	2.40
310	2.49
400	2.60
500	2.70
600	2.78
700	2.84
800	2.90
900	2.95
1000	3.00

Aggressive Index

- There are a number of formulae/equations available to estimate a water's corrosivity
- Corrosivity indices measure a water's ability to either precipitate out or dissolve CaCO_3 (corrosive)
- Both extremes of the scale cause problems
- EPA generally uses Langelier Index for drinking water systems
- Aggressive Index is much easier to calculate (need less data)

Corrosivity/Aggressiveness: What You Need to Know

- The carbonate cycle is dynamic process.
- Photosynthesis & respiration can change the pH of a system by adding or removing CO_2 .
- pH affects many aspects of water treatment including: disinfection, scale formation and corrosion potential.
- The interaction among pH, alkalinity and hardness has far reaching effect on water treatment.
- A basic knowledge of general water chemistry relationships can provide a better understanding of water treatment processes.
- Don't worry about equations & formulas--*that's what books are for*. It's far more important to understand the processes behind the equations.

Summary

CO_2	Carbon dioxide
H_2CO_3	Carbonic acid
CO_3^{2-}	Carbonate
HCO_3^-	Bicarbonate
$\text{Ca}(\text{HCO}_3)_2$	Calcium bicarbonate
CaCO_3	Calcium carbonate
H^+	Hydrogen ion
OH^-	Hydroxyl ion
PO_4^{3-}	Phosphate ion

Acronyms

Effective Disinfection

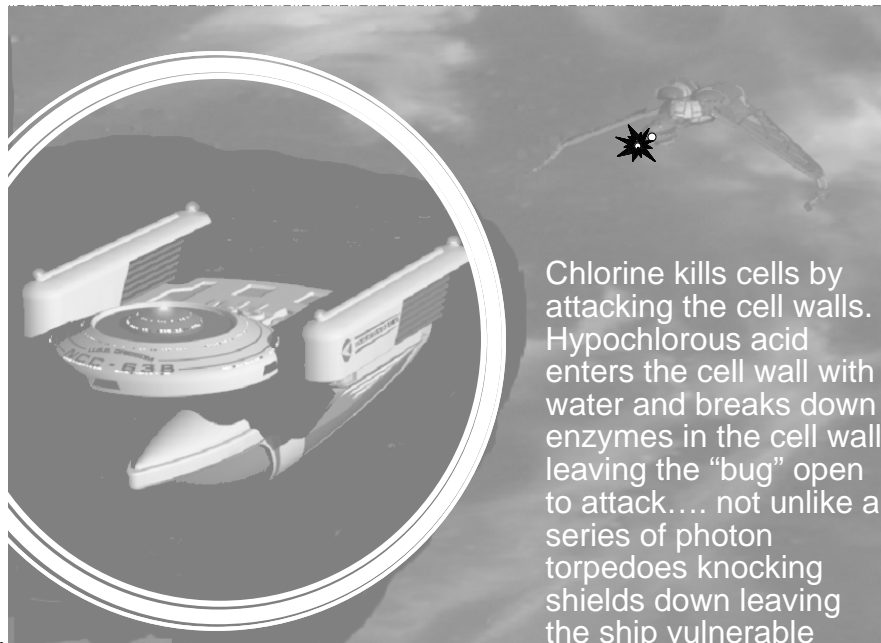


- kill the bugs

Disinfection
(Chlorination)

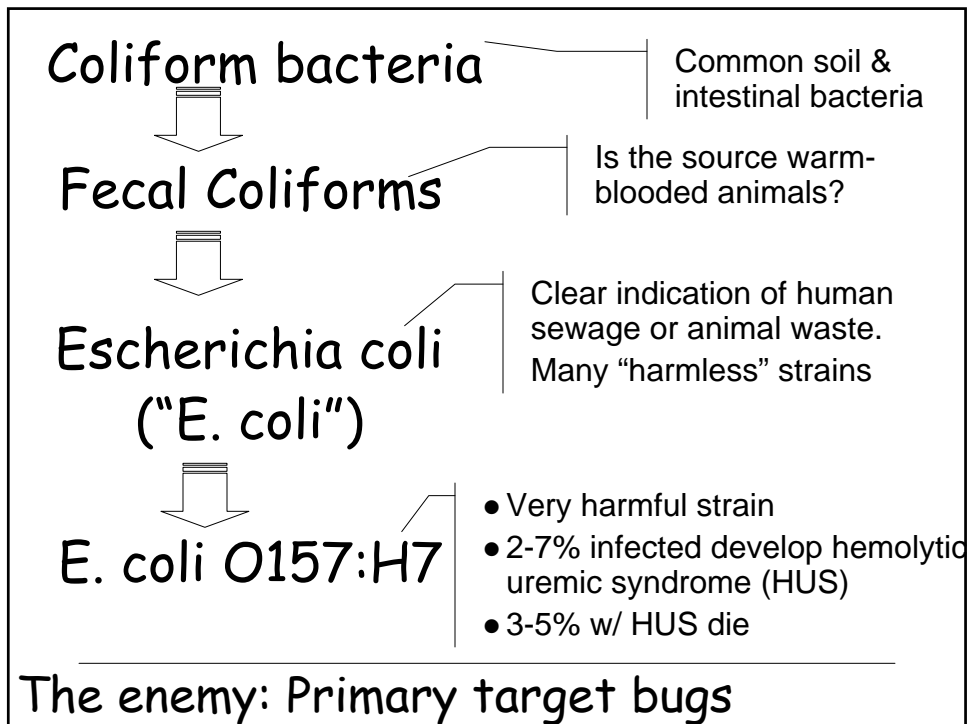


Focus Point: Disinfection



Chlorine kills cells by attacking the cell walls. Hypochlorous acid enters the cell wall with water and breaks down enzymes in the cell wall, leaving the "bug" open to attack... not unlike a series of photon torpedoes knocking shields down leaving the ship vulnerable

How does chlorine kill?



Chlorine gas rapidly hydrolyzes to hypochlorous acid according to:

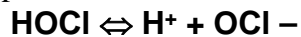


Aqueous solutions of sodium or calcium hypochlorite hydrolyze to:



The two chemical species formed by chlorine in water, hypochlorous acid (HOCl) and hypochlorite ion (OCl⁻), are commonly referred to as **"free" or "available"** chlorine.

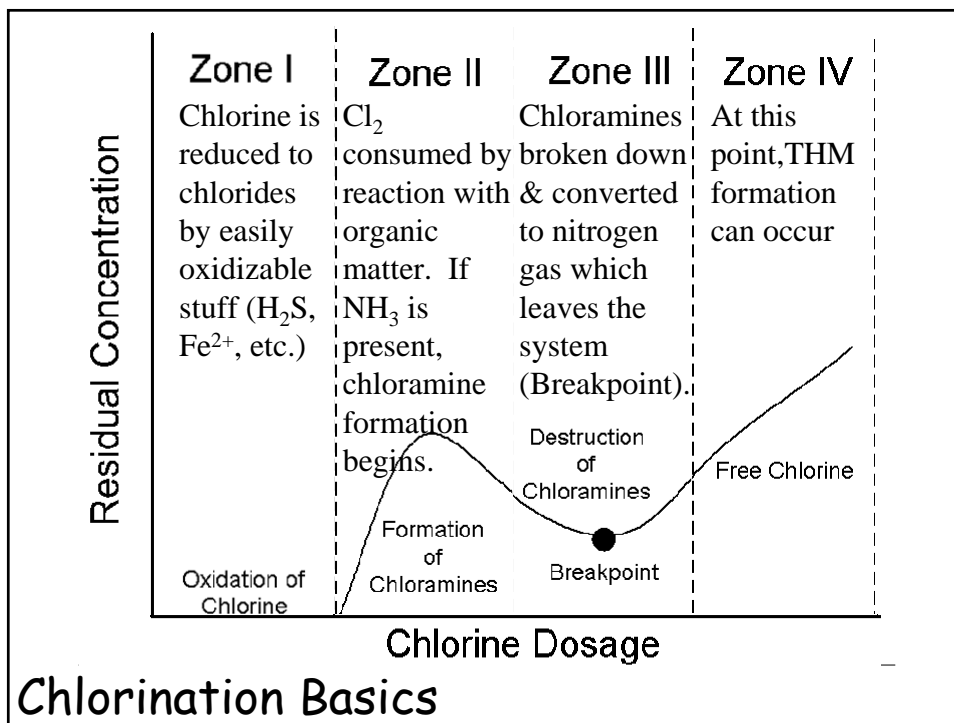
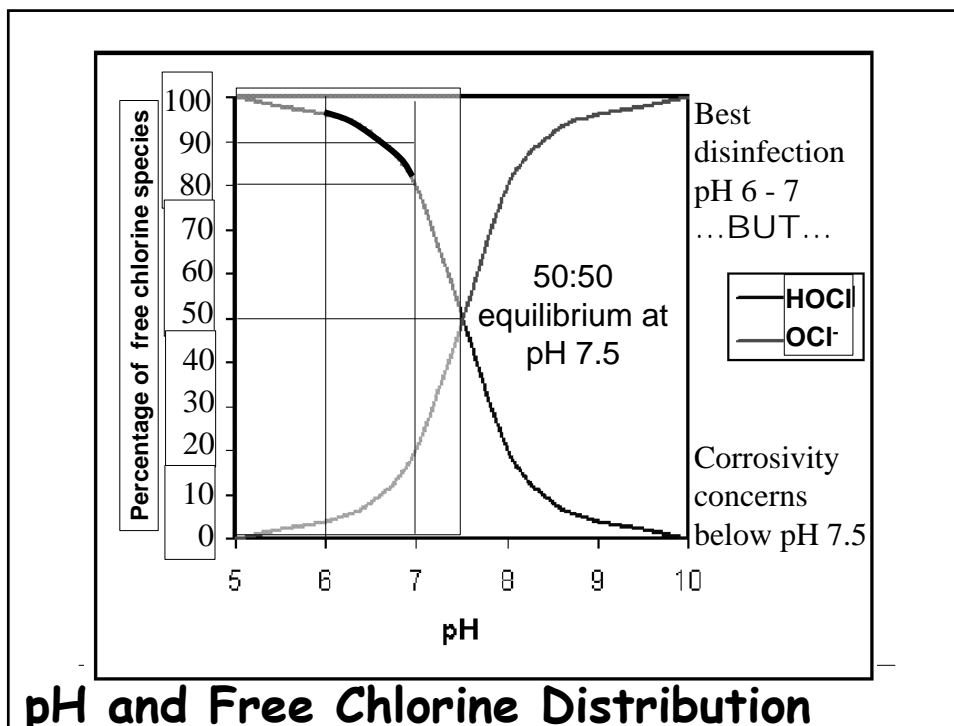
Hypochlorous acid is a weak acid and will disassociate according to:



In waters with pH between 6.5-8.5, the reaction is incomplete and both species (HOCl and OCl⁻) will be present.

Hypochlorous acid is the more germicidal of the two.

Chlorination



What is it? Free chlorine that has combined with ammonia (NH₃) or other nitrogen-containing organic substances. Typically, chloramines are formed.

Where does NH₃, etc come from? Present in some source waters (e.g., surface water). Some systems (about 25% of U.S. water supplies) actually ADD ammonia.

Why would you ADD ammonia? Monochloramine retains about 5% of free chlorine's disinfection power, but it's not powerful enough to continue producing toxic chlorinated organics. Lasts a lot longer in the mains than free chlorine,

Chloramine disinfection does not form nearly as many (*as chlorine alone*) disinfection byproducts:

- Trihalomethanes (THMs)
- Haloacetic Acids (HAAs)

THMs = suspect carcinogens (long term ingestion at high levels)

Combined Chlorine

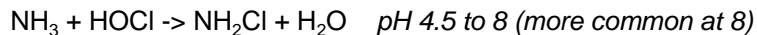
a) Cl₂ (gas) + H₂O reacts to form hypochlorous acid, HOCl & HCl hydrochloric acid.

b) If pH > 8, the HOCl dissociates to hypochlorite ion OCl⁻

If however, the pH << 7, then HOCl will not dissociate.

c) If NH₃ is present, HOCl will react to form one of 3 types of chloramines depending on the pH, temperature, and reaction time.

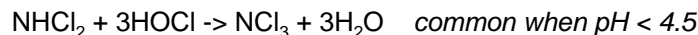
Monochloramine:



Dichloramine:



Trichloramine (stinks!):



Chloramines: effective vs. bacteria but NOT viruses.

Thus...add more chlorine to prevent the formation of chloramines and form other stronger forms of disinfectants.

d) additional free chlorine + chloramine = H⁺, H₂O, and N₂ gas which will come out of solution.

- Recent study on effect of chlorine on E. coli

- Tested 6 strains of O157:H7 at 4 Cl₂ levels

- ⊗ 0.25 mg/L

- ⊗ 0.5 mg/L

- ⊗ 1.0 mg/L

- ⊗ 2.0 mg/L

X 0 0.5 1 and 2 mins
contact time

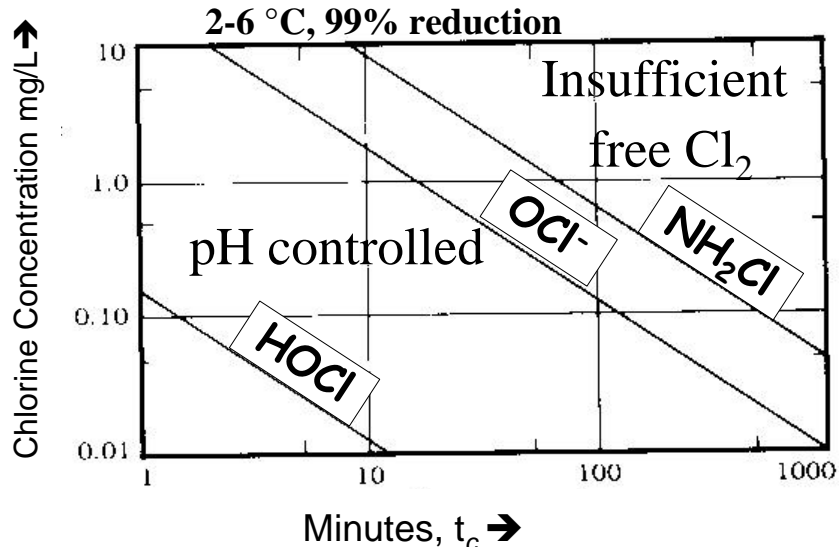
- 5/6 isolates + E. coli control strain were highly susceptible to chlorine

- >7 log₁₀ reduction of each of these strains by 0.25 mg/L free chlorine within 1 min

Each "log₁₀" = 90% reduction; 4 log₁₀ = 99.99% reduction
SDWA requires 4 log reduction

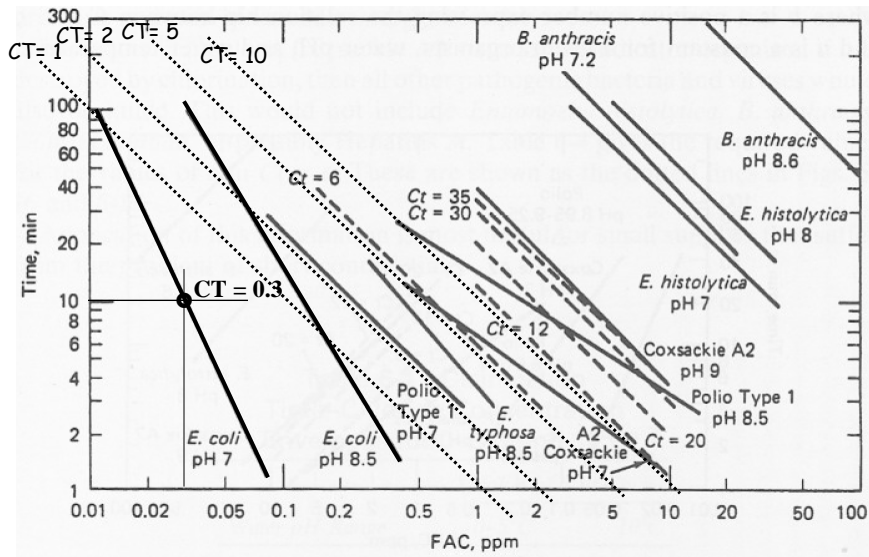
Effect of Cl₂ on E.coli

From: Reynolds & Richards, 1996. Unit Processes in Environmental Engineering.



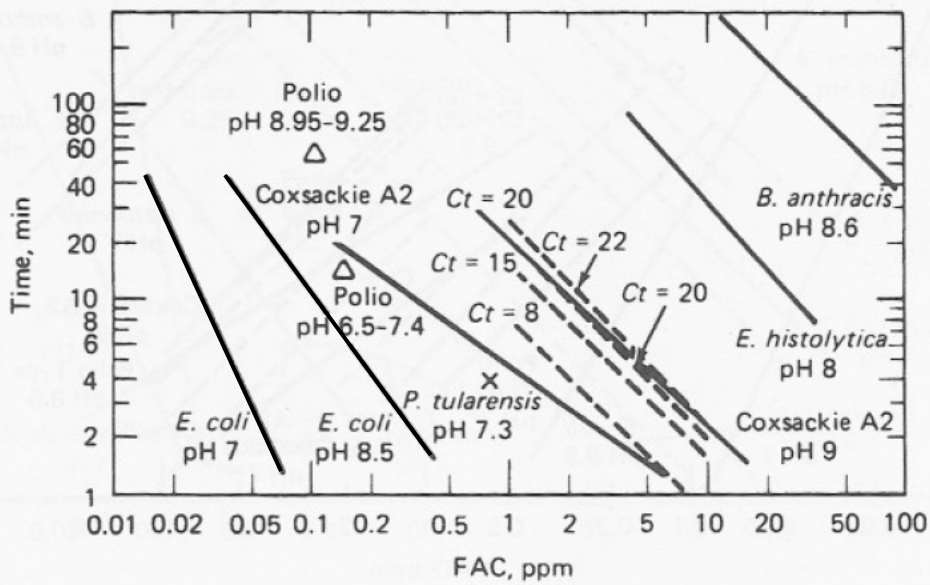
Effectiveness of chlorine forms vs. E. coli

Reprinted from *Journal American Water Works Association* 54, 1379, Nov.1962,



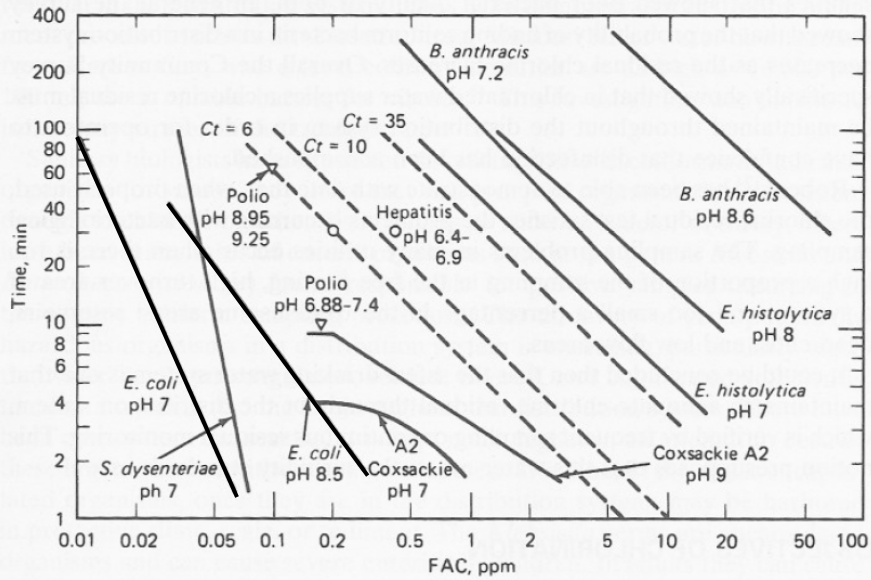
Chlorine vs. time at 0-5° C

Reprinted from *Journal American Water Works Association* 54, 1379, Nov.1962,

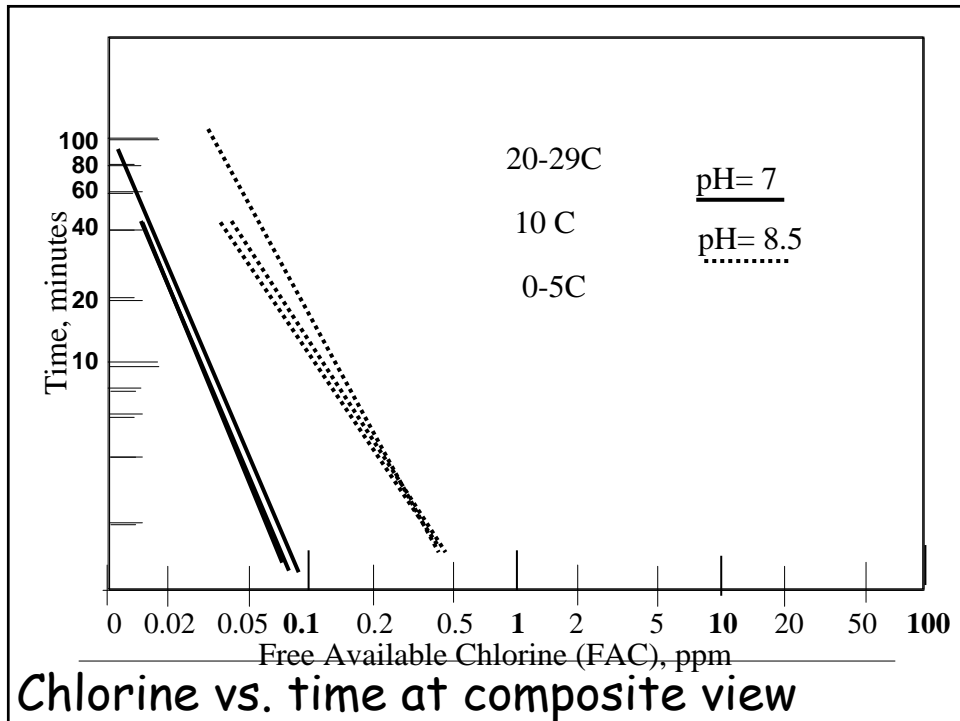


Chlorine vs. time at 10° C

Reprinted from *Journal American Water Works Association* 54, 1379, Nov.1962,



Chlorine vs. time at 20-29° C



Chlorine vs. time at composite view

PROCEDURE FOR DISINFECTION OF DRINKING WATER IN ONTARIO

CT VALUES FOR INACTIVATION OF VIRUSES BY FREE CHLORINE

Temperature (°C)	Log Inactivation					
	2		3		4	
	pH		pH		pH	
	6 to 9	10	6 to 9	10	6 to 9	10
0.5	6	45	9	66	12	90
5	4	30	6	44	8	60
10	3	22	4	33	6	45
15	2	15	3	22	4	30
20	1	11	2	16	3	22
25	1	7	1	11	2	15

June 2003

Virus inactivation by Chlorine

Summary of C.t values (mg/L. min)for 99% inactivation (2 log) at 5°C (Clark et al, 1993)

Organism	Disinfectant			
	Free chlorine, pH 6 to 7	Pre-formed chloramine, pH 8 to 9	Chlorine dioxide, pH 6 to 7	Ozone pH 6 to 7
<i>E. coli</i>	0.034-0.05	95-180	0.4-0.75	0.02
Polio virus 1	1.1-2.5	768-3740	0.2-6.7	0.1-0.2
Rotavirus	0.01-0.05	3806-6476	0.2-2.1	0.006-0.06
Bacteriophage f ₂	0.08-0.18	-	-	-
<i>G. lamblia</i> cysts	47->150	-	-	0.5-0.6
<i>G. muris</i> cysts	30-630	-	7.2-18.5	1.8-2.0 ^a
<i>C. parvum</i>	7200 ^b	7200 ^c	78 ^b	5-10 ^c

a Values for 99.9% inactivation at pH 6-9.

b 99% inactivation at pH 7 and 25°C.

c 90% inactivation at pH 7 and 25°C.

Disinfectant Options and Various "bugs"

Disinfectant	pH	<1°C	5°C	10°C	20°C	25°C
Free Chlorine at 2 mg/l ³	6	165	116	87	44	29
	7	236	165	124	62	41
	8	346	243	182	91	61
	9	500	353	265	132	88
Ozone	6-9	2.9	1.9	1.43	0.72	0.48
Chlorine Dioxide	6-9	63	26	23	15	11
Chloramine (performed ⁴)	6-9	3800	2200	1850	1100	750

² These CT values for free chlorine, ozone, and chlorine dioxide will guarantee greater than 99.99% inactivation of enteric viruses.

³ CT values will vary depending on concentration of free chlorine. Values indicated are for 2.0 mg/l of free chlorine. CT values for different free chlorine concentrations are specified in the Guidance Manual (U.S. EPA, 1990).

⁴ Obtaining 99.99% inactivation of enteric viruses with preformed chloramines requires CT values greater than 5,000 at temperatures of 1, 5, 10, and 15°C.

Disinfectant Options and Giardia

1. The best disinfection occurs at lower pH
2. If you have high alkalinity and high pH (> 8) consider longer chlorine contact time due to reduced efficiency of the hypochlorite form
3. Chlorine (hypochlorite) is a strong base. Therefore, in a low alkalinity system, be wary of pH changes with chlorination.

pH & disinfection (chlorine):

What you need to know

- Chloramination
- Bromination
- Iodination???
- Chlorine Dioxide
- Ozone
- UV

Chlorination Alternatives

- Addition of ammonia (NH₃) and chlorine (Cl₂) compounds separately. Compounds typically used:
 - Anhydrous ammonia
 - Hypochlorous acid (HOCl)
- Ammonia is applied first because it tends to prevent formation of trichloramine (chlorinous odor and taste)
- Adding ammonia first also prevents the formation of THMs.
- Target ratio: 3:1 HOCl to NH₃ produces the best tasting water
- Reactions
 - Monochloramine: $\text{NH}_3 + \text{Cl}_2 = \text{NH}_2\text{Cl} + \text{HCl}$ (at pH ≥ 8.5)
 - Dichloramine: $\text{NH}_3 + 2\text{Cl}_2 = \text{NHCl}_2 + 2\text{HCl}$ (at a pH 4.4 to 5.0)
 - Trichloramine: $\text{NH}_3 + 3\text{Cl}_2 = \text{NCl}_3 + 3\text{HCl}$ (at a pH < 5.0)

pH control is key to successful chloramination in public water supplies

(Note for breakpoint chlorination): To eliminate NH₃ in drinking water using the breakpoint process, (e.g., surface water supply) chlorine is fed at a ratio of 10-12 to 1 to the ammonia level.
- When chloramines are used, the distribution system must be continually monitored for mono- and dichloramine residuals and DO. ~~Total chlorine is not enough.~~

Chloramines as a disinfectant

- Potential problems with using chloramination:
 - Addition of NH_3 may compromise the water quality at the tap
 - Should the residual chloramine be depleted in the distribution system, serious dead-end problems can result.
 - Nitrification can occur.
 - Residual chloramines can pass through RO membranes on dialysis machines which can cause damage to red blood cells.
 - Chloramines are toxic to aquatic life in aquariums.
 - Requires longer contact time to be effective germicidal agent.
 - The process is complex, requires careful control and continual monitoring.
 - Taste and odor problems can occur without properly control.
 - Taste and odor thresholds concentrations:
 - Free chlorine (HOCl): 20 mg/L
 - Monochloramine (NH_2Cl): 5.0 mg/L
 - Dichloramine (NHCl_2): 0.8 mg/L
 - Trichloramine (nitrogen trichloride) (NCl_3): 0.02 mg/L

Chloramines as a disinfectant

					helium 2 He 4.0026
boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]

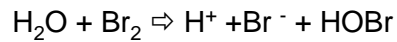
Those elements in the same column share similar properties, thus we can expect Bromine and Iodine to have some disinfectant capability.

As one moves downward through a column, molecular weight increases increasing toxicity potential.

[Notice the proximity of Iodine (I) to toxic heavy metals such as antimony (Sb) and lead (Pb)]

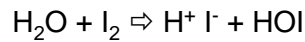
Periodic Table - Halogen sequence

Bromine



- Major difference (vs. Cl₂): effectiveness starts dropping at pH 8.5
- Does form bromamines...as effective as HOBr
- Bromine is relatively scarce, making it more expensive choice
- Bromine is more physiologically active thus its use is limited.

Iodine



- Effectiveness NOT affected by pH
- Does NOT react with ammonia (no iodamines)
- Iodine is very scarce, making it a very expensive choice
- Iodine is extremely physiologically active (i.e., thyroid gland)...thus its use is limited.

Bromine & Iodine Disinfection

Initially used at Niagara Falls water utility (ca. 1944) for taste & odor control.

Produced by reacting sodium chlorite with chlorine or an acid.

Advantages

- Strong disinfectant
- Does NOT produce THMs
- effective vs. Cryptosporidium & Giardia
- weakens organism allowing chlorine to work

DIS-Advantages

- Relatively expensive to generate; explosive above 10%
- Unstable--reverts to chlorite & chlorate (other DBPs)

Chlorine Dioxide Disinfection

- $3 \text{O}_2 \rightleftharpoons 2 \text{O}_3$ (ozone)
- $\text{O}_3 \rightarrow \text{O}_2 + \text{O}^\bullet$ (oxygen radical)
- Bugs killed immediately upon contact (cell rupture)
- Oxygen radical apparently is the actual cause
- strongest disinfectant used in water treatment
- effectiveness unimpaired by NH_3 or pH
- leaves DO in its wake

- Must be generated on-site
- no residual
- difficult to adjust to differing demand
- expensive

Ozone Disinfection

ADVANTAGES	DIS-ADVANTAGES
<ul style="list-style-type: none"> • Strong oxidizing power + short contact time = effective kill of bugs & viruses in seconds; • Produces no taste or odor; • Provides oxygen to the water after disinfecting; • Requires no chemicals; • Oxidizes iron and manganese; • Destroys and removes algae; • Reacts with and removes all organic matter; • Decays rapidly in water, avoiding any undesirable residual effects; • Removes color, taste, and odor; • Aids coagulation. 	<ul style="list-style-type: none"> • Toxicity \uparrow with concentration and exposure time; • Cost is > chlorination; • Installation can be complicated; • Ozone-destroying device is required at the exhaust • May produce undesirable aldehydes and ketones by reacting with certain organics; • No residual in distribution system, \therefore post-chlorination is required; • Much less soluble in water than chlorine; thus special mixing devices are necessary; and • Oxidizes some refractory organics either too slowly or not at all to be of practical significance.

Ozone - Advantages & Disadvantages

- ‡ Kill bugs by oxidizing their enzymes and destroying genetic material
- ‡ Most effective wavelength is 2,650 Angstroms(Å) (anything less than 3,100 is effective)
- ‡ Mercury vapor lamp is economical, produces 2,537 Å
- ‡ Water needs to be clear/colorless and shallow (3-5" deep)
- ‡ No residual effect
- ‡ Cost is high

UV Disinfection

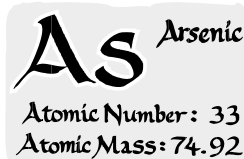
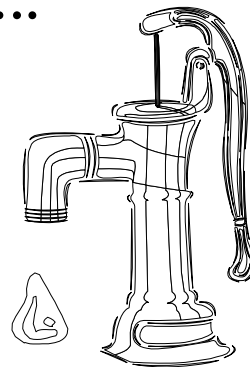
- Chlorine in very low doses and minimal contact time can easily kill even the most heinous of bacteria (E. coli O157:H7)
- Some of the alternative disinfection techniques CAN provide superior disinfection to chlorine, but there are cost and maintenance issues to consider
- Many alternative techniques still require post-chlorination to meet NR 809 requirements.

Disinfection Techniques Summary

Arsenic In Drinking Water.... And Treatment Options

The Safe Drinking Water Act requires EPA to revise the existing 50 parts per billion (ppb) standard for arsenic in drinking water.

On January 22, 2001 EPA adopted a new standard and public water systems must comply with the new 10 ppb standard beginning January 23, 2006

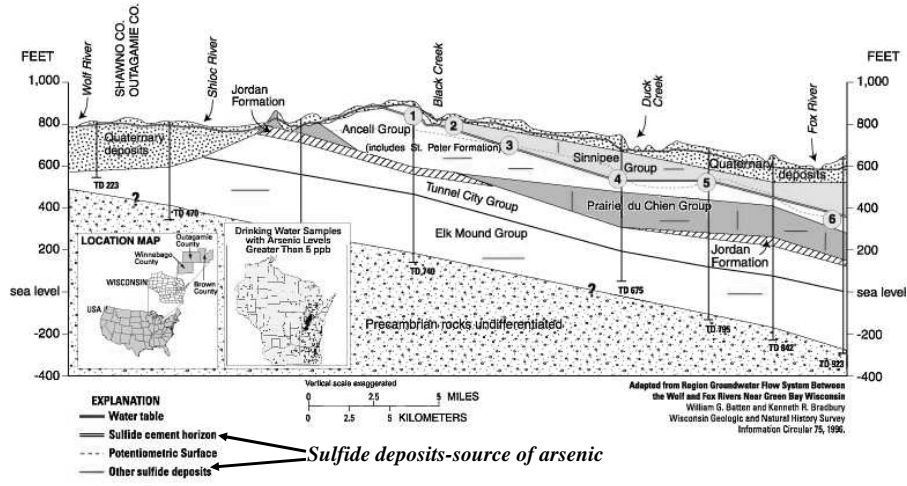


Arsenic and Treatment Options

- The valence states of As are: -3, 0, +1, +3, and +5 (Welch *et al.*, 1988).
- Elemental arsenic (valence 0) is rarely found under natural conditions.
- The +3 and +5 states are found in a variety of minerals and in natural waters.
- The valence state affects the toxicity of arsenic compounds.
 - arsine (-3) > organo-arsines > arsenites (+3) > arsenates (+5) > arsonium metals (+1) > elemental arsenic (0).
- Concentrations of As in the earth's crust range 1.5 - 5 mg/kg
- Arsenic is a major constituent of many mineral species in igneous and sedimentary rocks;
 - Igneous rock types-- the highest arsenic levels in basalts.
 - Sedimentary rocks-- higher As than igneous; particularly Fe/Mn

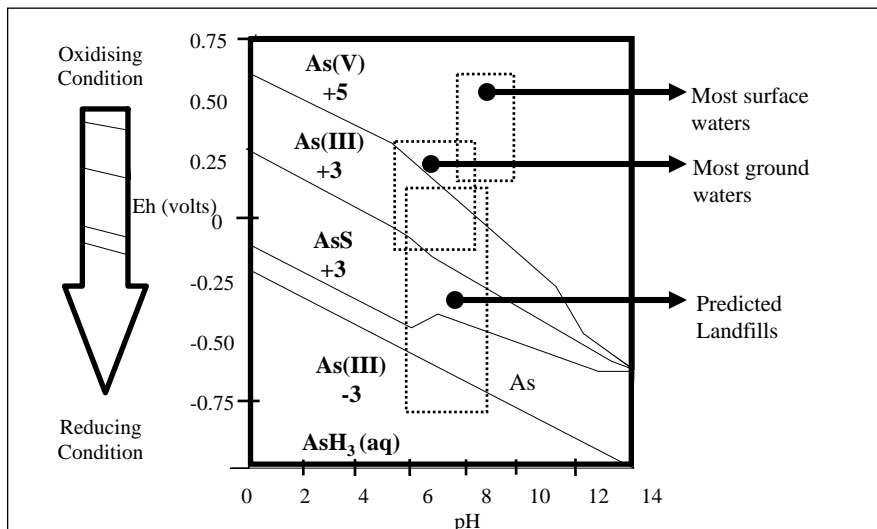
Arsenic (As) General Information

Illustration of well bored through bedrock containing arsenic bearing minerals



Arsenic - Where does it come from?

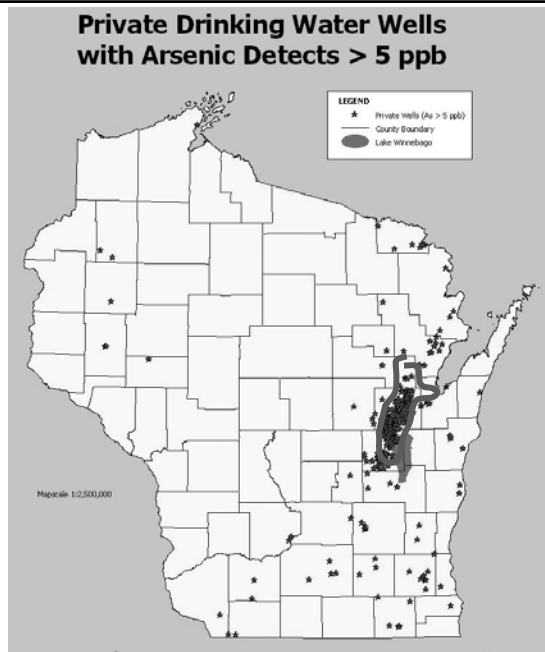
Kahn, B. July 2001. Arsenic Speciation at Landfill Facilities <http://www.ccaresearch.org>



- Measure of system state (O_2 /no O_2)
- Soluble As increases with decreasing Eh & increasing pH
- As (V) is expected to be the predominant form.

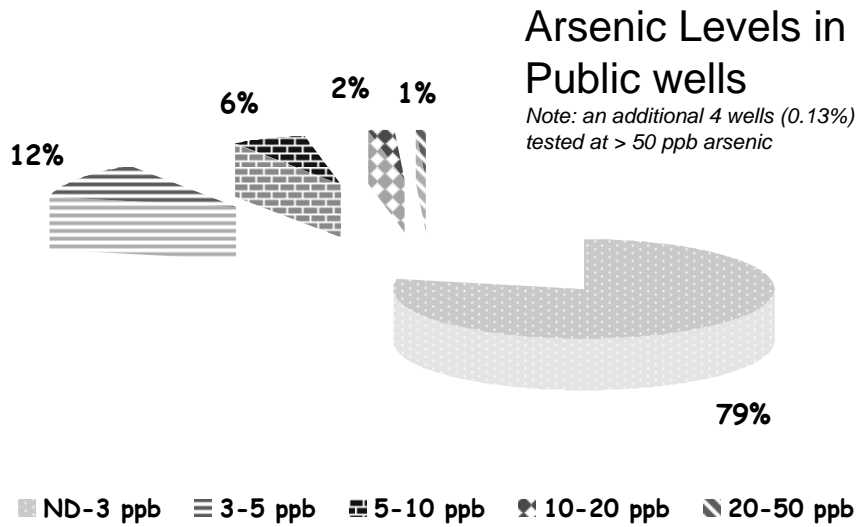
Arsenic Mobility - Eh-pH Diagram

An “Arsenic Advisory Area” was established by the Dept. of Natural Resources (DNR) in the early 1990s. This area includes a strip of land about ten miles wide extending, in a northeasterly trend, from a location just southwest of Oshkosh, to a location just west of Green Bay.



PWS with As Detects above 5 ppb

Source: <http://www.dnr.state.wi.us/org/water/dwg/arsenic/index.htm>



2000 DNR study of 3182 PWS wells

- ✓ Increased risk of skin cancer
- ✓ Increased risk of internal cancers (bladder, prostate, lung and other sites)
- ✓ Thick, rough skin on hands and feet
- ✓ Unusual skin pigmentation (dappling of dark brown or white splotches)
- ✓ Numbness in the hands and feet
- ✓ Circulatory disorders
- ✓ Tremors
- ✓ Stomach pain, nausea, diarrhea
- ✓ Diabetes (not confirmed)



Effects are irreversible

Arsenic Health Effects

<http://www4.nationalacademies.org/news.nsf/fc340309c47a1e43852567460067595e/c2f3467f548f460c85256ac4006d092a?OpenDocument>

☞ Both the US Environmental Protection Agency and the World Health Organization have set the standard at 10 µg/l.



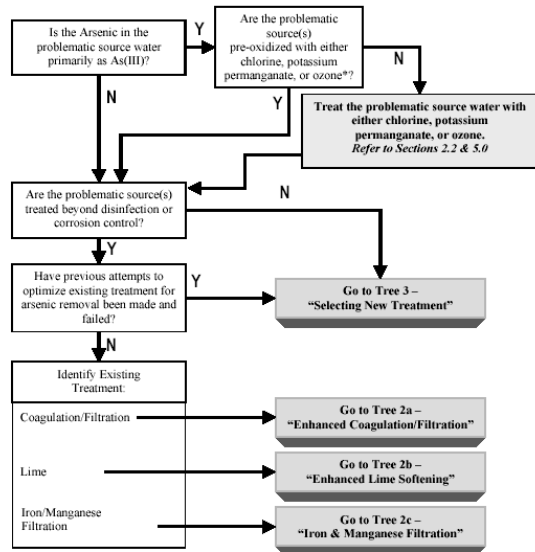
Here is the cancer risk:

0.5 ppb	-	1 in 10,000
1 ppb	-	1 in 5,000
3 ppb	-	1 in 1,000
5 ppb	-	1.5 in 1,000
10 ppb	-	>1 in 333
20 ppb	-	1 in 143

from: National Academy of Sciences

What level of Arsenic is safe?

Treatment Selection



*Pre-oxidized refers to the process of converting As(III) to As(V)

The EPA has developed an extensive Arsenic treatment decision tree.

Step 1= if As is in +3 form, you will have to oxidize it to the +5 form

EPA's Decision Tree for Arsenic Treatment

Existing Technology

Coagulation/Filtration	may require use of Fe; sludge issues
Polymer	requires pH < 7.5, may need to add Fe
Alum	lower pH to 5-7, increase Alum addition
Fe-based	pH to 5.5-8.5, increase Fe addition
Lime Softening	requires pH 10.5-11; add Mg or Fe
Fe/Mn Filtration	best with Fe: As of 20:1

Emerging Technology

Ion Exchange	TSS and Fe ppts clog, anions compete
Activated Alumina	other ions (Cl⁻, SO₄⁼) compete for sites
Filtration/Membranes	best with Fe: As of 20:1
Electrochemical	currently used in Europe only

Treatment Options Summary

www.htnweb.com/downloads/hhremove_ar.pdf

Viraraghvan, T., Subramaniam, K.S., and Swaminathan, T. V., - Drinking water without arsenic: A review of treatment technologies, March 1996, ENSIC, Asian Institute of Technology, Bangkok

Treatment method	As(III)	As(V)
Aeration and stripping	P	P
Coagulation, precipitation and filtration	F-G	G-E
Lime softening	F-G	G-E
Ion exchange		
<i>Anion</i>	G-E	G-E
<i>Cation</i>	P	P
Membrane Processes		
<i>Reverse Osmosis</i>	F-G	G-E
<i>Electrodialysis</i>	F-G	G-E
Chemical oxidation and disinfection	P	P
Adsorption		
<i>Granulated Activated Carbon</i>	F-G	F-G
<i>Powdered Activated Carbon</i>	P-F	P-F
<i>Activated Alumina</i>	G-E	E

P = Poor; F = Fair; G = Good and E = Excellent

As Treatment Technology Effectiveness

EPA: Technical Fact Sheet: Final Rule for Arsenic in Drinking Water (January 2001)

Total Annual Costs (\$) per Household for Community Water Systems (CWS)

System Size	25-500	501-3,300	3.3K-10K	>10K
Annual Household Costs	\$ 327-\$162	\$ 71-\$58	\$ 38	\$32-\$0.86

The estimated average annual costs for CWSs, which exceed the final MCL of 10 µg/L (required to treat) are shown below categorized by system size.

Average Annual Costs per CWS (Dollars)

CWS System Size	Costs (\$)
25-500	\$6,494-\$12,358
501-3,300	\$22,100-\$53,086
3,300-10,000	\$111, 646
10,000 and above	\$531,584-\$1,340,716

EPA 815-F-00-016

As Treatment Technology Costs

Treatment technologies for the removal of arsenic and their relative treatment Costs¹ in community treatment plants

Arsenic species	Treatment method	Percentage removal	Relative treatment cost (US Cents/1000gallons)		
			0.3 mgd	1.0 mgd	50 mgd
As(V) (Arsenate)	Alum coagulation/filtration, pH 6-7	>90	175	44	19
	Iron coagulation / filtration, pH 6-8	>90	175	44	19
	Excess lime softening	>90	305	63	40
	Activated alumina, pH 5-6	>95	122	62	51
	Ion exchange	<90	83	51	42
	Reverse osmosis	<90	332	164	129

Note : For As(III) removal, oxidation treatment of As(III) to As(V) is required

Viraraghvan, T., Subramaniam, K.S., and Swaminathan, T. V., - Drinking water without arsenic: A review of treatment technologies, March 1996, ENSIC, Asian Institute of Technology, Bangkok

As Treatment technology Costs