The complicated role of CO_2 in mine water treatment

Benjamin C Hedin[1,2]

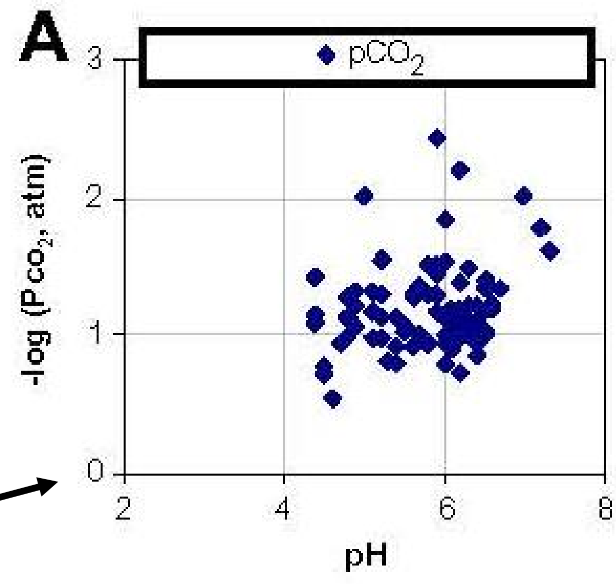
Robert S Hedin[1]

[1]Hedin Environmental

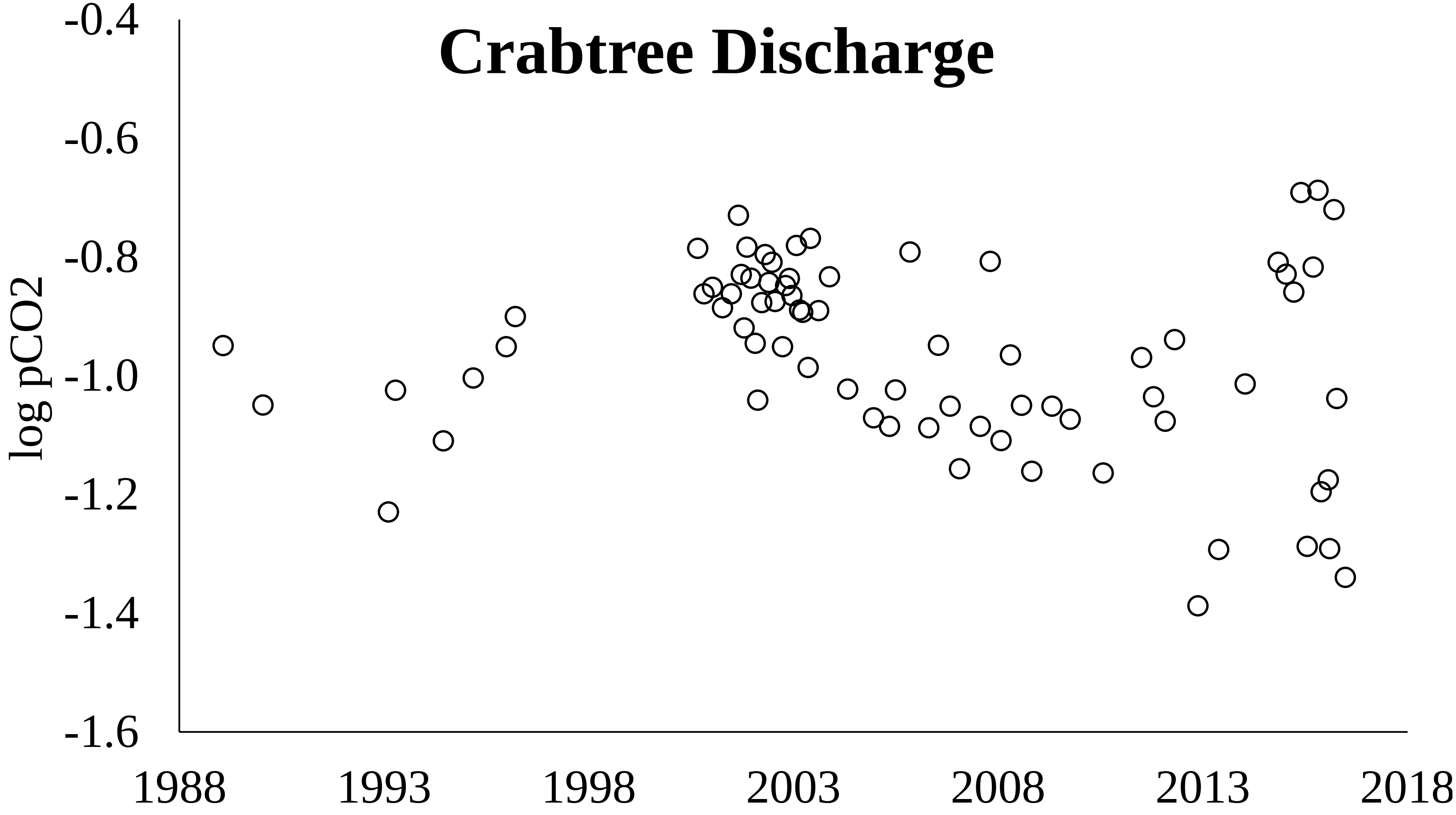
[2]University of Pittsburgh

CO_2 in PA coal mine drainage

Site	Log CO_2 partial pressure
Atmosphere	-3.50
Eastern U.S. groundwater (Appelo & Postma)	-1.60
Mine Waters	
Marchand	-0.76
Crabtree	-0.96
Pine Run	-1.14
Brinkerton	-1.14
Howe Bridge	-1.13
Morrison	-0.99
Wingfield	-0.94
Phillips	-1.01
Cravotta, 2008 (90 samples w/ alk > 0)	Median -1.00 -0.54 to -2.45



CO_2 over time



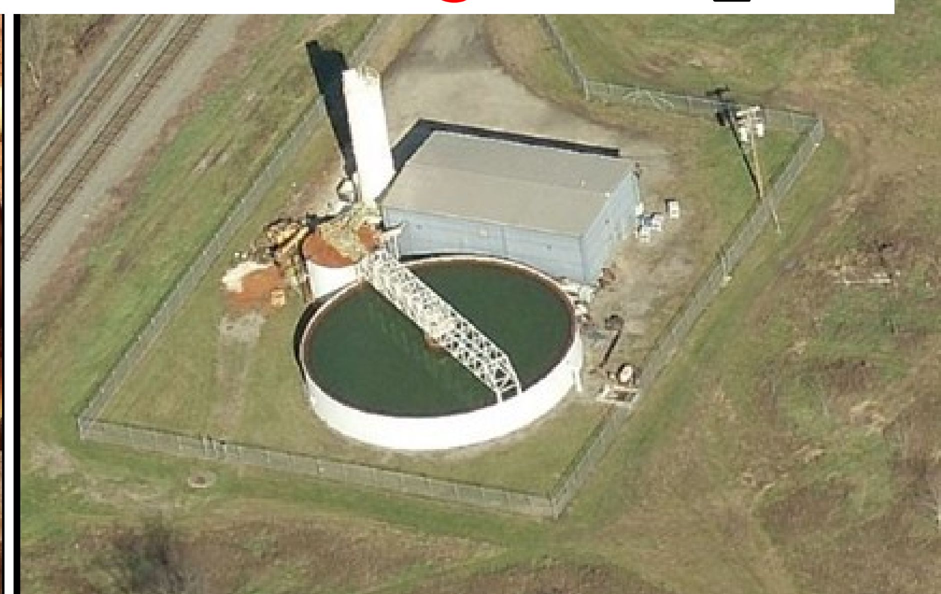
Presentation topics

- CO_2 and lime treatment
- CO_2 and passive Fe and Mn oxidation
- CO_2 and limestone dissolution

CO2 calculated

- Assume alkalinity is HCO_3^-
- H_2CO_3 <-> $H^+ + HCO_3^-$ $k_1 \sim 10^{-6.3}$ (temp dependent)
- $CO_{2(g)} + H_2O$ <-> H_2CO_3 $K_{co2} \sim 10^{-1.5}$ (temp dependent)

$$H_2CO_3 + CaO \rightarrow CaCO_3 + H_2O$$



Lime Treatment Inefficiency due to CO_2

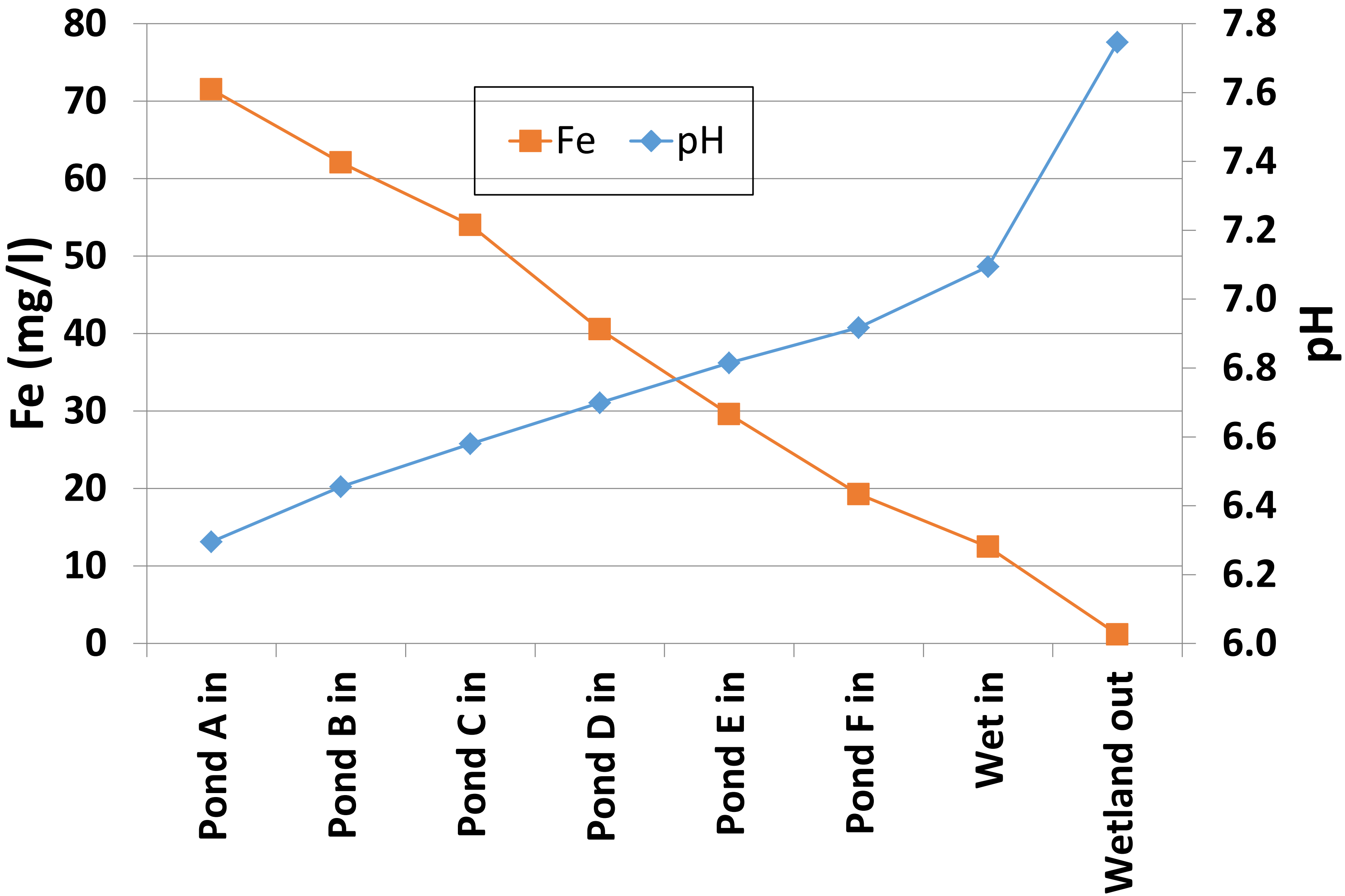
- Nine lime treatment sludges from Pennsylvania
  - 10 – 92% $CaCO_3$ equivalency, average 56%
- Clyde lime treatment plant (Pennsylvania)
  - 25% of lime addition → calcite formation
  - $117,000/yr in extra reagent cost

But…

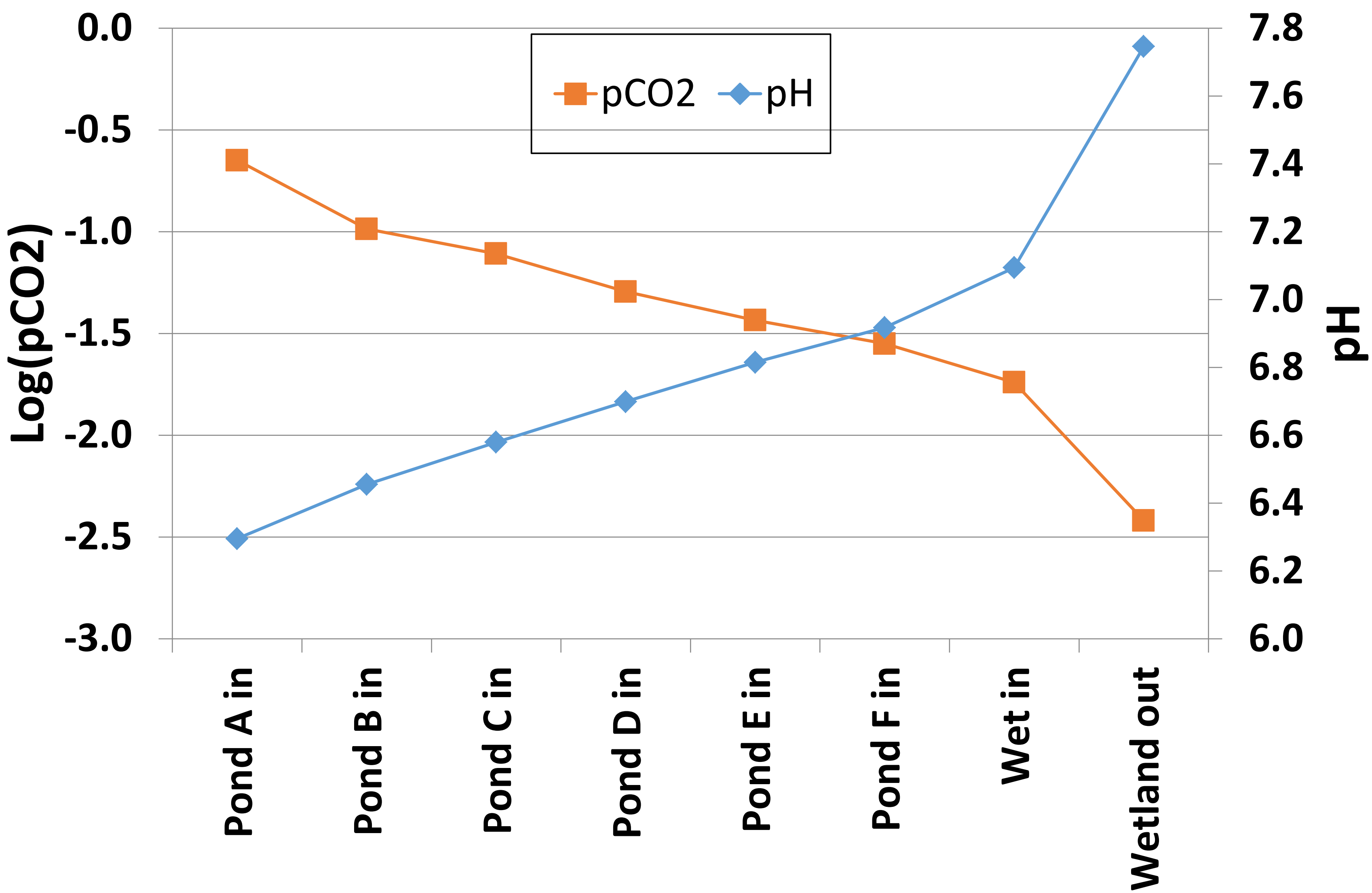
- Hollywood lime treatment plant (Pennsylvania) needed to discharge more alkalinity, so the plant's CO_2 aeration was scaled back
- Schleenbain lime treatment plant (Germany) produces a calcite-containing iron sludge that is valued for its neutralization potential in the mine pit

CO_2 and passive treatment of net alkaline mine waters

- Fe^{2+} and Mn^{2+} oxidation rates are both directly affected by pH
- $HCO_3^- \rightarrow CO_{2(g)} + OH^-$
- Degassing of CO_2 from alkaline water increases pH



Fe (mg/l)
80
70
60
50
40
30
20
10
0
pH
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
Fe
pH
Pond A in
Pond B in
Pond C in
Pond D in
Pond E in
Pond F in
Wet in
Wetland out


pCO2
pH
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
Log(pCO2)
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
pH
Pond A in
Pond B in
Pond C in
Pond D in
Pond E in
Pond F in
Wet in
Wetland out

CO_2 and alkalinity generation with limestone

$CO_{2(g)} + H_2O \leftrightarrow H_2CO_3$

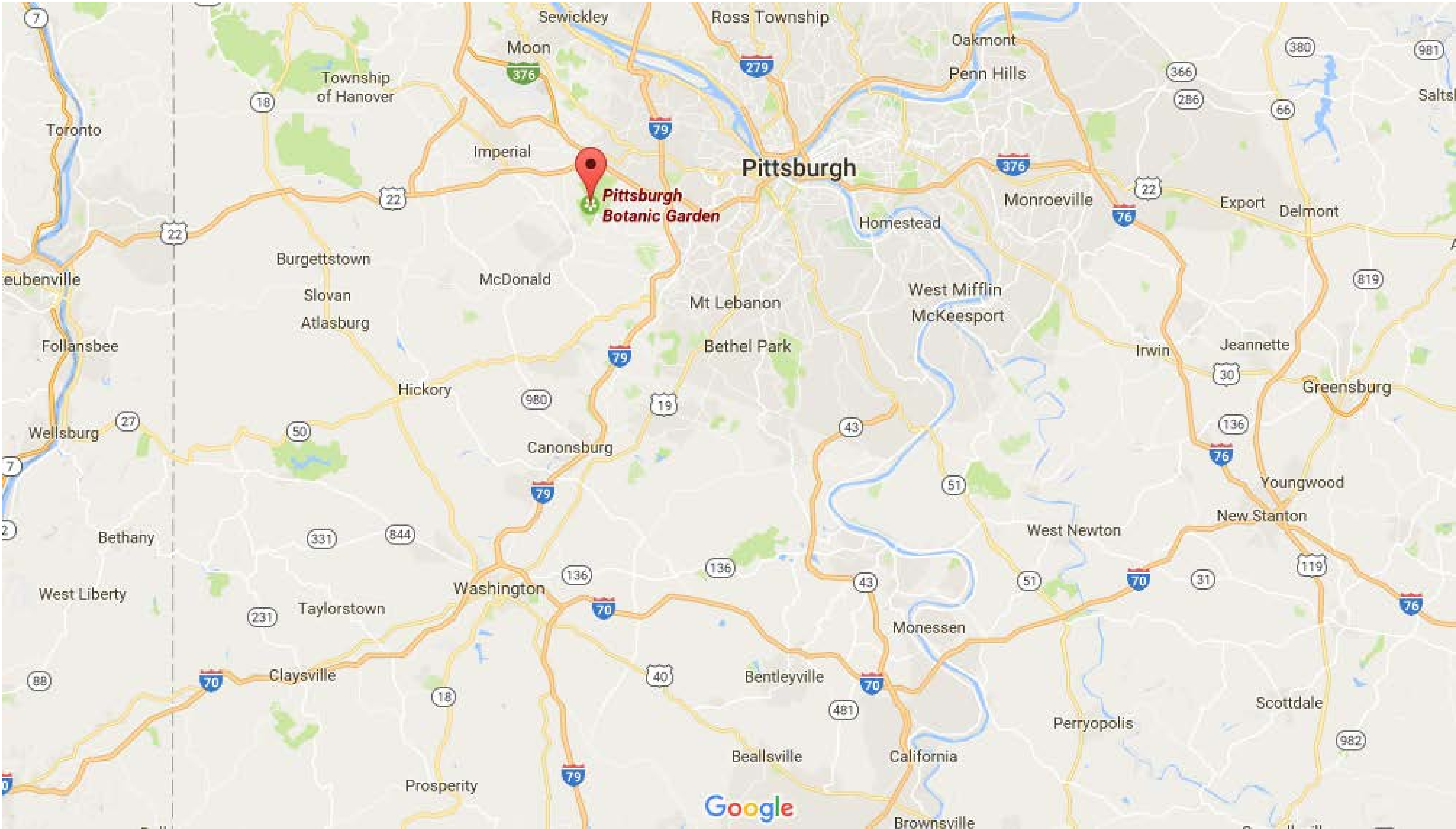
$H_2CO_3 + CaCO_3 \rightarrow 2HCO_3^- + Ca^{2+}$

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

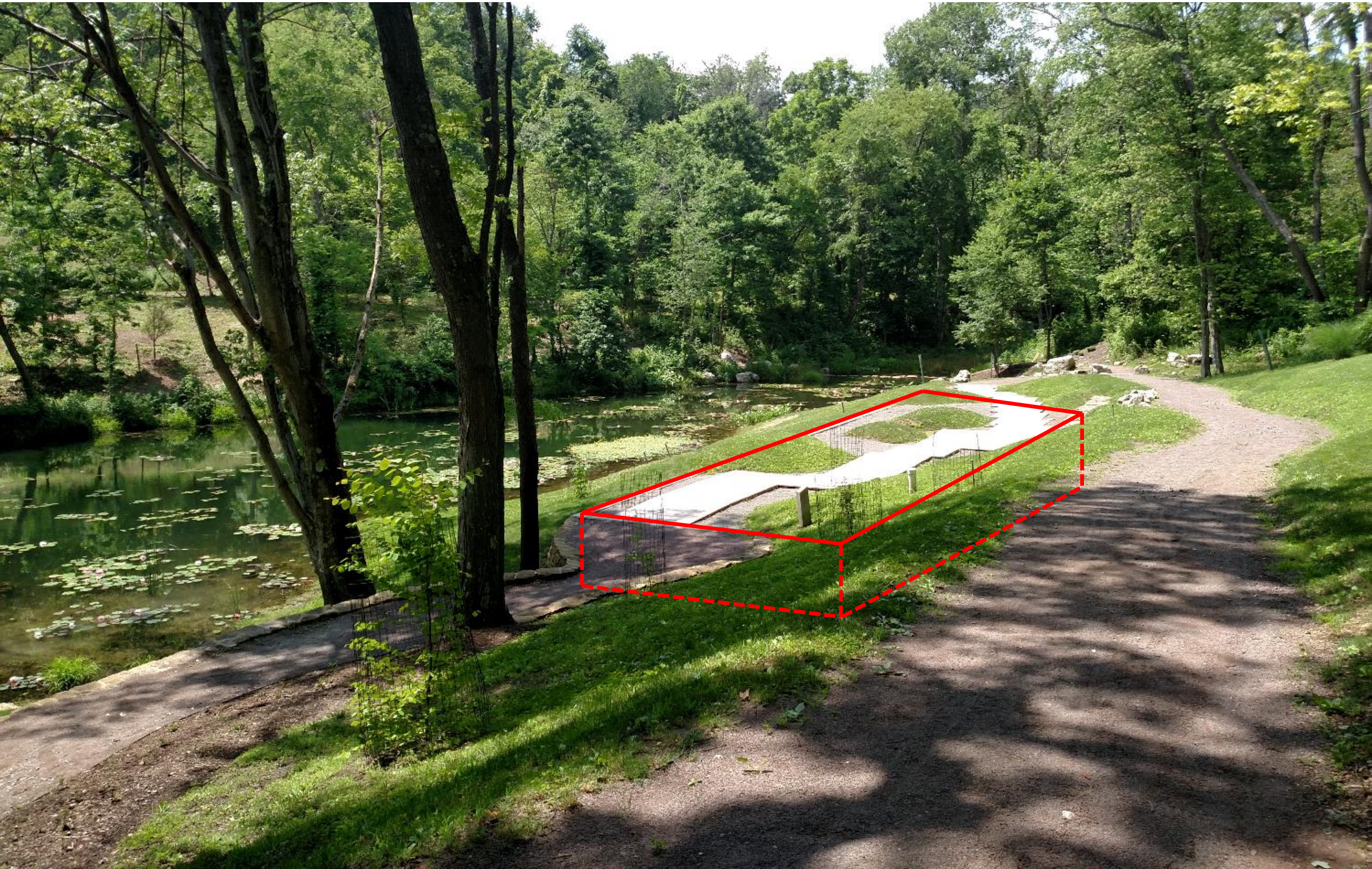
How important is the CO_2 reaction?

ALKasts

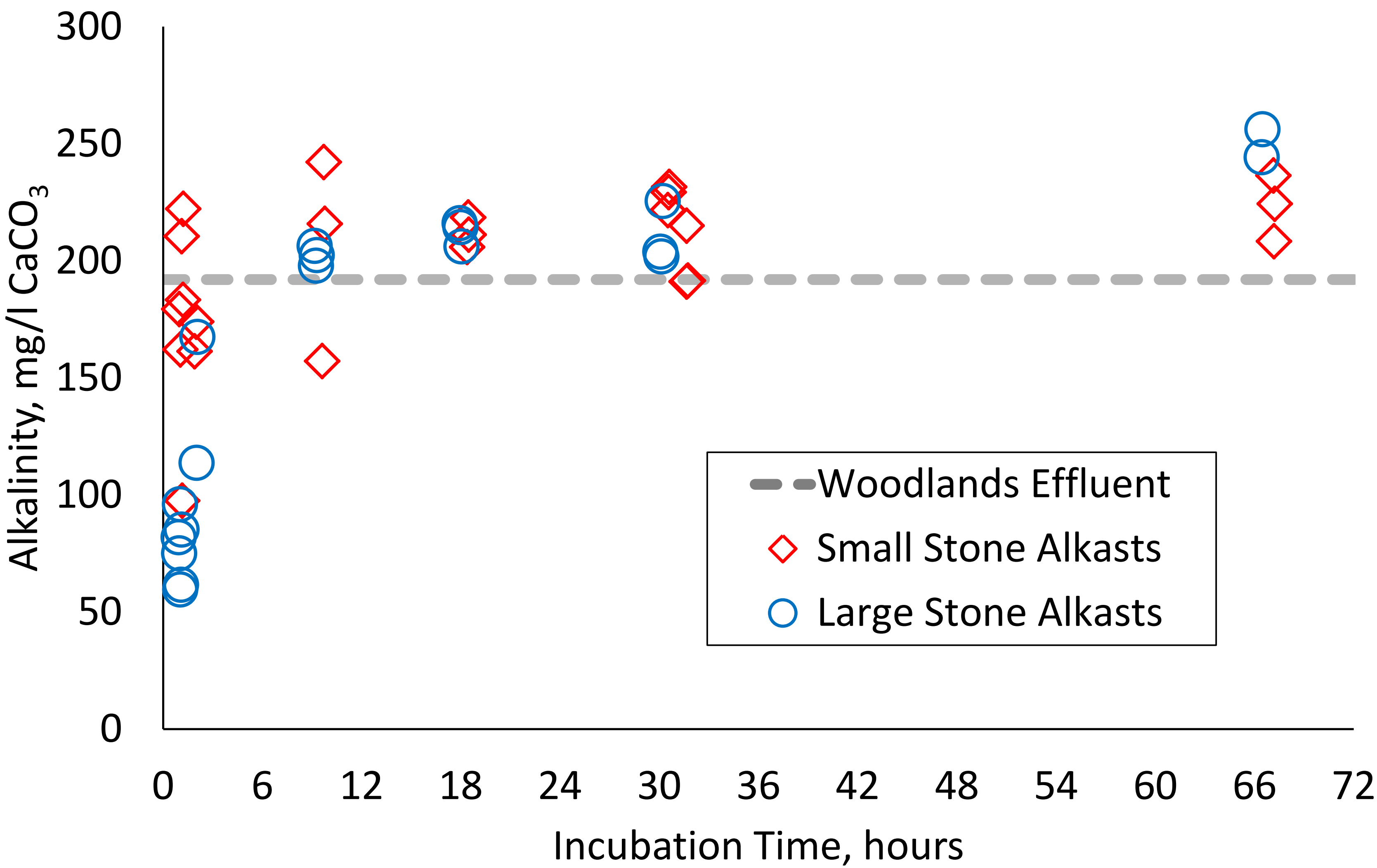
Woodlands treatment system at the Pittsburgh Botanic Garden



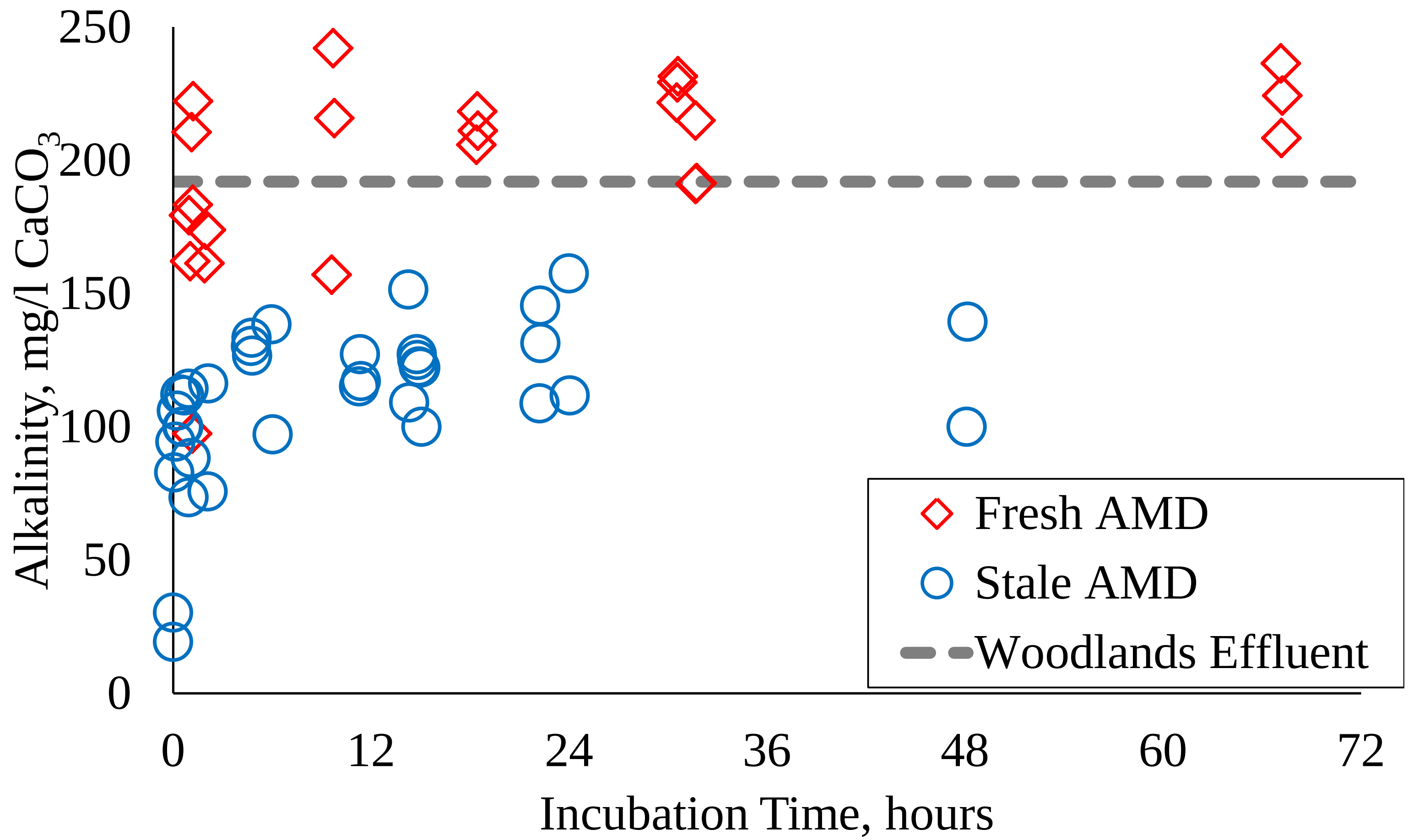
Collected from pipe out of abandoned underground mine



Do Alkasts mimic limestone beds?
Influence of particle size?



Does CO_2 matter?



Condition	Alkalinity (mg/l $CaCO_3$)	St. Dev.	log pCO_2
Woodlands Effluent	202	11	
Fresh AMD (>4 hr incubation)	217	21	-1.53
Stale AMD (>4 hr incubation)	124	16	-2.24

Fall Brook north/south Treatment System

North: Boring buried pipe
South: ~250 ft channelized flow before in stream collection

Fall Brook

- Fall Brook North = Fresh
- Fall Brook South = Stale
- ALKasts on North/South DLB influent/effluent
- ALKasts on South AMD at source (fresh)
- ALKasts on South AMD at variable flows

	Influent	flow	pH	Acid	Fe	Al	Mn	SO4
		gal/min		$CaCO_3$	---------- mg/L ------------			
Woodlands	Pipe	8	3.2	143	0.6	16.3	0.8	474
FB North	Pipe	135	3.5	67	2.7	11.5	9.4	213
FB South	Stream	2,070	3.5	66	0.5	9.9	10.1	285
FB South	Stream	666	3.6	59	0.4	9.4	10.2	274

How do ALKast measurements on the influent water compare to alkalinity generated by the system?

	FBN	**FBS**	**FBS**
System influent water type	Fresh	Stale	Stale
System theoretical retention, hr	14	15	5
System effluent, alk	125	78	61
Retention time = hours. Alk = alkalinity as mg/l $CaCO_3$			

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Alkast, system influent, alk	158	97	76
Retention time = hours. Alk = alkalinity as mg/l $CaCO_3$			

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Alkast, system influent, alk	158	97	76
Alkast, system effluent, alk	147	97	89
Retention time = hours. Alk = alkalinity as mg/l $CaCO_3$			

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System theoretical retention, hr	14	15	5
System effluent, alk	125	78	61
Alkast, system influent, alk	158	97	76
Alkast, system effluent, alk	147	97	89
Alkast, fresh influent, alk	---	206	162
Retention time = hours. Alk = alkalinity as mg/l $CaCO_3$			

CO_2 and Limestone Conclusions

What happens when the *fresh* influent is allowed to aerate and become stale before ALKast testing?

	Wood	FBN	FBS	FBS
System influent water type	Fresh	Fresh	Stale	Stale
System theoretical retention, hr	36	14	15	5
System effluent, alkalinity mg/L	202	125	78	61
Alkast, system influent, alkalinity mg/L	217	158	97	76
Alkast, system effluent, alkalinity mg/L	---	147	97	89
Alkast, fresh influent, alkalinity mg/L	217	---	206	162
Alkast, stale influent, alkalinity mg/L	124	---	---	---

Loose ~ 93 mg/l alkalinity if allow water to aerate

What happens if water is collected from the source and kept *fresh* for Alkast testing?

	Wood	**FBN**	**FBS**	**FBS**
System influent water type	Fresh	Fresh	Stale	Stale
System theoretical retention, hr	36	14	15	5
System effluent, alkalinity mg/L	102	125	78	61
Alkast, system influent, alkalinity mg/L	217	158	97	76
Alkast, system effluent, alkalinity mg/L	---	147	97	89
Alkast, fresh influent, alkalinity mg/L	217	---	206	162
Alkast, stale influent, alkalinity mg/L	124	---	---	---

Gain ~ 100 mg/l alkalinity if collected at source

Lower CO_2 with high flow rate

How to handle CO_2 in treatment systems?

- Lime system
  - Degassing CO_2 substantially decreases chemical costs
  - Preserving CO_2 increases effluent alkalinity and makes sludge more alkaline
- Fe^{2+} or Mn^{2+} passive oxidation system
  - Degassing CO_2 increases pH and oxidation rates
- Limestone system
  - Preserving CO_2 substantially increases alkalinity generation
  - Maximize alkalinity generation vs maximize lifespan of bed

Recommendations

- Measure CO_2 or simply assume fresh AMD has high CO_2 content
- Consider the effect of CO_2 on the treatment processes and handle it appropriately

Use ALKasts to experiment with alkalinity generation