How Much Buffer Do You Need to Adjust Aquifer pH?

A Design Tool to Estimate Amount of Buffer Required

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Overview

- Importance of pH
- Factors Affecting Aquifer Acidity
- Aquifer Buffering Capacity
- Common Additives to Adjust pH
- Alkali Addition Design Tool
- Example

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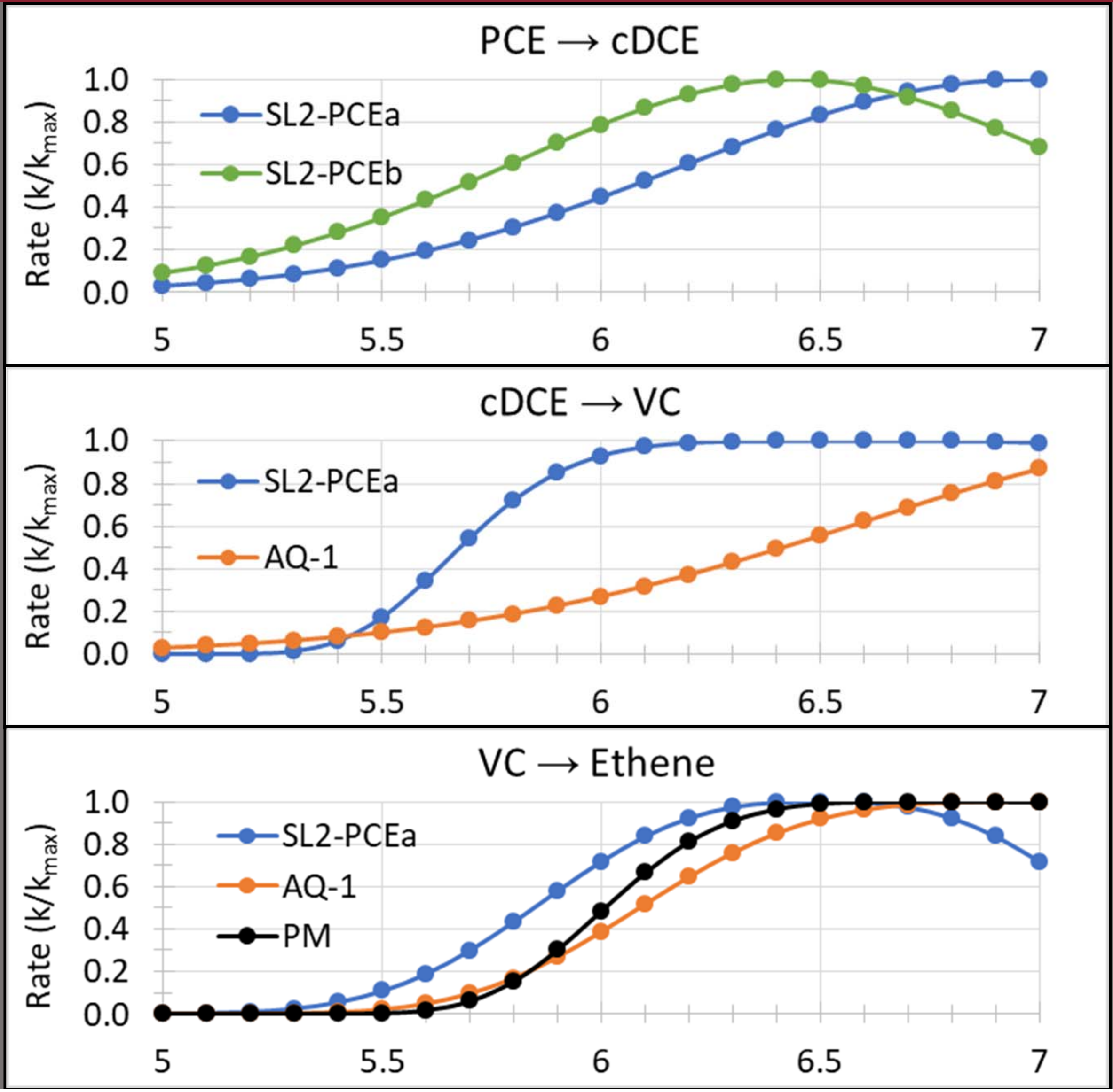
Importance of pH for ERD



Dechlorination rates are highest at circumneutral pH

Lacroix et al.,
Appl. Environ. Micro,
July 2014

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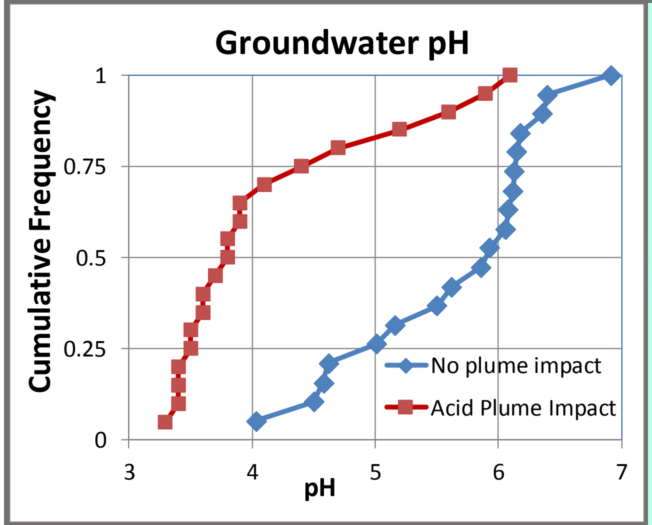
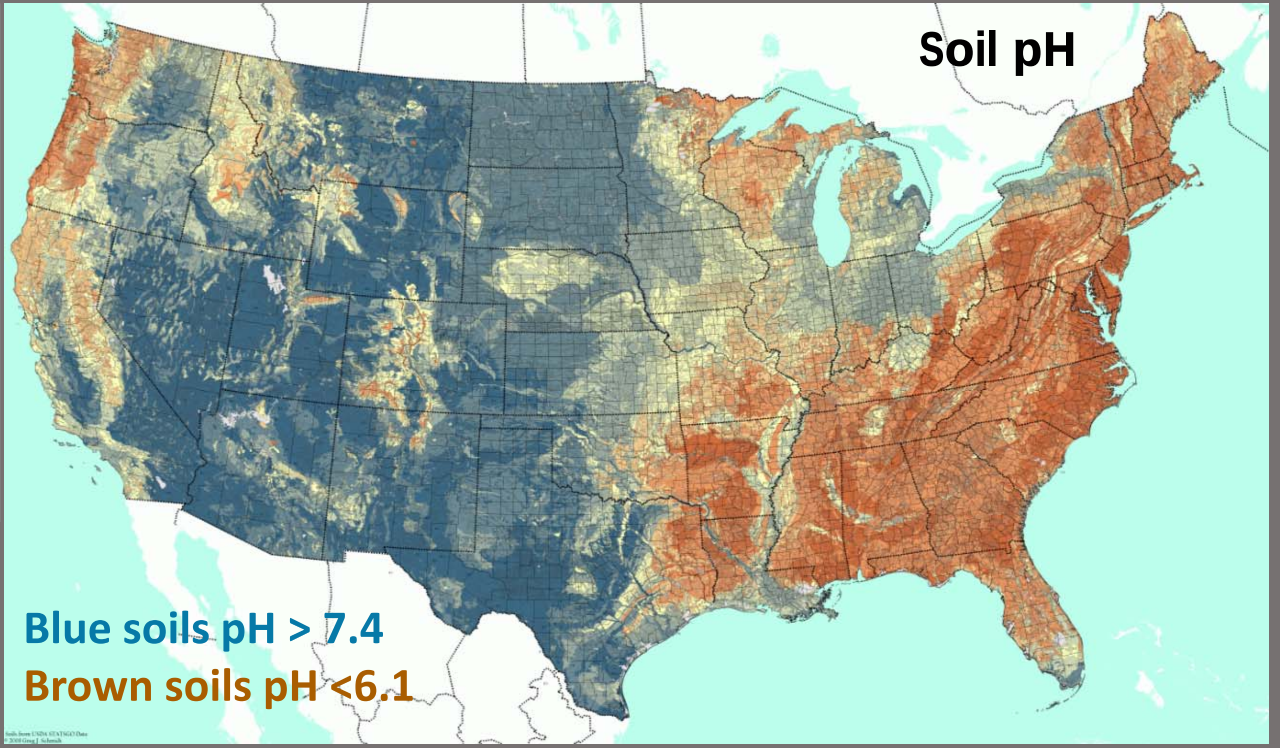
Factors Affecting Aquifer pH

Prevailing Site Conditions



Industrial Site in Eastern North Carolina with sulfuric acid plume



(http://www.bonap.org/2008_Soil/pH20110321.png)

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Factors Affecting Aquifer pH

Acidity from Fermentation of Substrate

Sodium Lactate ($NaC_3H_5O_3$)

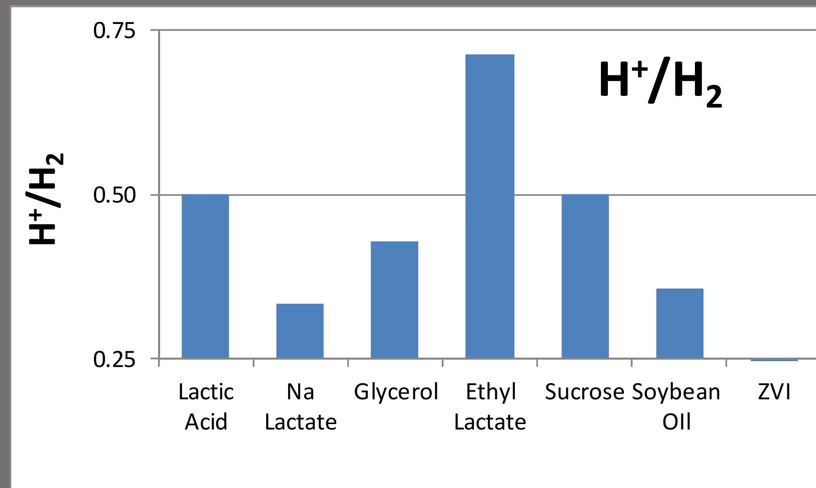
$NaC_3H_5O_3 + 6H_2O \rightarrow$

$\mathbf{6H_2} + 3HCO_3^- + Na^+ + \mathbf{2H^+}$

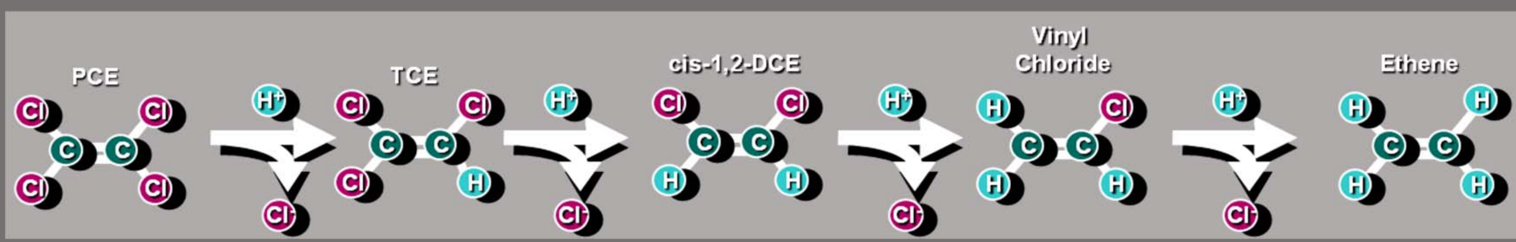
Soybean Oil ($C_{56}H_{100}O_6$)

$C_{56}H_{100}O_6 + 162H_2O \rightarrow$

$\mathbf{156H_2} + 56HCO_3^- + \mathbf{56H^+}$



Acidity from Reductive Dechlorination



C_2Cl_4 (PCE) + $4H_2 \rightarrow C_2H_4$ (ethene) + $\mathbf{4HCl}$

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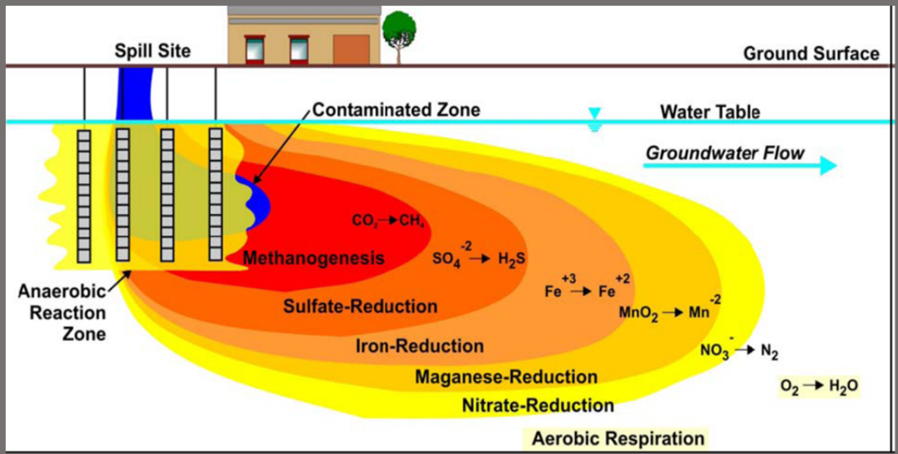
Factors Affecting Aquifer Acidity



Electron Acceptor Reduction

- Nitrate-Reduction
  $NO_3^- + 2\frac{1}{2} H_2 \rightarrow 2 H_2O + \frac{1}{2} N_2 + OH^-$
- Iron-Reduction
  $Fe(OH)_3 + \frac{1}{2} H_2 \rightarrow Fe^{2+} + H_2O + 2 OH^-$
- Sulfate-Reduction
  $SO_4^{2-} + 4 H_2 + Fe^{2+} \rightarrow Fe^{2+} + H_2S + 2 H_2O + 2 OH^- \rightarrow FeS_2 + 4 H_2O$
- Methanogenesis
  $HCO_3^- + 4 H_2 \rightarrow CH_4 + 2 H_2O + OH^-$

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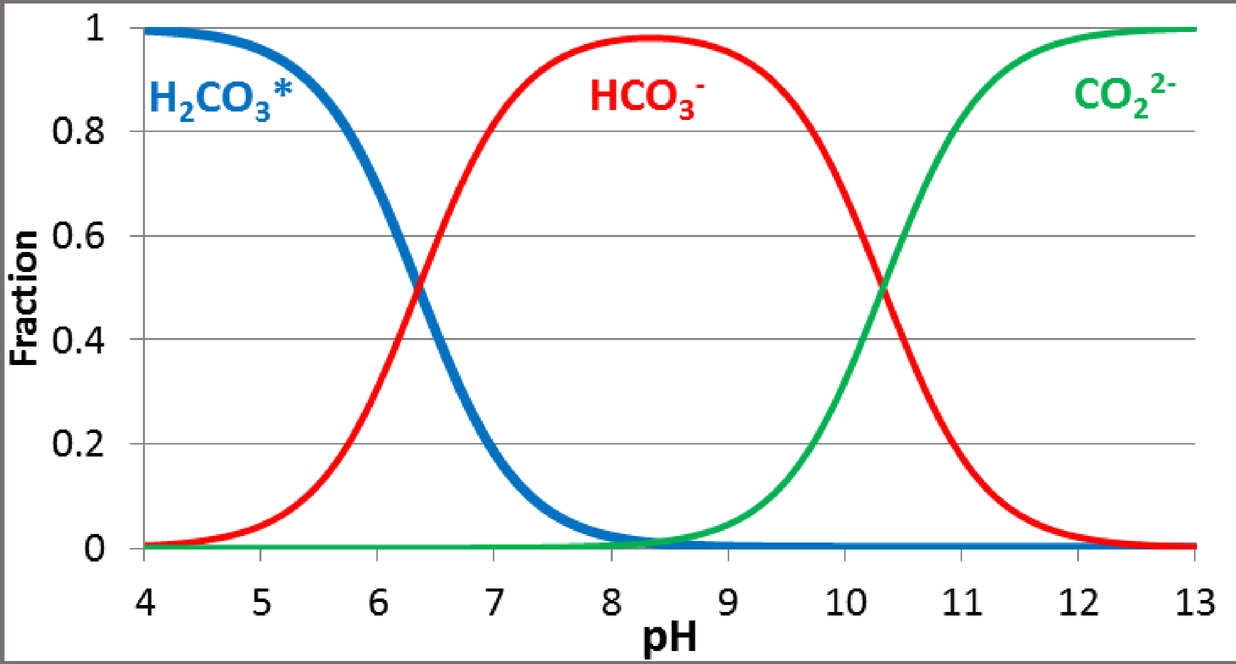
Aquifer Buffering Capacity

Buffering by Carbonates

$CO_2(g) + H_2O \Leftrightarrow H_2CO_3^* \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2\,H^+ + CO_3^{2-}$

- Near the water table, CO_2 degas, stripping acid
- Open system , buffering capacity: a function of PCO_2
- Closed system, buffering capacity: a function of total dissolved carbonate (assuming no minerals)



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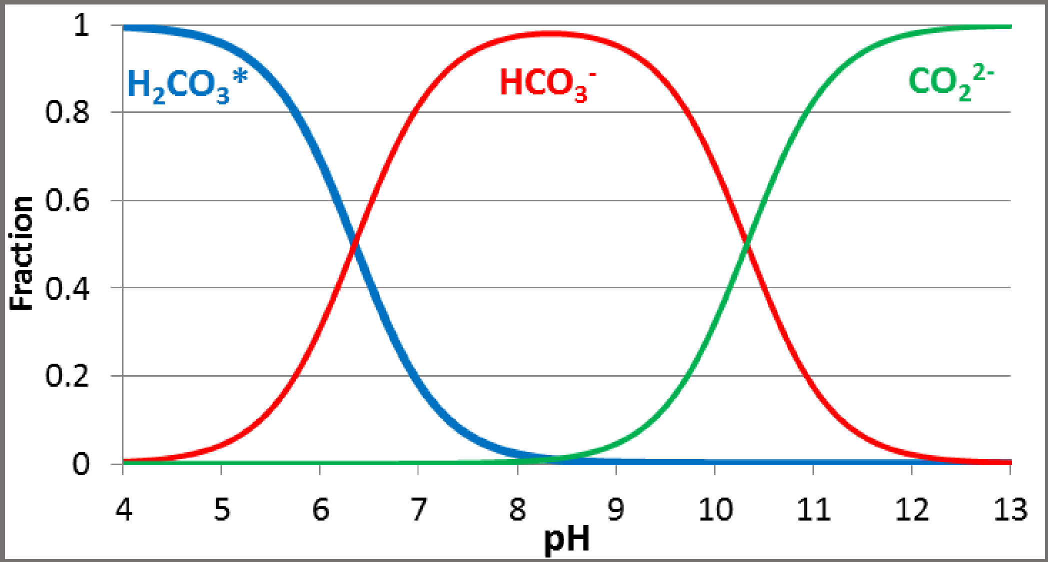
Aquifer Buffering Capacity

Buffering by Carbonates

- Solid carbonate minerals: $CaCO_3(s)$, $MgCO_3(s)$
- Limit pH declines caused by strong acids (e.g. HCl)
- Relatively low solubility so less effective in limiting pH declines due to CO_2 production in saturated zone
- $H_2CO_3^* + Ca_2+ + CO_3^{2-} \rightarrow 2H^+ + Ca^{2+} + 2CO_3^{2-} \rightarrow\rightarrow H^+ + HCO_3^- + CaCO_3(s)$ (precipitation with accumulation of H^+)



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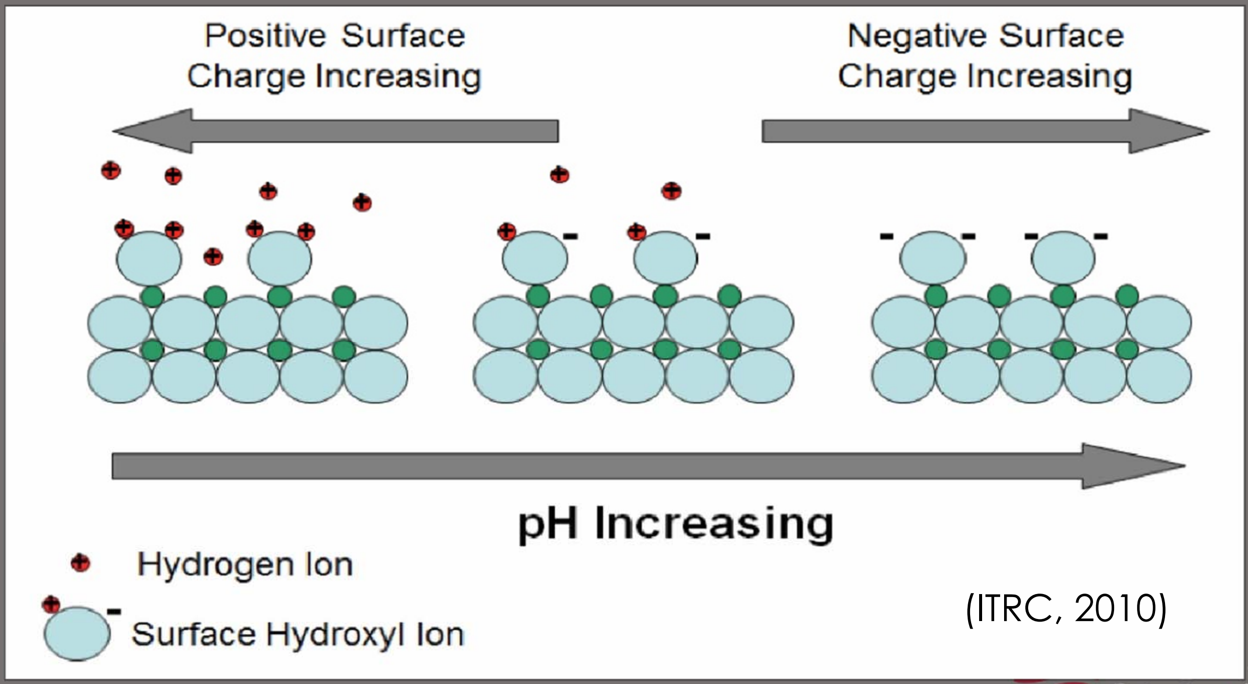
Aquifer Buffering Capacity

Surface Complexation and Ion Exchange

- H^+ and OH^- exchange on Fe and Al oxide surfaces and clay minerals
- Strong buffer, reduce the pH decline → adsorbing H^+
- Increase required base amount to increase aquifer pH → adsorbing OH^-



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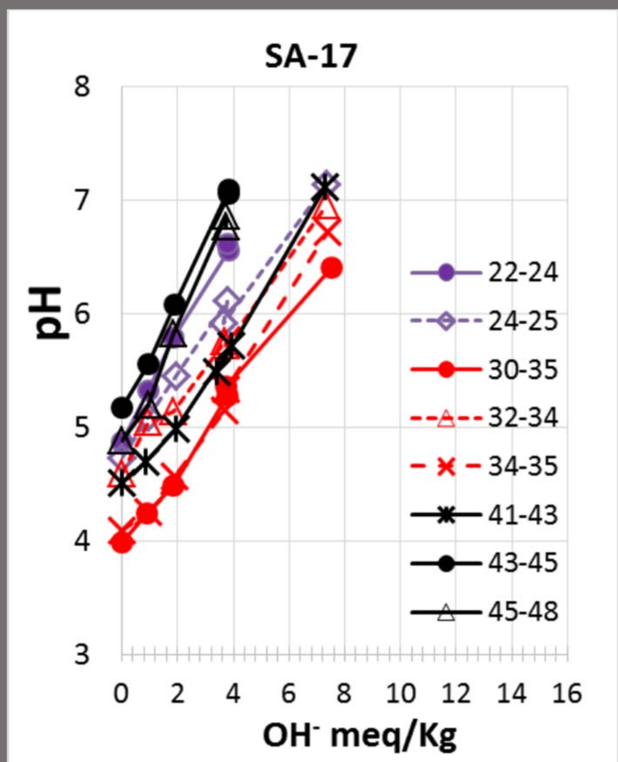
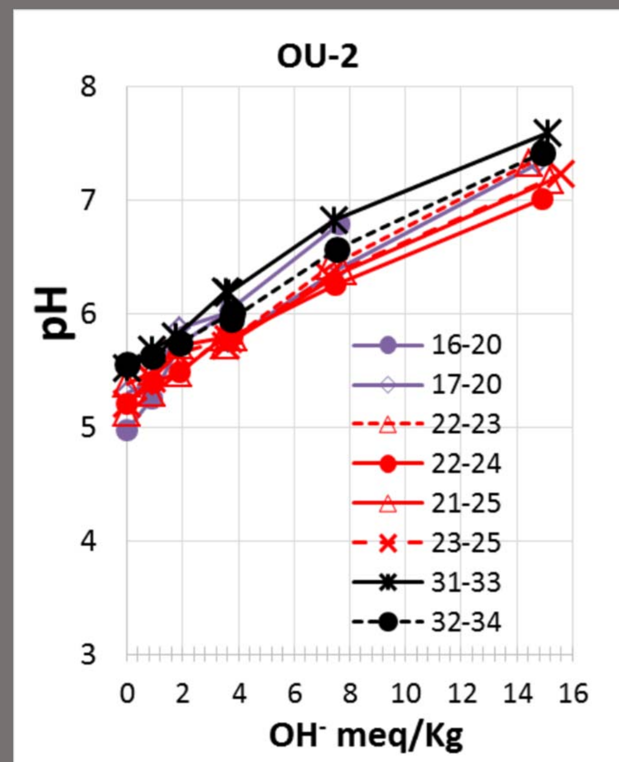
Aquifer Buffering Capacity

Estimating Aquifer Buffering Capacity

- Titrations with strong base
- Buffering curves are typically linear in the pH range of 4.5 to 6.5
- Inverse slope: pH buffer capacity (pHBC)=meq OH^- sorbed/pH unit





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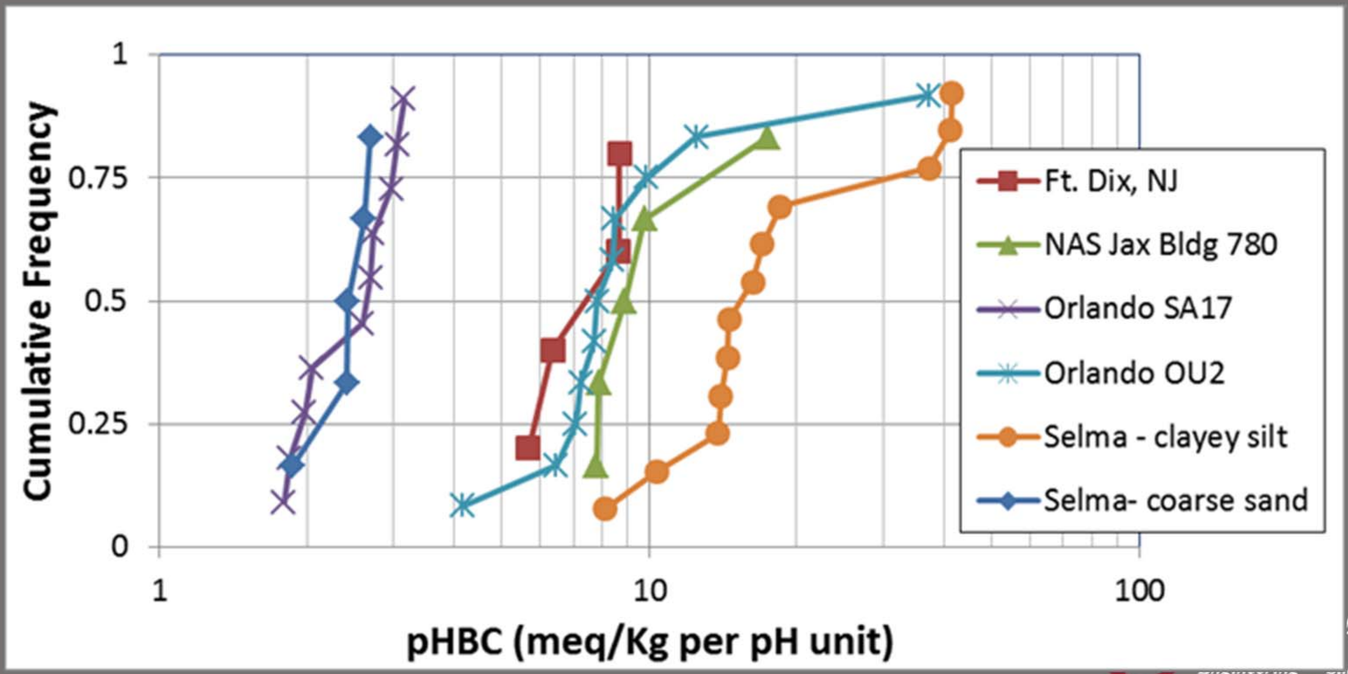
Aquifer Buffering Capacity

Estimating Aquifer Buffering Capacity

- 6 contaminated aquifers
- Vary by a factor of 10 between sites
- Increases with silt/clay



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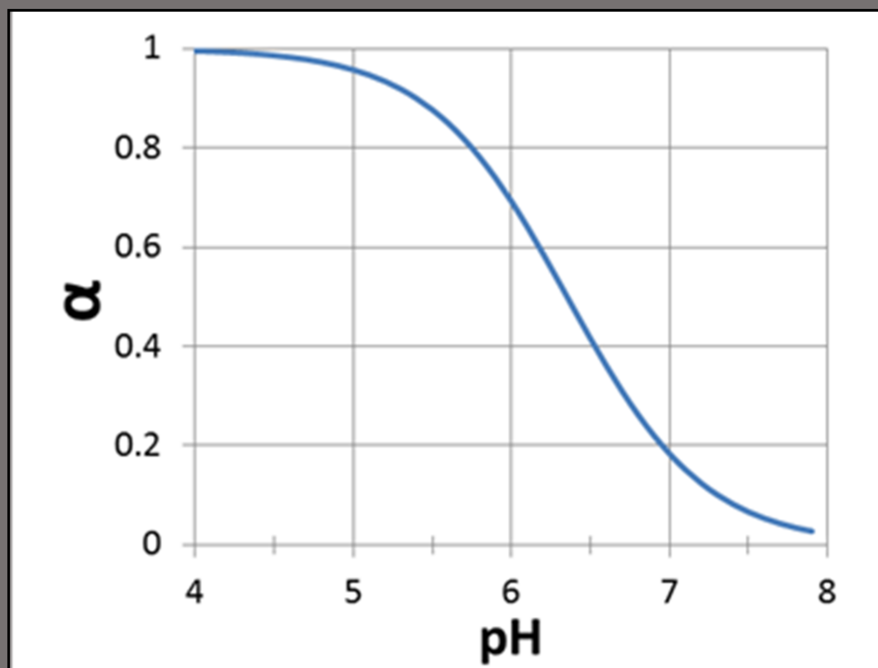
Acid and Base Production

- $pH < 8$ (CO_3^{2-} insiginificant)
- $a = (1+ 10^{-6.352} /[H+])^{-1}$ ($5 > pH > 8$)
- H^+ release: $H_2CO_3^* \rightarrow aH_2CO_3^* + (1-a)H^+ + (1-a)HCO_3^-$
- H^+ consumed : $NaHCO_3 + aH^+ \rightarrow Na^+ + aH_2CO_3^* + (1-a)HCO_3^-$

  $Na_2CO_3 + (1+a)H^+ \rightarrow 2Na^+ + aH_2CO_3^* + (1-a)HCO_3^-$



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Net Acid Production

e- Acceptor	e- Donor	Product	Reaction	H^+ Produced
PCE	H_2	TCE	$C_2Cl_4 + H_2 \rightarrow C_2HCl_3 + H^+ + Cl^-$	1
TCE	H_2	*c*DCE	$C_2HCl_3 + H_2 \rightarrow C_2H_2Cl_2 + H^+ + Cl^-$	1
DCE	H_2	VC	$C_2H_2Cl_2 + H_2 \rightarrow C_2H_3Cl + H^+ + Cl^-$	1
VC	H_2	Ethene	$C_2H_3Cl + H_2 \rightarrow C_2H_4 + H^+ + Cl^-$	1
H_2O	Acetic Acid	H_2, HCO_3^-	$C_2H_4O_2 + 4\ H_2O \rightarrow 2\ H_2CO_3^* + 4\ H_2$	2(1-a)
H_2O	Lactic Acid	H_2, HCO_3^-	$C_3H_6O_3 + 3\ H_2O \rightarrow 3\ H_2CO_3^* + 6\ H_2$	3(1-a)
H_2O	Glucose	H_2, HCO_3^-	$C_6H_{12}O_6 + 12\ H_2O \rightarrow 6\ H_2CO_3^* + 12\ H_2$	6(1-a)
H_2O	Soybean Oil	H_2, HCO_3^-	$C_{56}H_{100}O_6 + 162H_2O \rightarrow 56H_2CO_3^* + 156H_2$	56(1-a)
Oxygen	H_2		$O_2 + 2\ H_2 \rightarrow 2\ H_2O$	0
Nitrate	H_2	N_2	$NO_3^- + 2\frac{1}{2}\ H_2 \rightarrow 2\ H_2O + \frac{1}{2}\ N_2 + OH^-$	-1
Goethite	H_2	Fe^{2+}	$FeO(OH) + \frac{1}{2}\ H_2 \rightarrow Fe^{2+} + 2\ OH^-$	-2
Sulfate	H_2	HS^-	$SO_4^{2-} + 4\ H_2 + Fe^{2+} \rightarrow FeS + 4\ H_2O$	0
$H_2CO_3^*$	H_2	CH_4	$H_2CO_3^* + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$	a-1

Common Alkalis

Base	Formula	MW (g/mole)	OH^- per mole	OH^- per Kg	Solubility (g/L)	Saturated solution pH
Caustic Soda	$NaOH$	40.0	1	25.0	1,100	>14
Caustic Potash	KOH	56.1	1	17.8	1,200	>14
Soda Ash	Na_2CO_3	106	1+ a	11.2	300	~11.7
Baking Soda	$NaHCO_3$	84	a	2.2	78	~8.3
Hydrated Lime	$Ca(OH)_2$	74.1	2	27.0	1.85	~12.4
Milk of Magnesia	$Mg(OH)_2$	58.3	2	34.3	<0.01	~10.3

Alkali Addition Design Tool

- Spreadsheet based design tool developed to estimate base addition required to maintain target pH during ERD
- Inputs
  - Treatment zone dimensions, design period
  - Site characteristics (K, porosity, dh/dL)
  - Geochemistry (Background pH, pHBC)
  - Contaminant concentrations and electron acceptors
  - Substrates added
  - Target pH
- Results
  - OH^- required to neutralize H^+ produced and raise pH
  - Amount of different reagents required

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Operational Unit 2 (OU2)

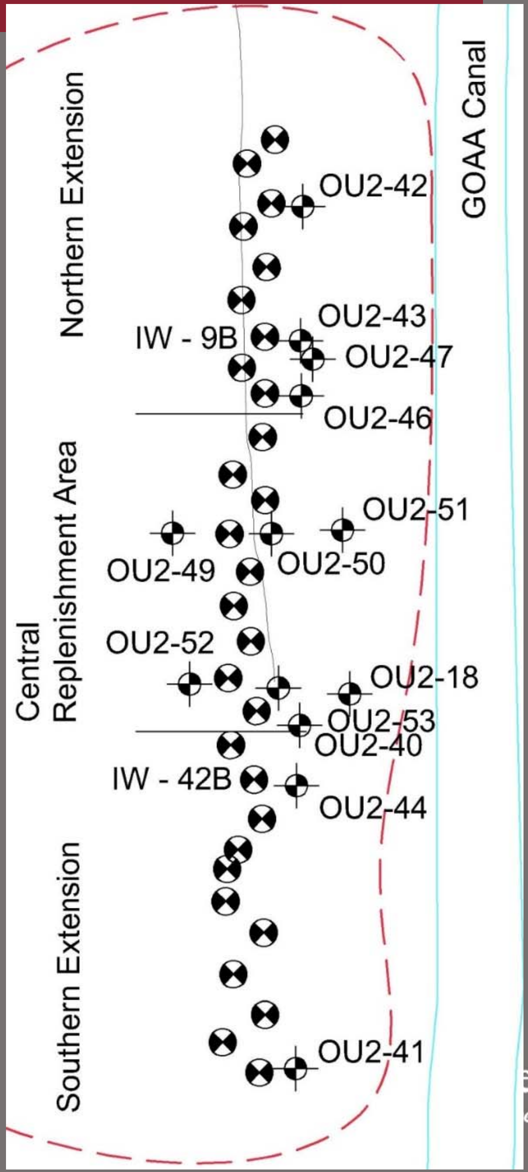
- Former Naval Training Center (NTC), Orlando, FL
- Former landfill with GW flow to GOAA canal / drainage ditch
- TCE and related CVOCs
- Low pH

2008

- 150 ft barrier (central portion)
- 11 Inject well pairs (15-25 ft and 25-35 ft)
- Two rows, 30 ft OC
- EVO injections

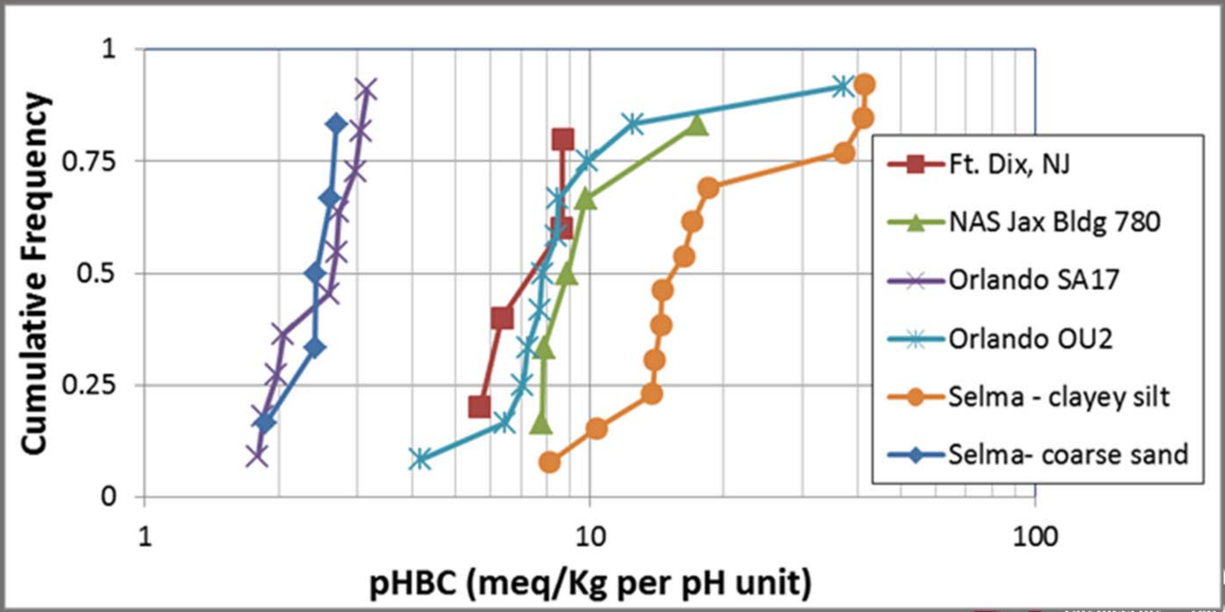
2012

- Reinject central area
- Extend barrier 135 ft north and 135 ft south in 25-35 ft zone
- EVO and buffer ($Mg(OH)_2$) injections



Operational Unit 2 (OU2)

- 5 year design life
- Background pH = 5.0
- pHBC = 8 meq OH^-/Kg/pH
- Vegetable oil added = 20,224 lb
- Buffer added = 240 lb



Site Information

Facility Name:	Former NTC Orlando
Site Name:	OU2
Owner:	US NAVY

Aquifer Characteristics				
Description:	fine sand and fine silty sand			
Hydraulic Gradient:	0.002	m/m	0	ft/ft
Hydraulic Conductivity:	7.62	m/d	25	ft/d
Sediment Specific Gravity:	2.50	g/cm^3		
Porosity:	0.28	mL/cm^3		
Effective Porosity	0.20	mL/cm^3		
Bulk Density:	2	g/cm^3	112	lb/ft^3
Transport Velocity:	28	m/yr	91	ft/yr

Geochemistry			alpha
Target pH:	7.0	SU	0.184
Background pH:	5.0	SU	0.957
Total Inorganic Carbon:	12	mg/L	
Background CO2 Acidity:	0.8	meq/L	
Background CO2 Alkalinity:	0.0	meq/L	
Mineral Acidity:	0	meq/L	
Total GW Acidity	1	meq/L	
Aquifer Buffering Capac.:	8.00	meq/Kg/pH	
Base to raise starting pH	114,556	OH^- eq	

Average GW and Soil Concentrations	GW (mg/L)	Soil (mg/Kg)	GW+Soil (Kg)
PCE	0	0	0
TCE	5	0	61
DCE	0	0	0
VC	0	0	0
Oxygen	0	NA	0
Nitrate	0	NA	0
Fe(II)	2	100	740
Sulfate	15	NA	183
Methane	549	NA	6,684

Bioremediation Info.

Treatment Zone Dimensions					
Design Period:	5	yr			
Width:	133	m	435	ft	(perpendicular to GW flow)
Length:	10	m	33	ft	(parralel to GW flow)
Vertical Thickness:	3	m	10	ft	(depth)
Volume:	3,978	m^3	140,469	ft^3	
Soil Mass:	7,159,752	Kg	15,751,430	lb	(treated soil mass)
Pore Volume:	1,113,739	L	294,220	gal	(Treatment zone PV)
GW Flux:	2,212,602	L/yr	584,509	gal/yr	(GW entering per year)
Total GW Vol:	12,176,749	L	3,216,767	gal	(Total GW vol. treated over)
HRT:	1	yr			

Reagents Added				
Acetic Acid		lb	0	Kg
Lactic Acid	1,078	lb	490	Kg
Glucose		lb	0	Kg
Soybean Oil	20,224	lb	9,193	Kg
Caustic Soda		lb	0	Kg
Caustic Potash		lb	0	Kg
Soda Ash		lb	0	Kg
Baking Soda		lb	0	Kg
Hydrated Lime		lb	0	Kg
Milk of Magnesia	240	lb	109	Kg

Influent Acidity	9,423	OH^- eq
Base to raise starting pH	114,556	OH^- eq
Acidity from Dechlorination	1,390	OH^- eq
Acidity from Added Substrate	496,733	OH^- eq
Acidity from e^- accept / donors	-366,647	OH^- eq

Total Base Required	255,455	OH^- eq
Total Base Added	3,742	OH^- eq
Fraction of Base Demand Satisfied	1%	

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Description:	fine sand and fine silty san		
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Hydraulic Conductivity:	7.62	m/d	25
Sediment Specific Gravity:	2.50	g/cm^3	
Porosity:	0.28	mL/cm^3	
Effective Porosity	0.20	mL/cm^3	
Bulk Density:	2	g/cm^3	112

Geochemistry			alpha
Target pH:	7.0	SU	0.184
Background pH:	5.0	SU	0.957
Total Inorganic Carbon:	12	mg/L	
Background CO2 Acidity:	0.8	meq/L	
Background CO2 Alkalinity:	0.0	meq/L	
Mineral Acidity:	0	meq/L	
Total GW Acidity	1	meq/L	

Average GW and Soil Concentrations	GW (mg/L)	Soil (mg/Kg)	GW+Soil (Kg)
PCE	0	0	0
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Nitrate	0	NA	0
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Background CO2 Acidity:	0.5	meq/L	
Background CO2 Alkalinity:	0.0	meq/L	
Mineral Acidity:	0	meq/L	
Total GW Acidity	1	meq/L	
Aquifer Buffering Capac.:	8.00	meq/Kg/pH	
Base to raise starting pH	85,917	OH^- eq	

Average GW and Soil Concentrations	GW (mg/L)	Soil (mg/Kg)	GW+Soil (Kg)
PCE	0	0	0
TCE	5	0	61
DCE	0	0	0
VC	0	0	0
Oxygen	0	NA	0
Nitrate	0	NA	0
Fe(II)	2	100	740
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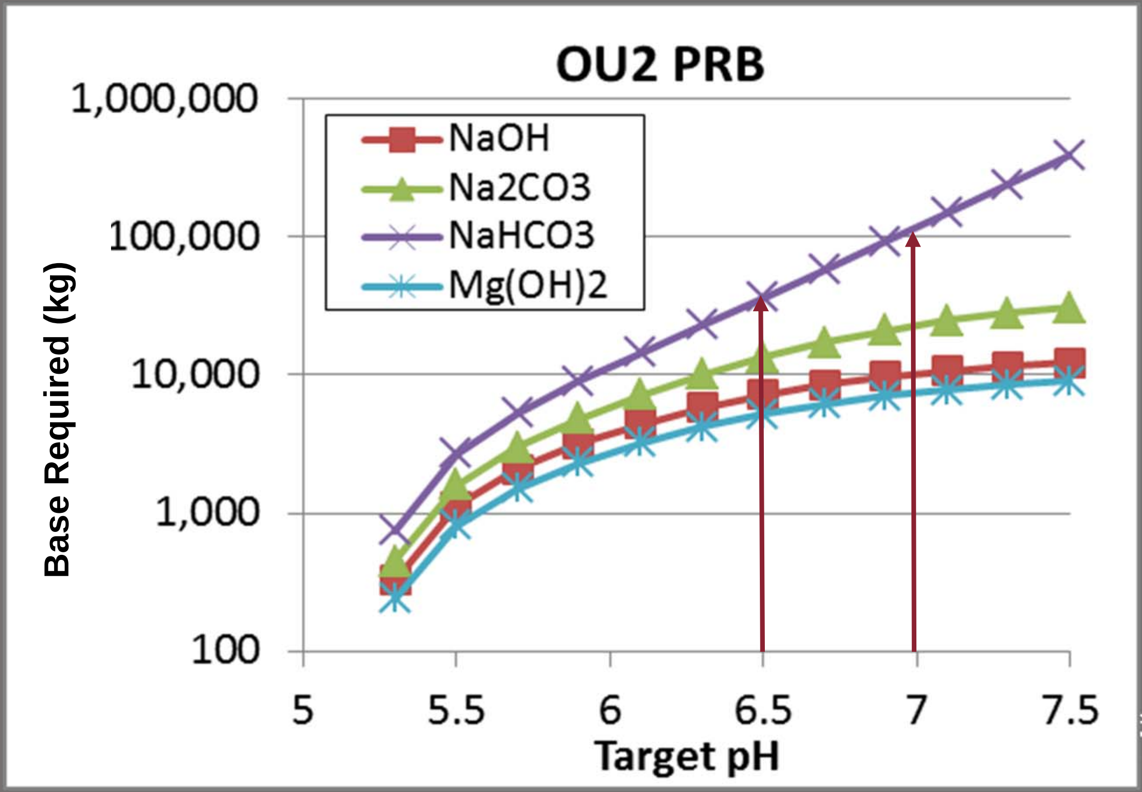
Milk of Magnesia	240	lb	109	Kg

Influent Acidity	6,597	OH^- eq
Base to raise starting pH	85,917	OH^- eq
Acidity from Dechlorination	1,390	OH^- eq
Acidity from Added Substrate	355,567	OH^- eq
Acidity from e^- accept / donors	-269,985	OH^- eq

Total Base Required	179,486	OH^- eq
Total Base Added	3,742	OH^- eq
Fraction of Base Demand Satisfied	2%	

Lessons Learned

- Target pH has major impact on amount of base required
- When the aquifer pH < 6.3, measure pHBC
- Base required can be equal or greater than organic substrate required



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QUESTIONS ?

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