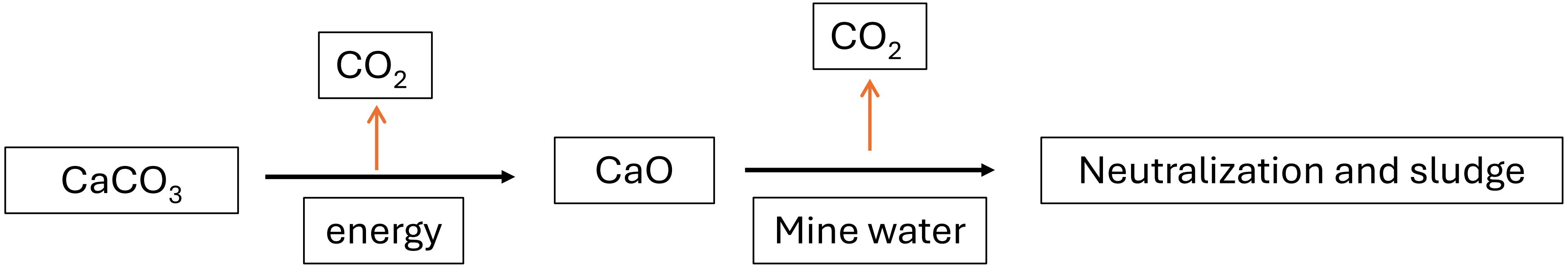
Carbonation of Mine Water to Increase Calcite Dissolution

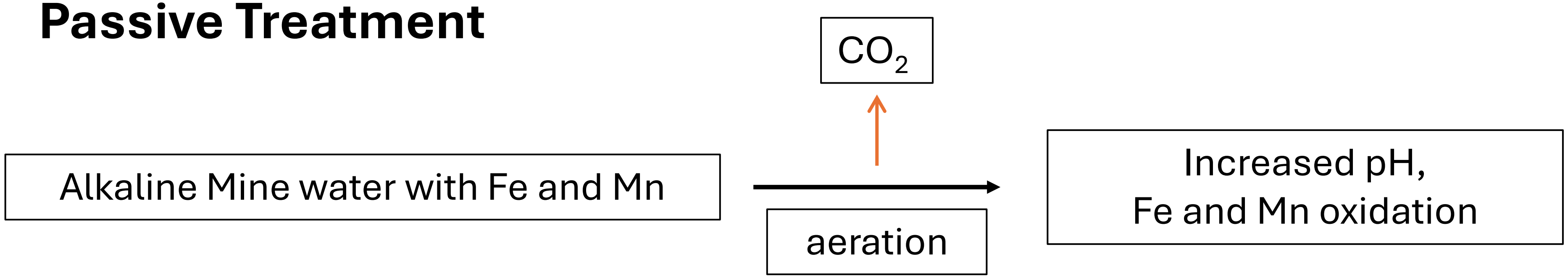
Robert Hedin
Benjamin Hedin

Hedin Environmental
Pittsburgh PA

Active Treatment



Passive Treatment



CO_2 can be an Important Contributor to Passive Treatment

Limestone (calcite) Dissolution

- $CaCO_3 + H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$
- $CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$
- $CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + HCO_3^-$

CO_2 partial pressure affects H_2CO_3 and alkalinity generation

- atmosphere, $pCO_2 = 10^{-3.4} \rightarrow$ ~40 mg/L alk
- mine waters , $pCO_2 = 10^{-2} - 10^{-1} \rightarrow$ 150 – 300 mg/L alk

Passive systems that use limestone to generate alkalinity should preserve CO_2

Outcome of Pre-treating Mine Water with Anoxic Limestone Beds

- Alkalinity generated > acid-producing potential of Fe^{2+} and Mn
  - aeration and retention can yield effluent with neutral pH and low metals

- Alkalinity generated < acid-producing potential of Fe^{2+} and Mn
  - Aeration and retention will lower Fe, but final pH will be < 6 and little removal of Mn will occur
  - Accept incompletely treated effluent or add another alkalinity-generating step

Mine waters that do not generate sufficient alkalinity from limestone (under anoxic, closed conditions)

Site	pH	Alk	CO_2	Fe	Mn	Al	Zn	Ca	Metal Acid	LS-Alk	Deficit
		$CaCO_3$	$\log(P_{CO2})$	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L $CaCO_3$		
Howe (PA)	5.6	47	-0.98	128	21	<1	na	86	267	177	90
Clarion (PA)	5.1	16	-0.94	187	37	2	na	115	401	280	121
Tyler #1 (PA)	5.6	31	-1.16	133	9	<1	na	na	254	189	65
Lambert (PA)	5.9	58	-1.19	161	12	<1	0.1	227	310	169	141
Inclined Plane (PA)	5.9	111	-0.89	142	2	<1	<1	131	257	236	21
Truetown (OH)	5.2	21	-0.93	264	5	2	na	170	482	266	216
Red&Bon (CO)	5.9	40	-1.35	95	31	4	14	432	247	160	87
Elizabeth (VT)	6.5	163	-1.34	150	3	<1	<1	430	274	220	54

How can calcite dissolution (alkalinity generation) be increased?

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

$$[Ca^{2+}]\,[HCO_3^-]^2 / [P_{CO2}] = K$$

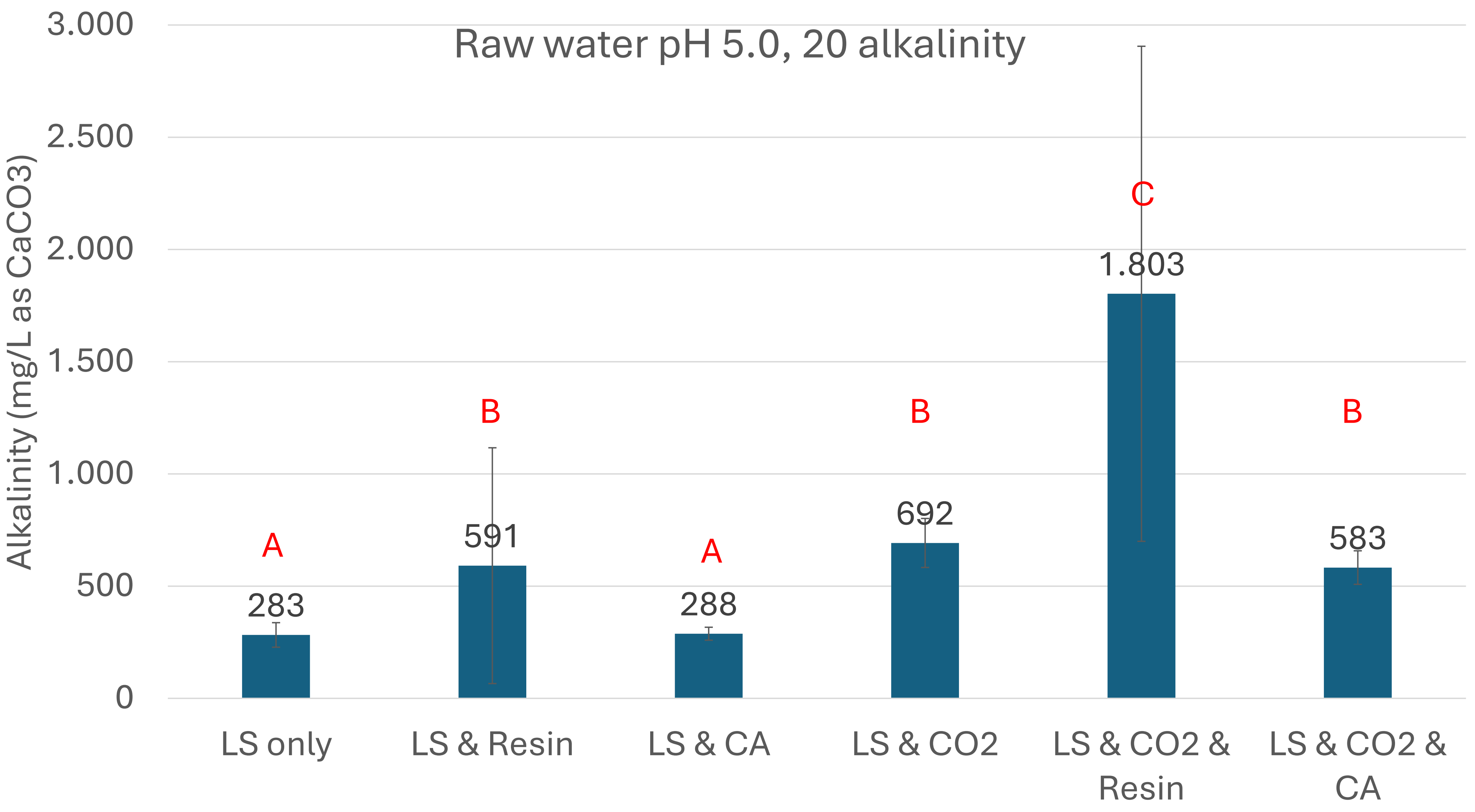
$$[HCO_3^-] = [P_{CO2}] \;/\; [Ca^{2+}]$$

Increase decrease

Evaluating ways to influence $CaCO_3$ dissolution

Tools of the kitchen experimentalist

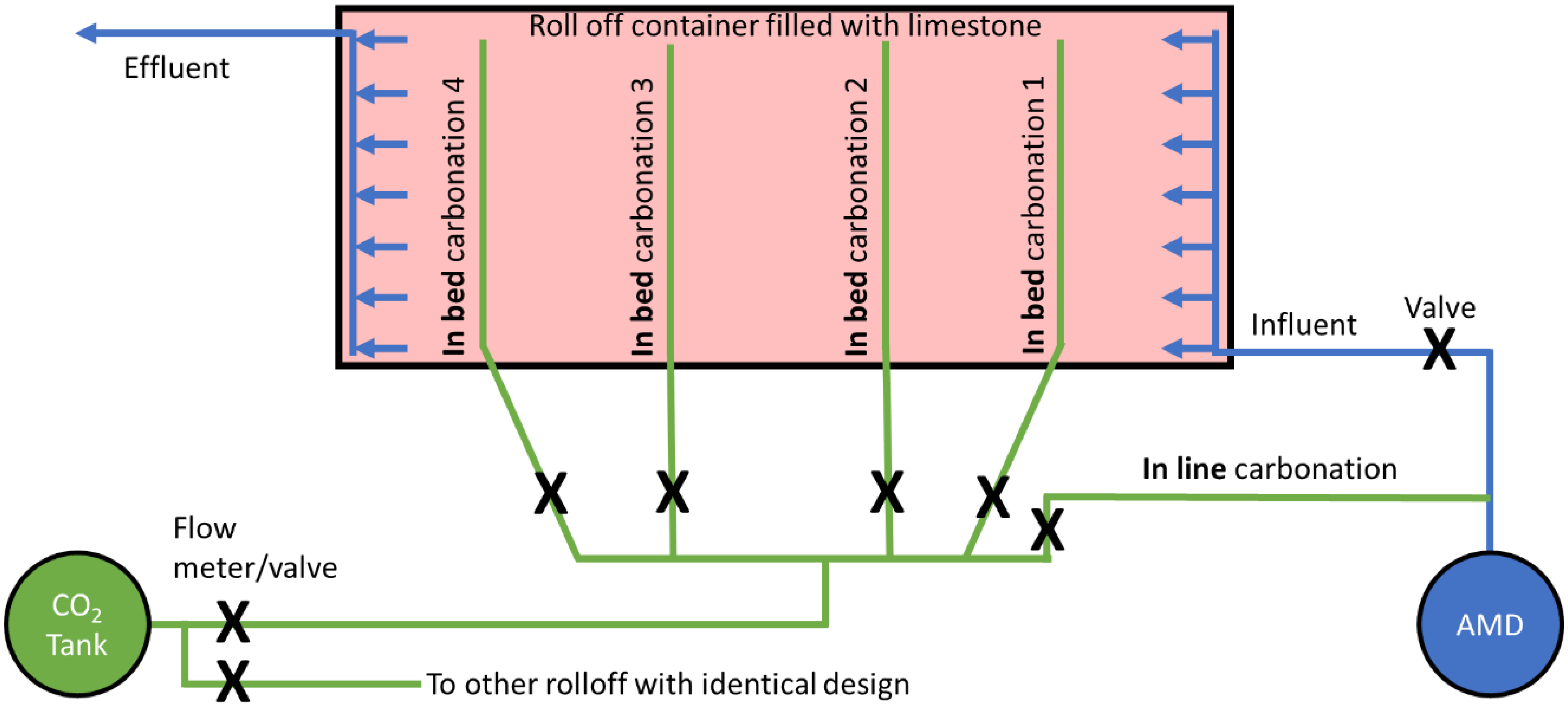
Willing volunteer labor


Raw water pH 5.0, 20 alkalinity
Alkalinity (mg/L as CaCO3)
3.000
2.500
2.000
1.500
1.000
500
0
A
283
B
591
A
288
B
692
C
1.803
B
583
LS only
LS & Resin
LS & CA
LS & CO2
LS & CO2 & Resin
LS & CO2 & CA

Carbonatization of Mine Water to Increase Limestone Dissolution and Alkalinity Generation

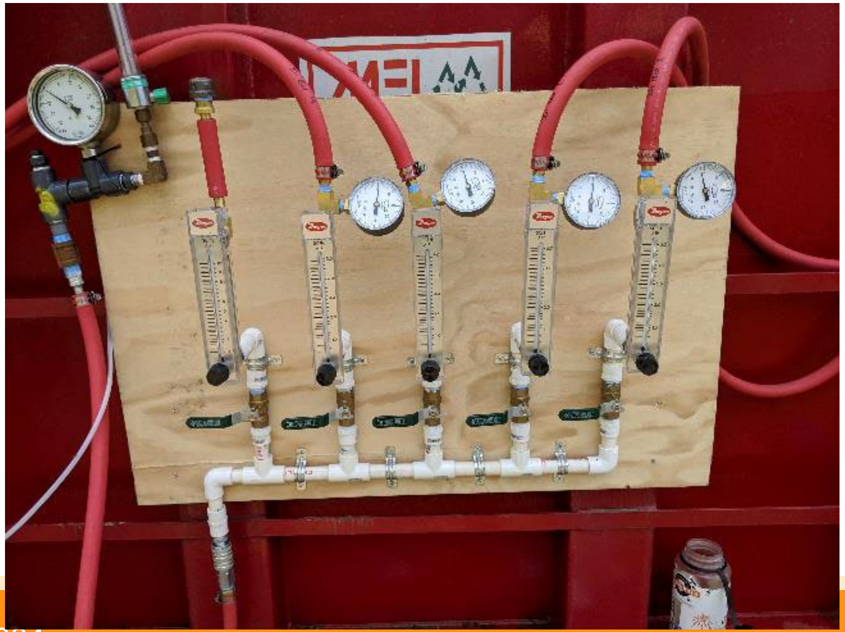
EPA Small Business Innovation Research Award

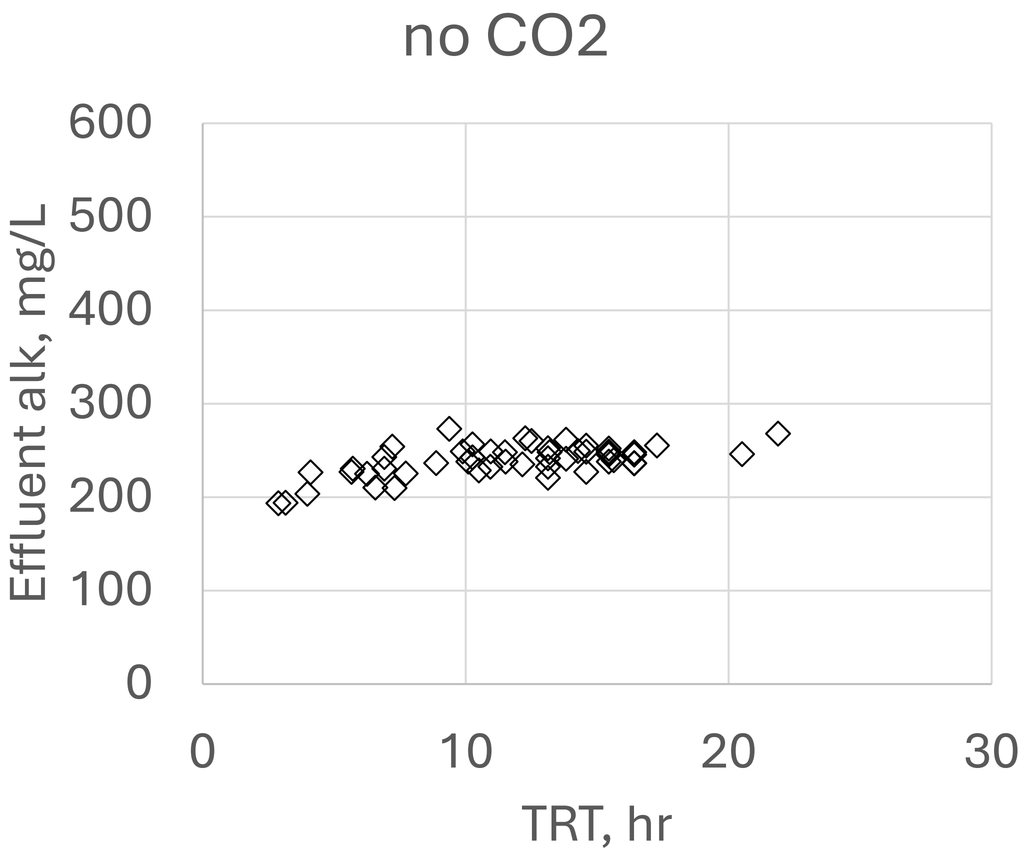
Phase I, 2020; Phase II, 2021-24

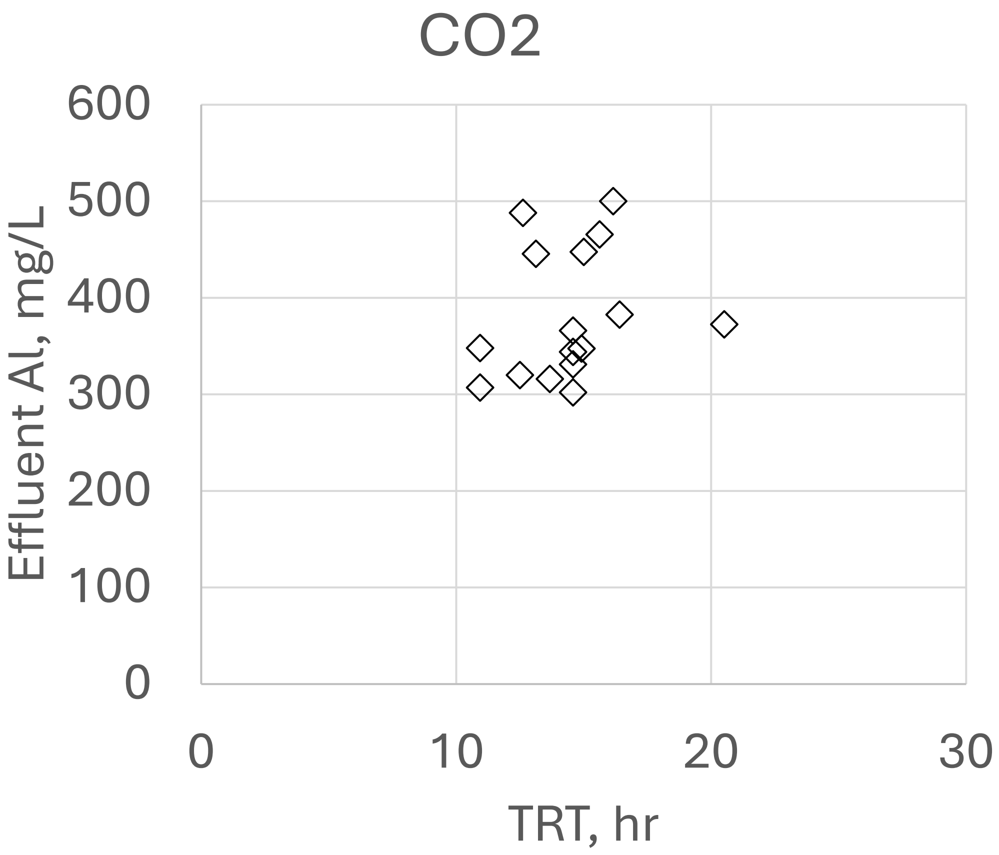


Roll off container filled with limestone
Effluent
In bed carbonation 4
In bed carbonation 3
In bed carbonation 2
In bed carbonation 1
Influent
Valve
In line carbonation
Flow meter/valve
CO_2 Tank
To other rolloff with identical design
AMD

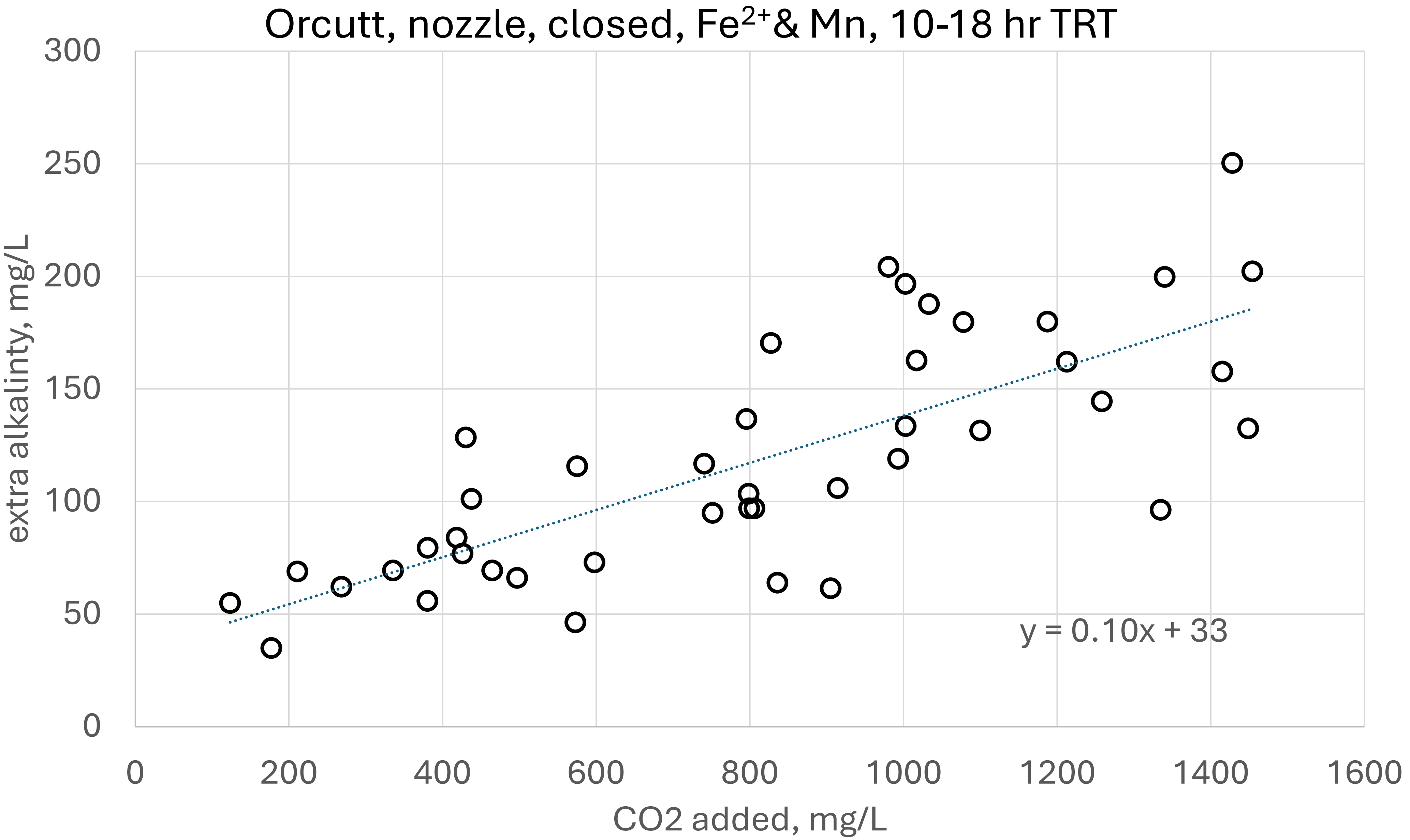




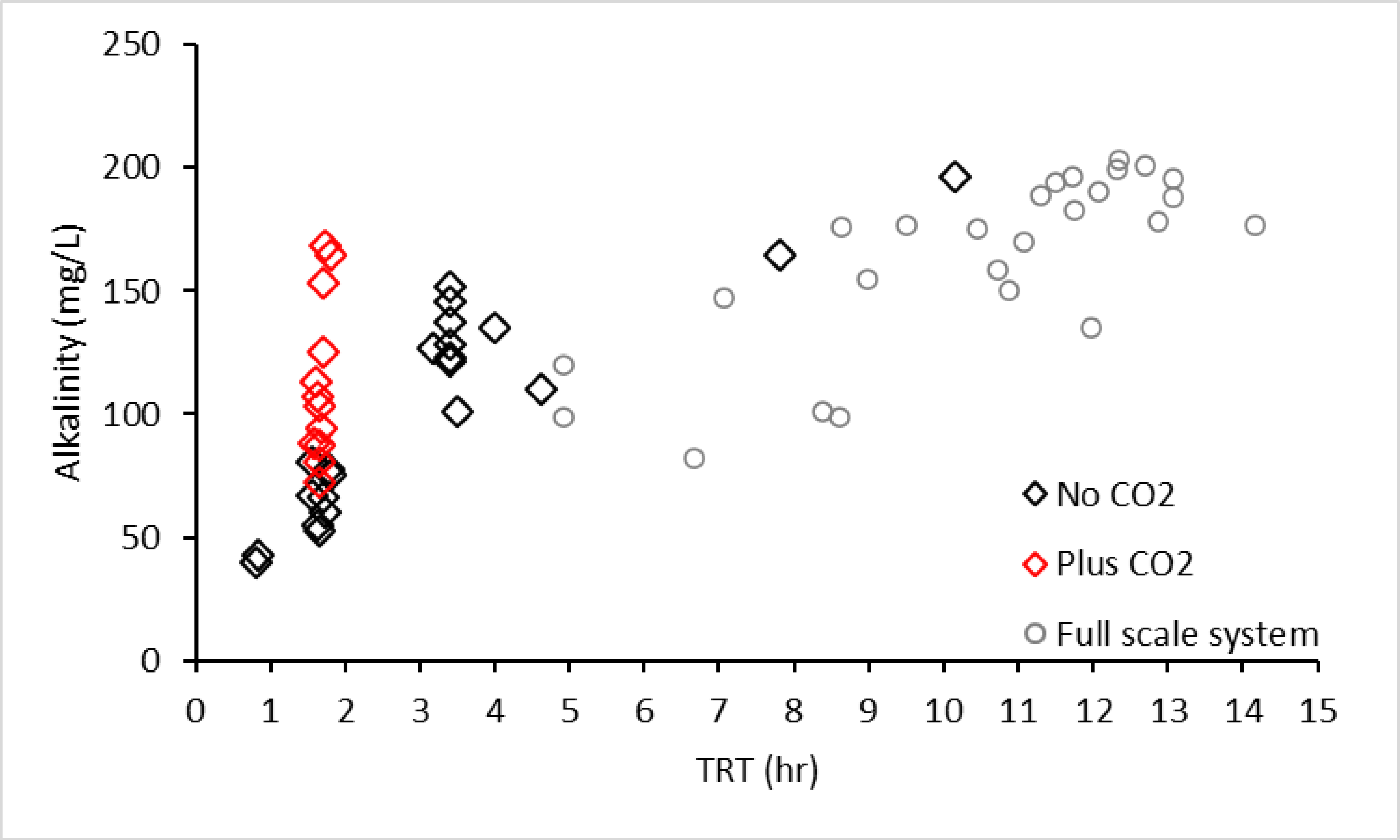


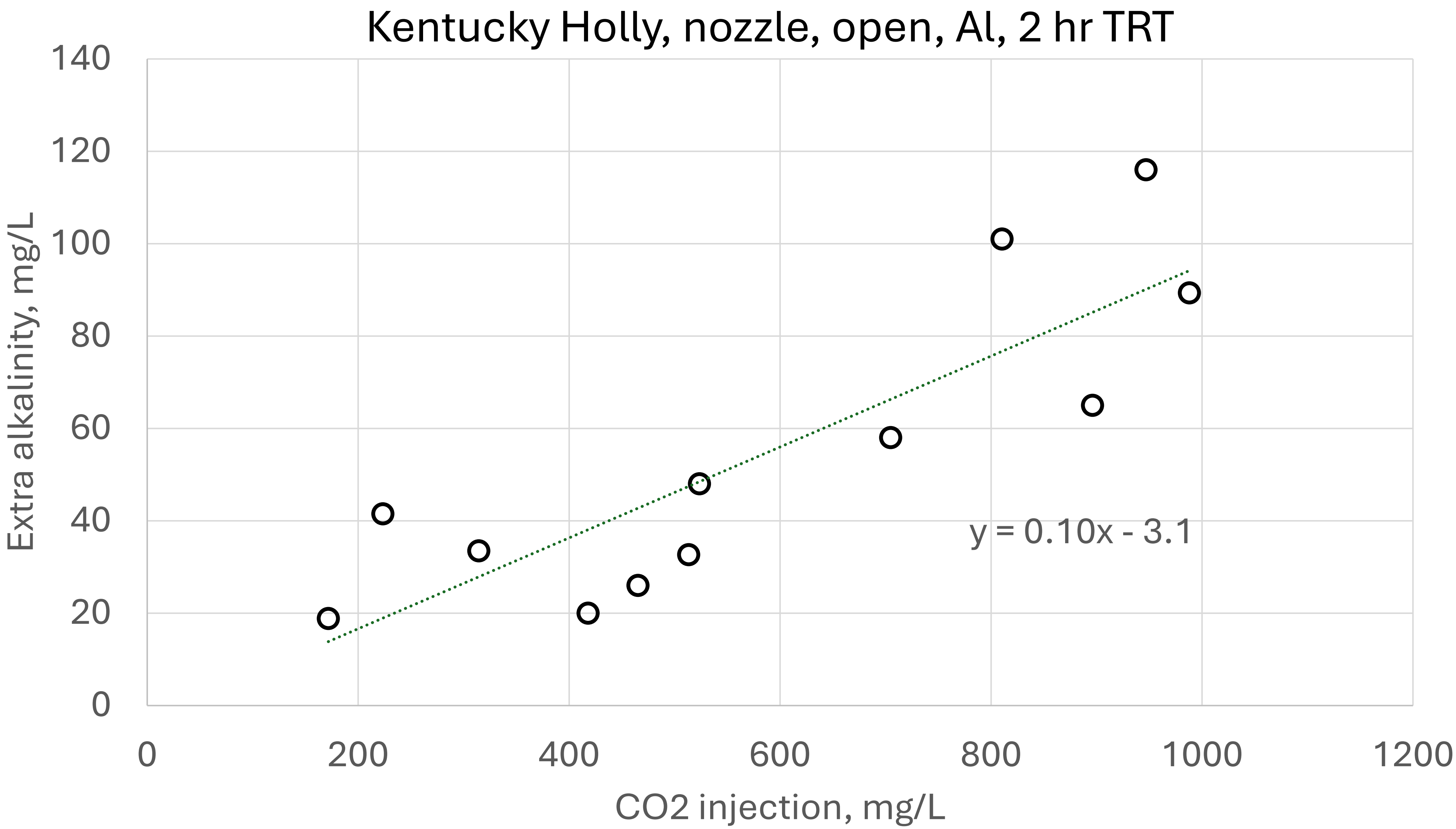
The important measure is increased alkalinity with respect to CO_2 injection

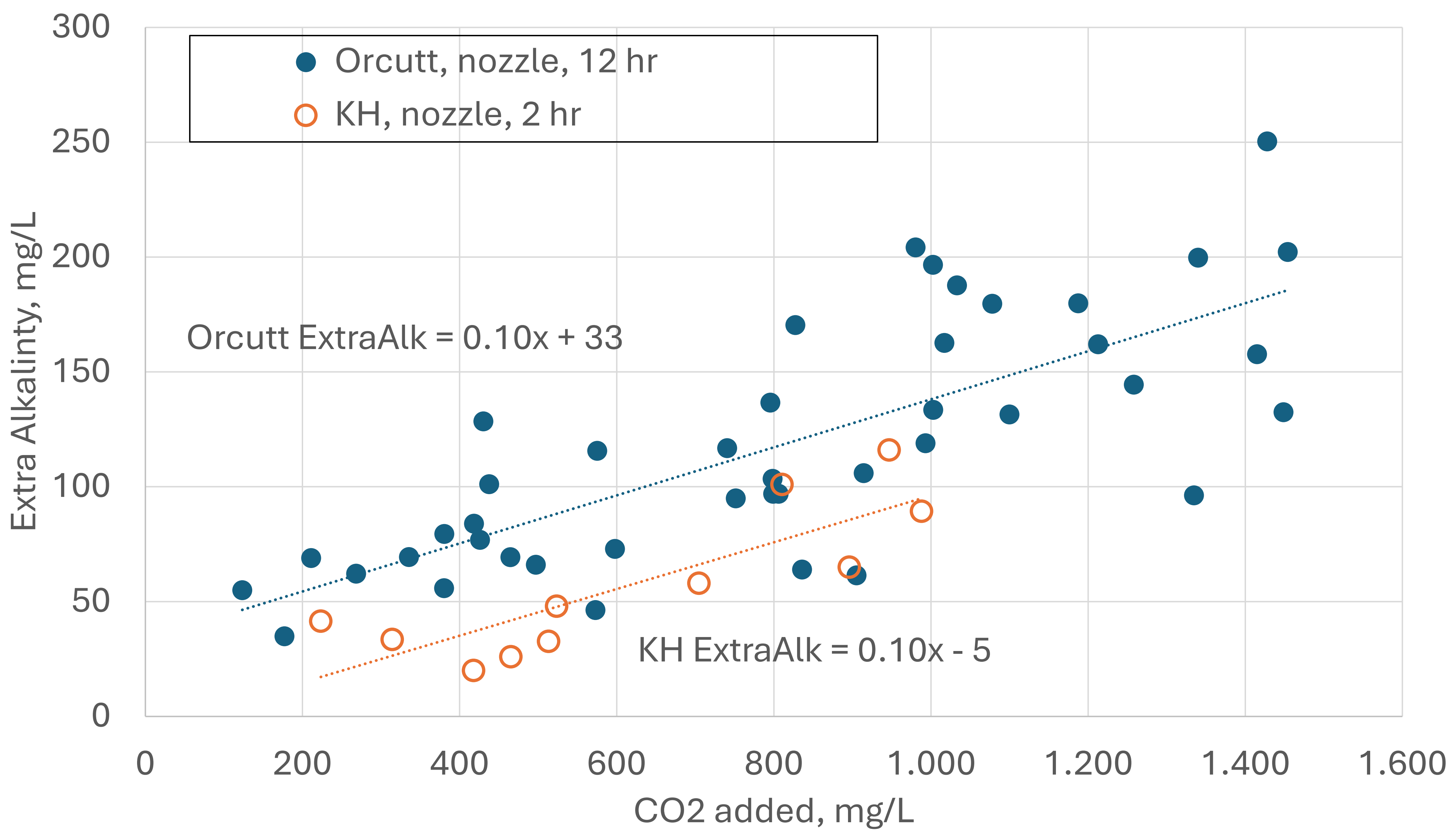


Orcutt, nozzle, closed, Fe2+& Mn, 10-18 hr TRT
extra alkalinty, mg/L
300
250
200
150
100
50
0
0
200
400
600
800
1000
1200
1400
1600
CO2 added, mg/L
y = 0.10x + 33

Kentucky Hollow	pH	Acid	Fe	Al	Mn	SO_4
	s.u.	mg/L	mg/L	mg/L	mg/L	mg/L
Unit influent	3.5	126	0.8	16.1	1.3	515

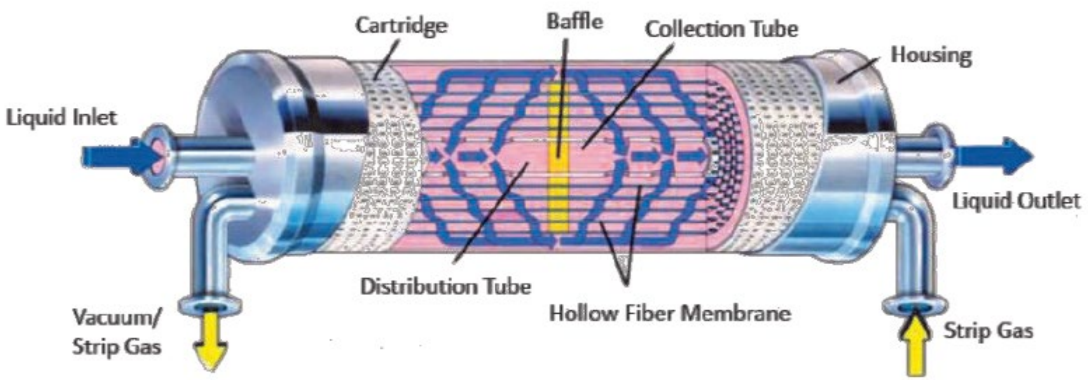

250
200
150
100
50
0
Alkalinity (mg/L)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
TRT (hr)
No CO2
Plus CO2
Full scale system


Kentucky Holly, nozzle, open, Al, 2 hr TRT
140
120
100
80
60
40
20
0
Extra alkalinity, mg/L
0
200
400
600
800
1000
1200
CO2 injection, mg/L
y = 0.10x - 3.1


Orcutt, nozzle, 12 hr
KH, nozzle, 2 hr
Orcutt ExtraAlk = 0.10x + 33
KH ExtraAlk = 0.10x - 5
Extra Alkalinty, mg/L
CO2 added, mg/L
300
250
200
150
100
50
0
0
200
400
600
800
1.000
1.200
1.400
1.600

Site	MW chem	System	LS size	CO_2 injection	TRT, hr	CO_2 / (extra alk)
Orcutt In-bed	pH 5, Fe 95, Mn 30	ALD Roll-off	19 mm	Nozzle	12	7.7
Orcutt In-line	pH 5, Fe 95, Mn 30	ALD Roll-off	19 mm	Nozzle	12	6.0
Kentucky Hollow	pH 3, Al 20	DLB Roll- off	38 mm	Nozzle	2	11.0

Active Carbonation



BV-1	Beer Inlet Valve	GV-1	Gas Inlet Valve	M-1	Air Flow Meter
BV-2	Beer Outlet Valve	GR-1	Gas Pressure Regulator with Gauge	SV-1	Sample Valve
BV-3	Beer Drain Valve				
BPG-1	Beer Pressure Gauge	GV-2	Gas Outlet Valve with Gauge		
BPG-2	Beer Pressure Gauge				

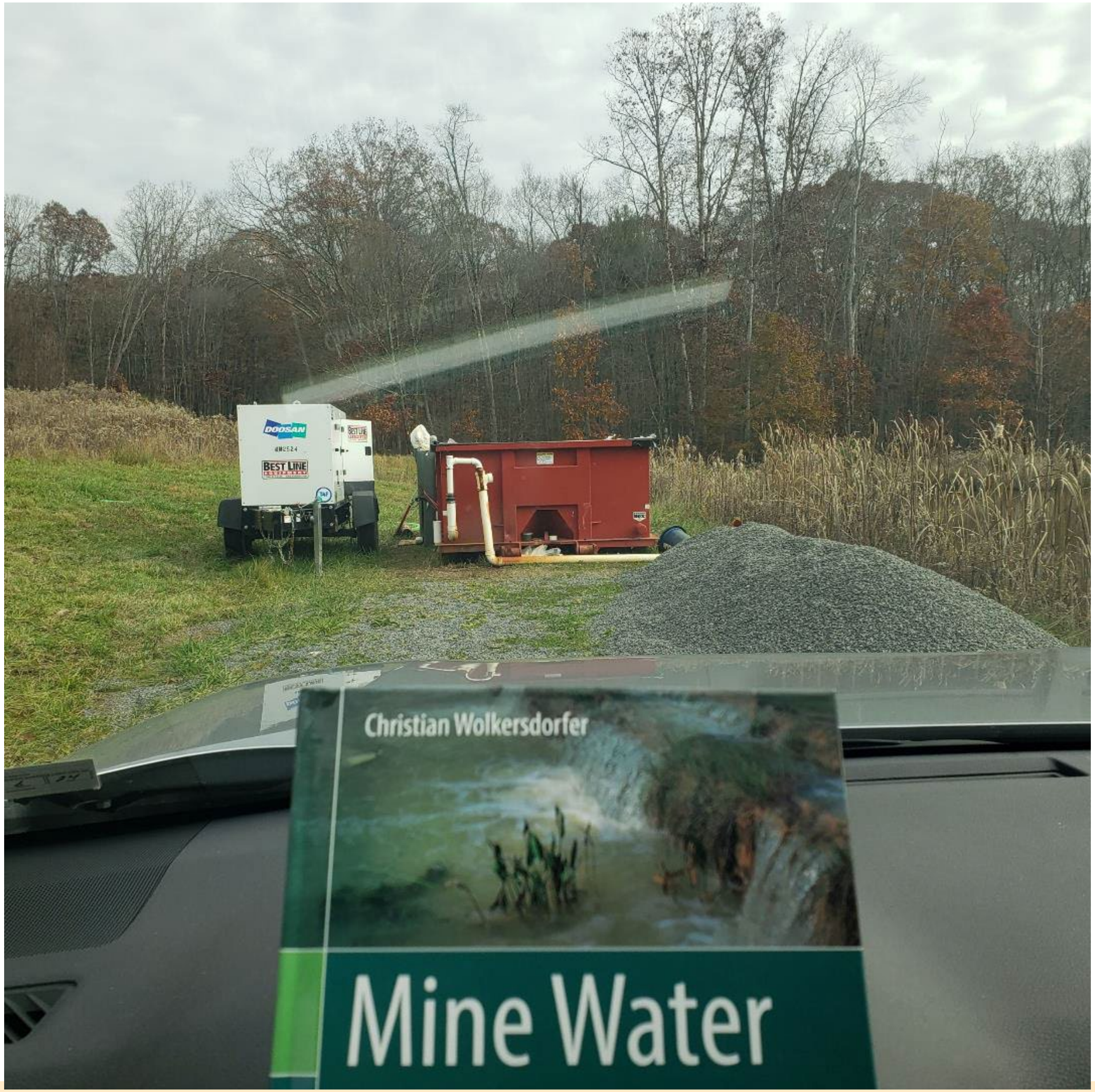
Membrane experiments

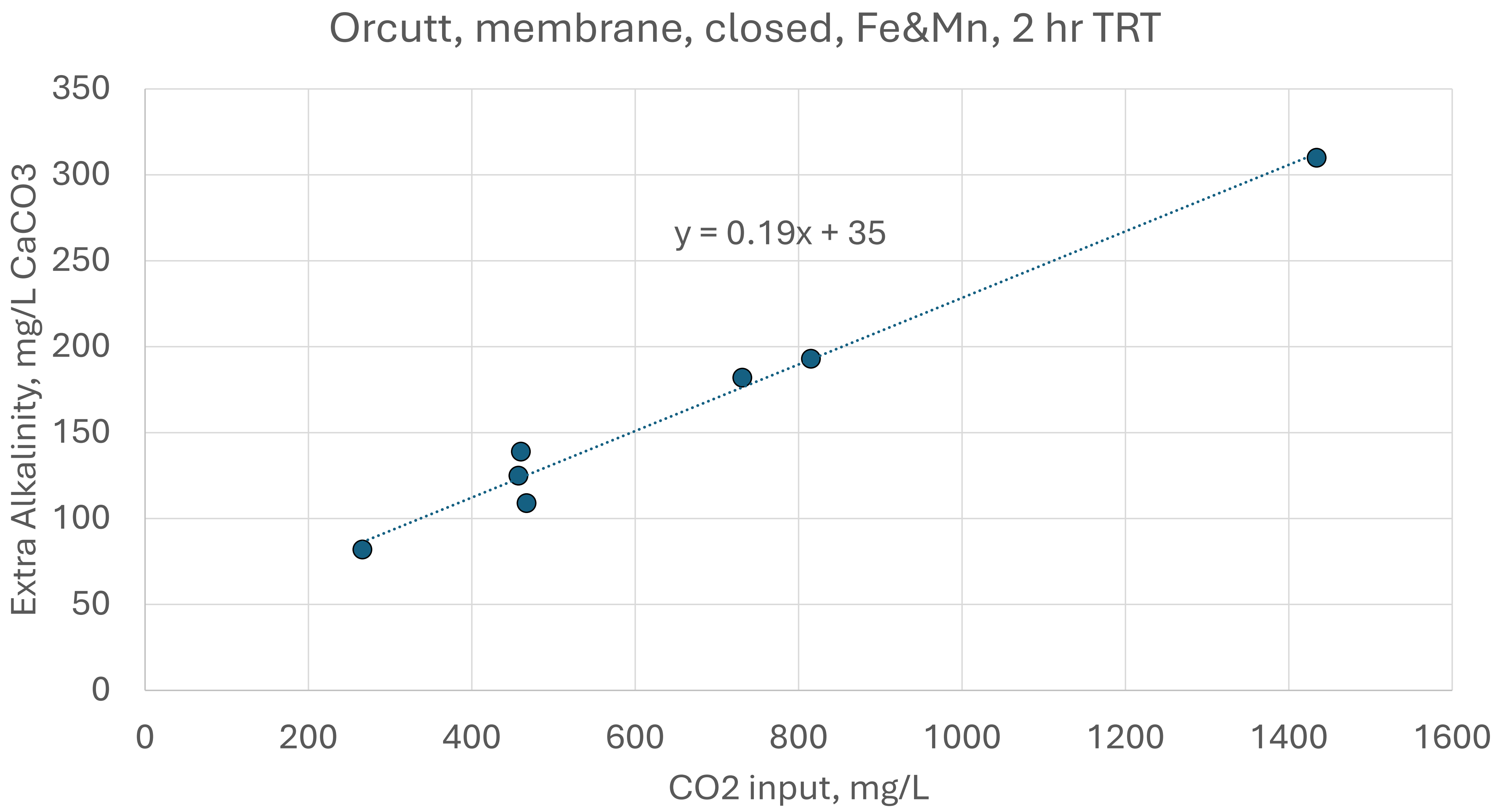
Device

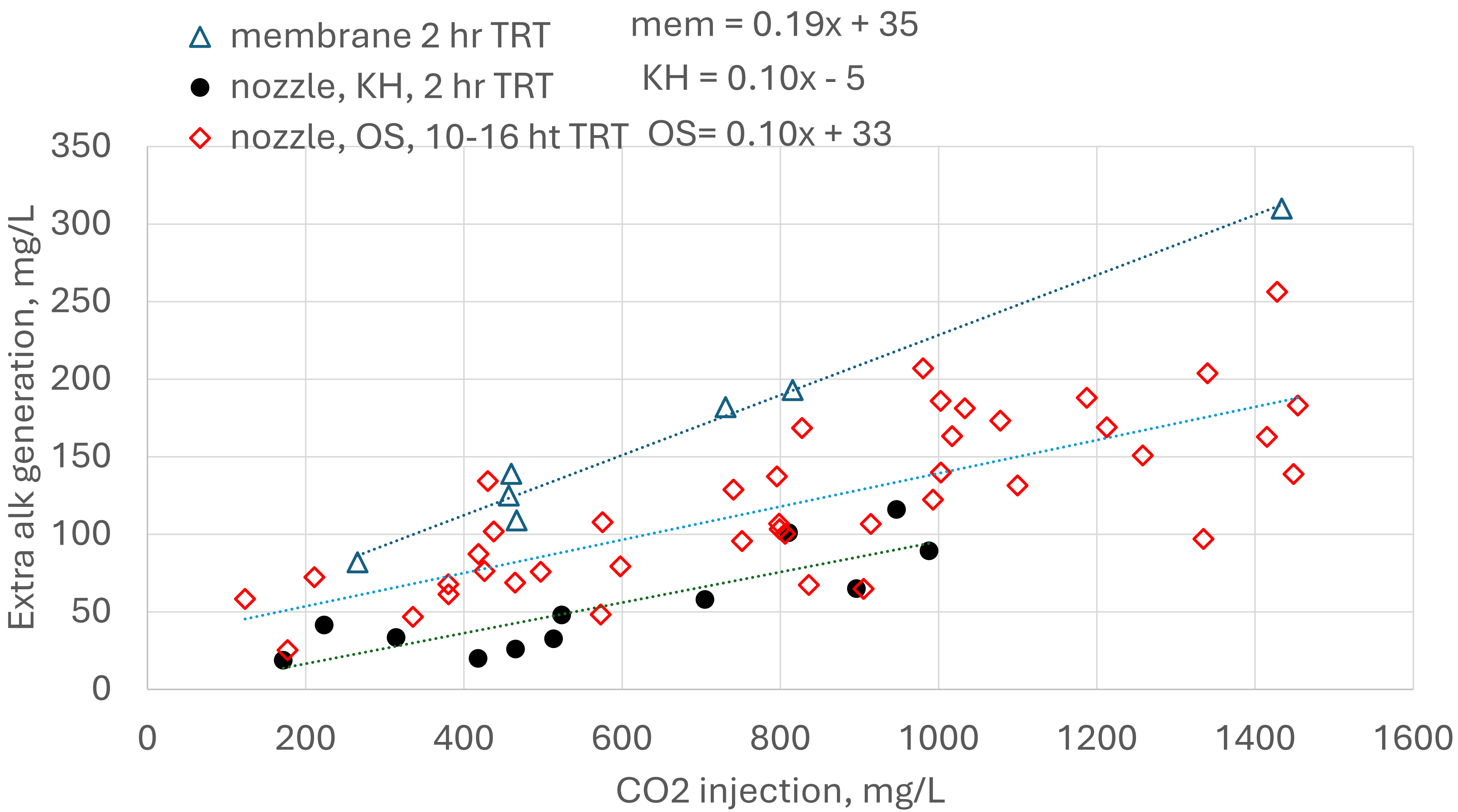
- Carbonation unit made by MG Newell (Greensboro, NC)
  - CO_2 is pressurized from source
  - Water is pressurized by pump
  - Membrane is made by 3M
- Very easy to control inputs and pressures
- Need electricity
- 11 mm aggregate (ASSHTO 8)

Experimental

- No CO_2 alkalinity generation (100 minute TRT): 204 mg/L
- All experiments at 90-100 minute TRT
- Experiments were at least 3 hr (1.5 TRT)


DOOSAN
BEST LINE
Christian Wolkersdorfer
Mine Water


Orcutt, membrane, closed, Fe&Mn, 2 hr TRT
350
300
250
200
150
100
50
0
Extra Alkalinity, mg/L CaCO3
y = 0.19x + 35
0
200
400
600
800
1000
1200
1400
1600
CO2 input, mg/L


membrane 2 hr TRT
nozzle, KH, 2 hr TRT
nozzle, OS, 10-16 ht TRT
mem = 0.19x + 35
KH = 0.10x - 5
OS= 0.10x + 33
Extra alk generation, mg/L
350
300
250
200
150
100
50
0
0
200
400
600
800
1000
1200
1400
1600
CO2 injection, mg/L

Site	MW chem	System	LS size	CO_2 injection	TRT, hr	CO_2 / (extra alk)
Orcutt In-bed	pH 5, Fe 95, Mn 30	ALD Roll-off	19 mm	Nozzle	12	7.7
Orcutt In-line	pH 5, Fe 95, Mn 30	ALD Roll-off	19 mm	Nozzle	12	6.0
Kentucky Hollow	pH 3, Al 20	DLB Roll- off	38 mm	Nozzle	2	11.0
Orcutt	pH 5, Fe 95, Mn 30	ALD Roll-off	11 mm	membrane	2	3.9

Rough AMD neutralization costs

Treatment	Assumptions	CO_2 \$/ton	Alk:CO_2	\$/ton $CaCO_3$
NaOH	20%, $2.00/gal	na	na	$1,600
Lime slurry	$4,100/load	na	na	$900
Limestone	$50/ton	na	na	$60
CO_2 & Limestone, nozzle	$50/ton limestone	$160	8.0	$1,340
CO_2 & Limestone, membrane	$50/ton limestone	$160	4.0	$700
CO_2 & Limestone, membrane	$50/ton limestone	$80	4.0	380

Comments and Questions?