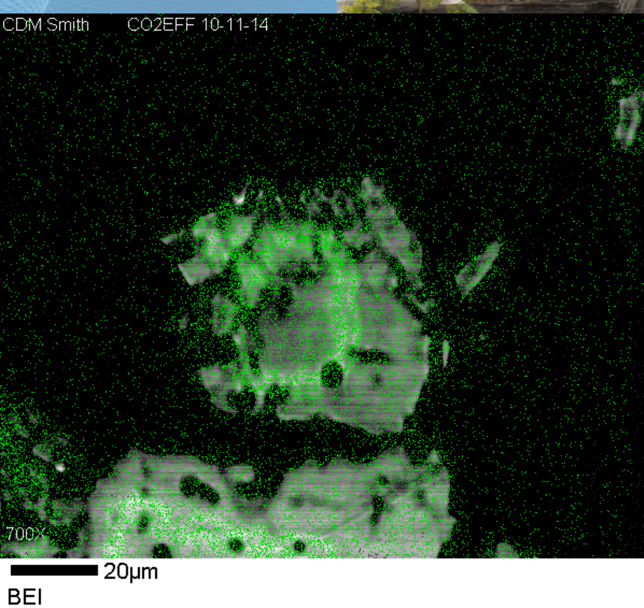
Treatment of Zinc-, Lead-, and Cadmium-bearing Mine Drainage at the Rex Mine Site Coeur d' Alene, Idaho.



Kent Whiting, L.G. – CDM Smith
Nick Anton, P.E. – CDM Smith
Todd Burgesser CHMM – CDM Smith
Roger Olsen, Ph.D., BCES – CDM Smith

June 6, 2018

CDM Smith

Presentation Outline

- Brief summary of Rex Mine site and water quality
- Water Treatment Challenges
- Introduction of Calcite Precipitation Technology (CPT)
- CPT Modeling and Batch Study Findings
- CPT Column Study Findings
- Conclusions

Successor Coeur d'Alene Custodial and Work Trust

- In December 2009, U.S. EPA announced a $1.7 Billion settlement with ASARCO, the largest Superfund settlement in EPA history.
- $494 Million toward the cleanup of the Bunker Hill Superfund Site
- Settlement funds were placed in a Successor Coeur d'Alene Custodial and Work Trust (Coeur d'Alene Trust)
- The Rex Mine project is part of the Coeur d'Alene Trust work

Rex Mine Site, Coeur d'Alene District, Idaho

CDM Smith

Rex MIW Treatment Approach

Water Was Collected from the Rex Adit on April 17, 2014

Rex MIW Treatment Approach

Adit Water Quality on April 17, 2014 (mg/L)

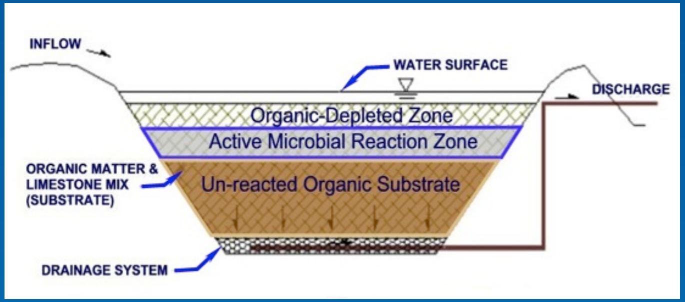
Parameter	Rex Mine Adit Discharge (4-17-14)	Parameter	Rex Mine Adit Discharge (4-17-14)
Temperature (C)	4.03	Sodium	2.9
pH (su)	**5.62**	Potassium	1.10
Bicarbonate Alkalinity (as mg $CaCO_3$/L)	**15**	**Zinc**	**5.10**
Phosphate (as P)	0.57	Chloride	0.42
Aluminum	0.018	Fluoride	0.13
Barium	0.014	**Sulfate**	**36**
Iron	0.022	Silica (as SiO2)	38.5
Manganese	0.043	Nitrite	0.049
Calcium	**10**	Nitrate	0.130
Cadmium	**0.029**	Ammonia	0.022
Lead	0.380	Barium	0.014
Magnesium	2.5	TDS	97

Flow of 4.5 to 58 gpm

CDM Smith

Water Treatment Technologies

- Common MIW treatment approaches
  - Active neutralization-based treatment
  - Passive treatment
    - Limestone channels/drains
    - Biochemical reactors (sulfate reducing bioreactors)
    - Wetland systems
- MIW Treatment Challenges
  - Active treatment cost limitations
  - Lack of electrical power
  - Stringent treatment standards



CDM Smith

Calcite Precipitation Technology

The Technology Includes the Following Steps

- Step 1 - Adjust the pH of the MIW (using CO_2) to make it aggressive to calcite (undersaturated with respect to calcite), if necessary
- Step 2 - Contact the zinc-bearing MIW with calcite via a limestone bed, resulting in dissolution of some of the calcite.
- Step 3 - After the MIW exits the limestone bed (into a pond), strip the water of carbon dioxide using an air sparging system
- Step 4 - The pH increases resulting in precipitation of zinc-, and cadmium-bearing calcite.

Calcite Precipitation Technology

The Relevant Reactions Include

- Step 1 – CO2 Addition

$CO_2\ (\downarrow) + H_2O \rightarrow H_2CO_3 \rightarrow HCO_3^- + H^+$

- Step 2 – Calcite dissolution

$H^+ + CaCO_3\ (\text{Calcite}) \rightarrow Ca^{+2} + HCO_3^-$

- Step 3 – CO_2 Stripping

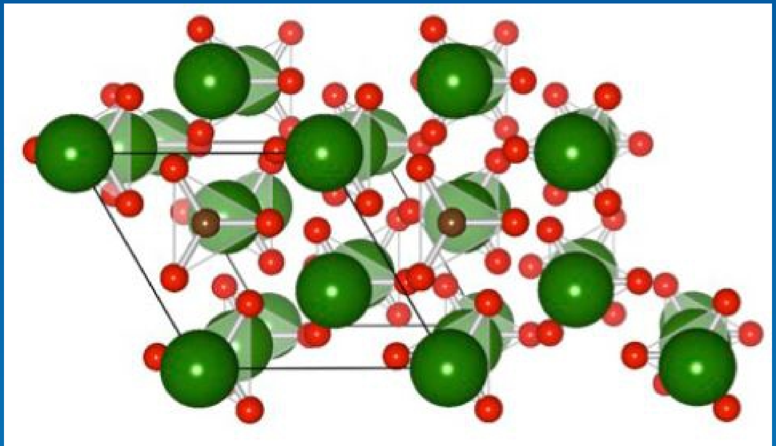
$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2\ (\uparrow) + H_2O$

- Step 4 – Calcite Precipitation

$Ca^{+2} + Zn^{+2} + HCO_3^- \rightarrow (Ca, Zn)CO_3(s) + H^+$

Calcite Precipitation Removal Mechanisms

- Cadmium is removed by replacing calcium within the calcite structure.
  - Ca^{+2} and Cd^{+2} have the same charge and very similar ionic radii allowing substitution within minerals



- Zinc is removed by the formation of the mineral hydrozincite ($Zn_5(CO_3)_2(OH)_6$) onto the calcite surfaces
- Lead is removed by the pH increase as either a carbonate or phosphate phase.

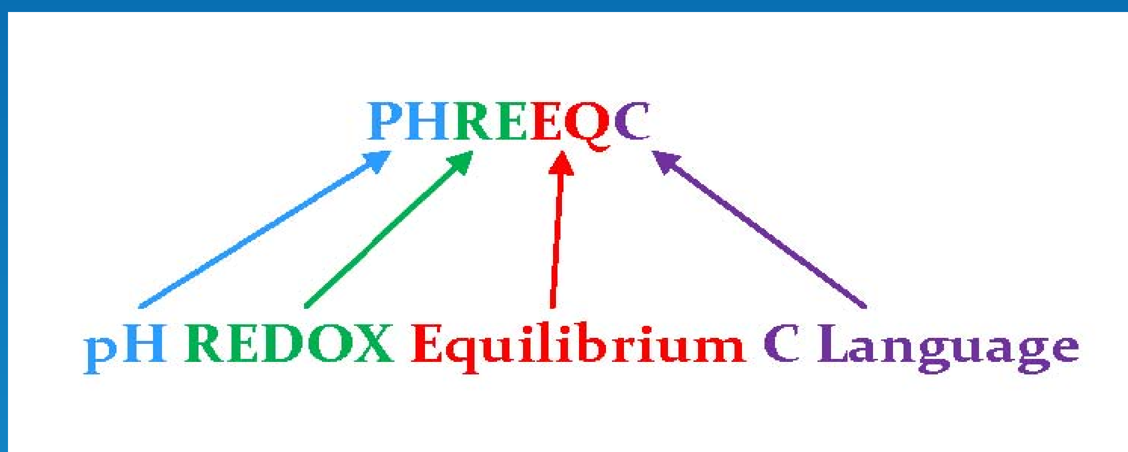
Applicability of Technology

- Works well for cadmium, zinc, lead, and possibly other metals (copper, nickel, manganese, etc.). Does not work for arsenic.
- Does not work for waters high in iron and aluminum (limestone armoring)
- Useful for waters low in sulfate where use of biochemical reactors is more challenging (would require sulfate addition).
- Works for waters which have pH values 4.5 to about 6.0 (lower pH water can often be obtained by collecting at the discharge point)

Rex MIW Treatment Approach

PHREEQC Modeling was performed to confirm that the water was aggressive to calcite

USGS
science for a changing world



Rex MIW Treatment Approach

PHREEQC Modeling Results

Phase	Saturation Index
Calcite ($CaCO_3$)	-3.80
P_{CO2} (atm)	$10^{-1.46}$

Results show:

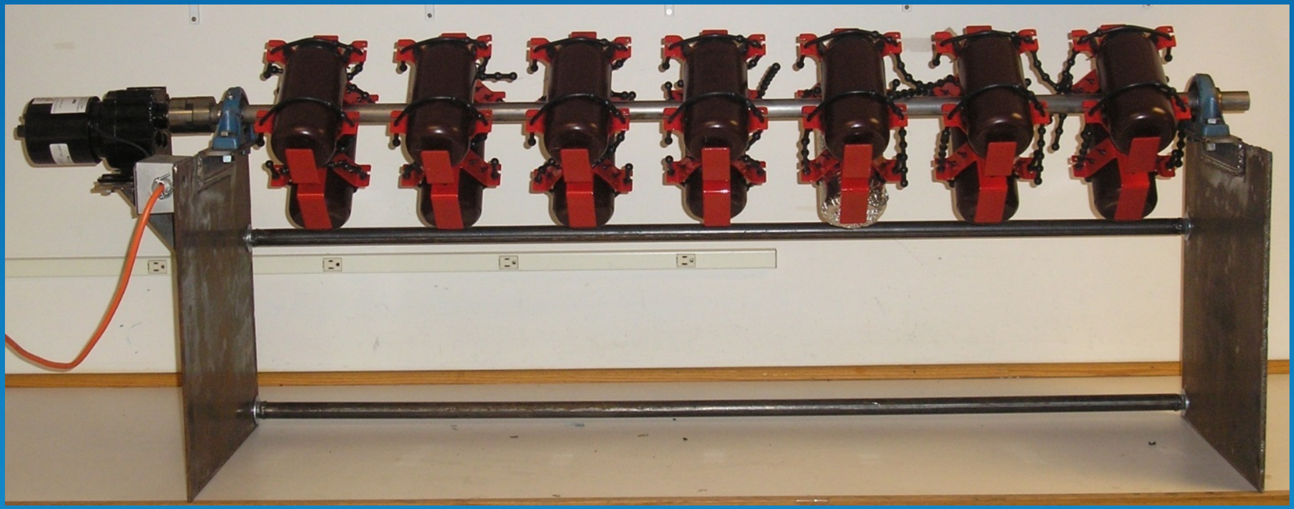
- Water is aggressive toward calcite (can dissolve calcite)
- Carbon dioxide is supersaturated with respect to the atmospheric value (can be stripped following calcite dissolution)

Batch Study Design

- Adit water pH was 5.62 su when the water was analyzed on April 17, 2014
- The bulk sample for bench-scale testing collected on May 29, 2014 had a pH of 6.17 when received at the lab.
- Carbon dioxide degasses under normal conditions during transport.
- Carbon dioxide addition was implemented in the lab to mimic field conditions (to reduce pH)

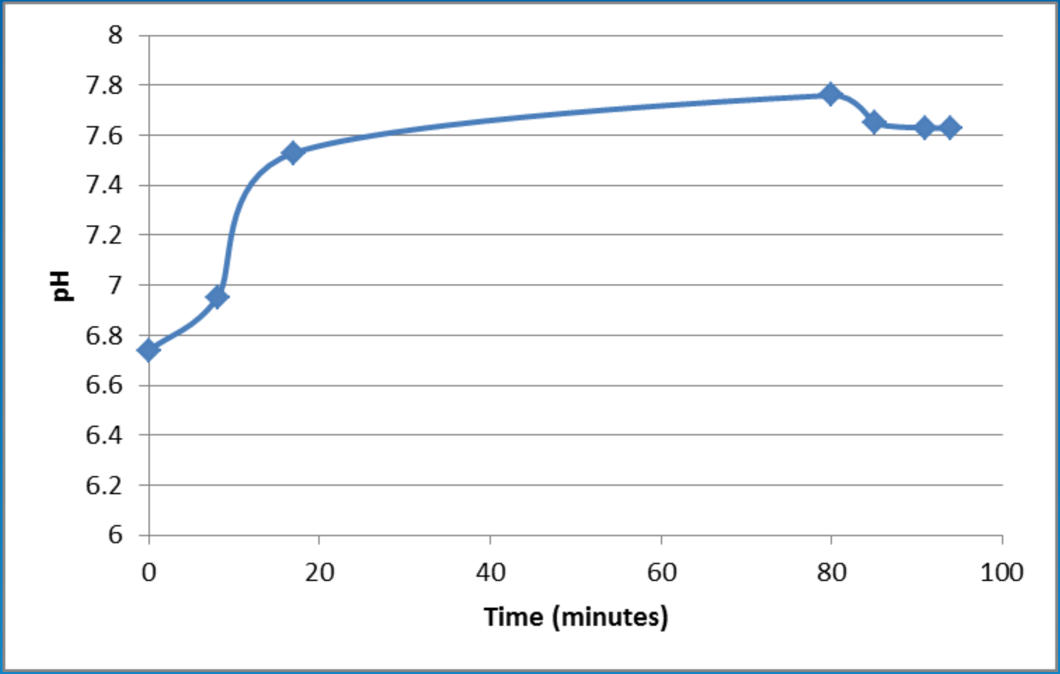
Batch Study Design

- Batches utilized ¼-inch minus limestone, sieved to remove fines
- Batches were prepared by combining adit water and limestone in a 2:1 ratio
- Batches were allowed to react for 24 hrs in a rotary tumbler

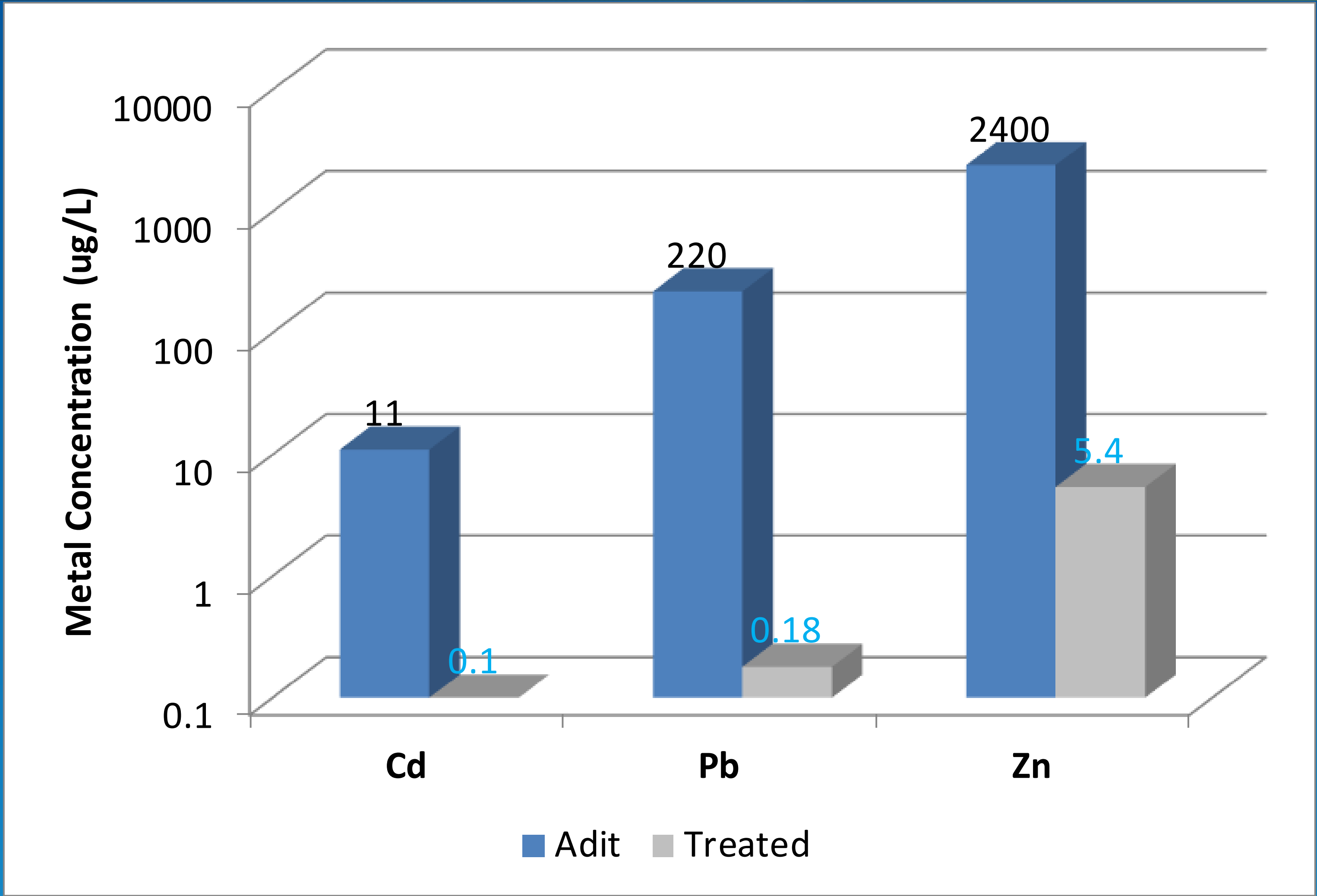


Batch Study Design (cont.)

- Following tumbling, the water was decanted from the limestone and placed in a beaker containing an aquarium stone.
- Air was bubbled into the beaker through the stone, to strip carbon dioxide from the solution.
- The pH was measured periodically during air stripping.
- Following tumbling the pH had increased to 6.67



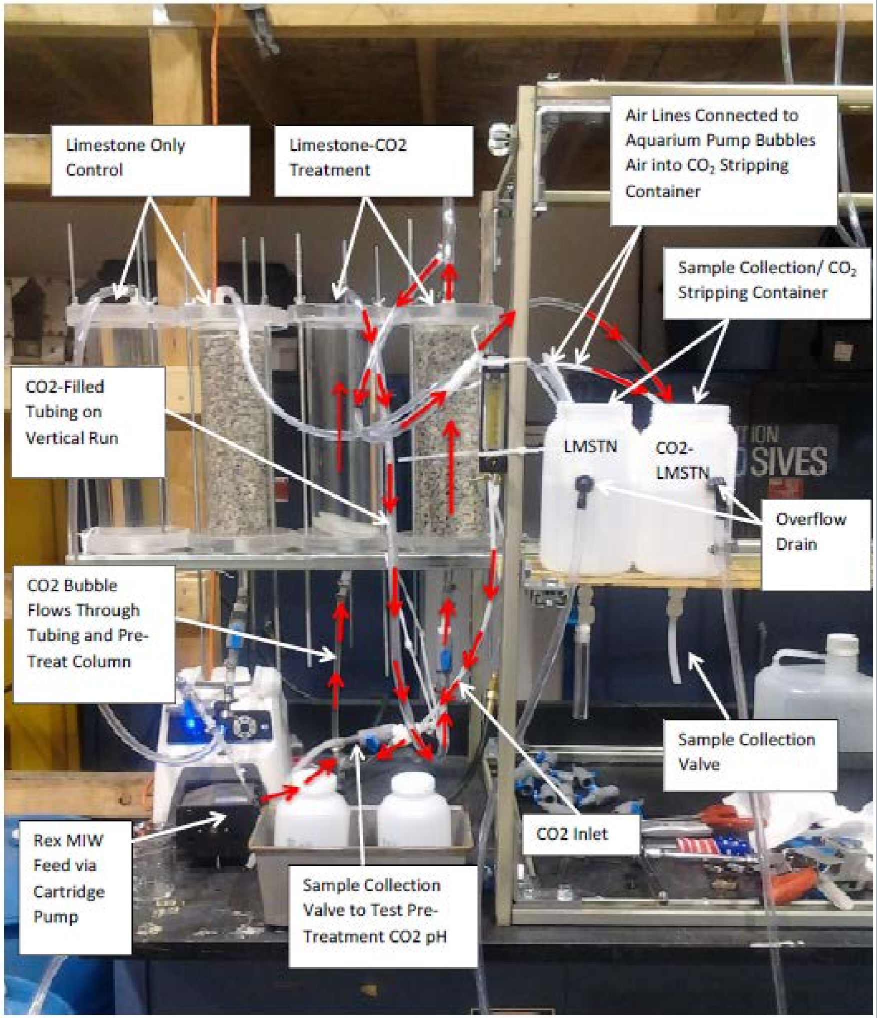
Batch Study Results



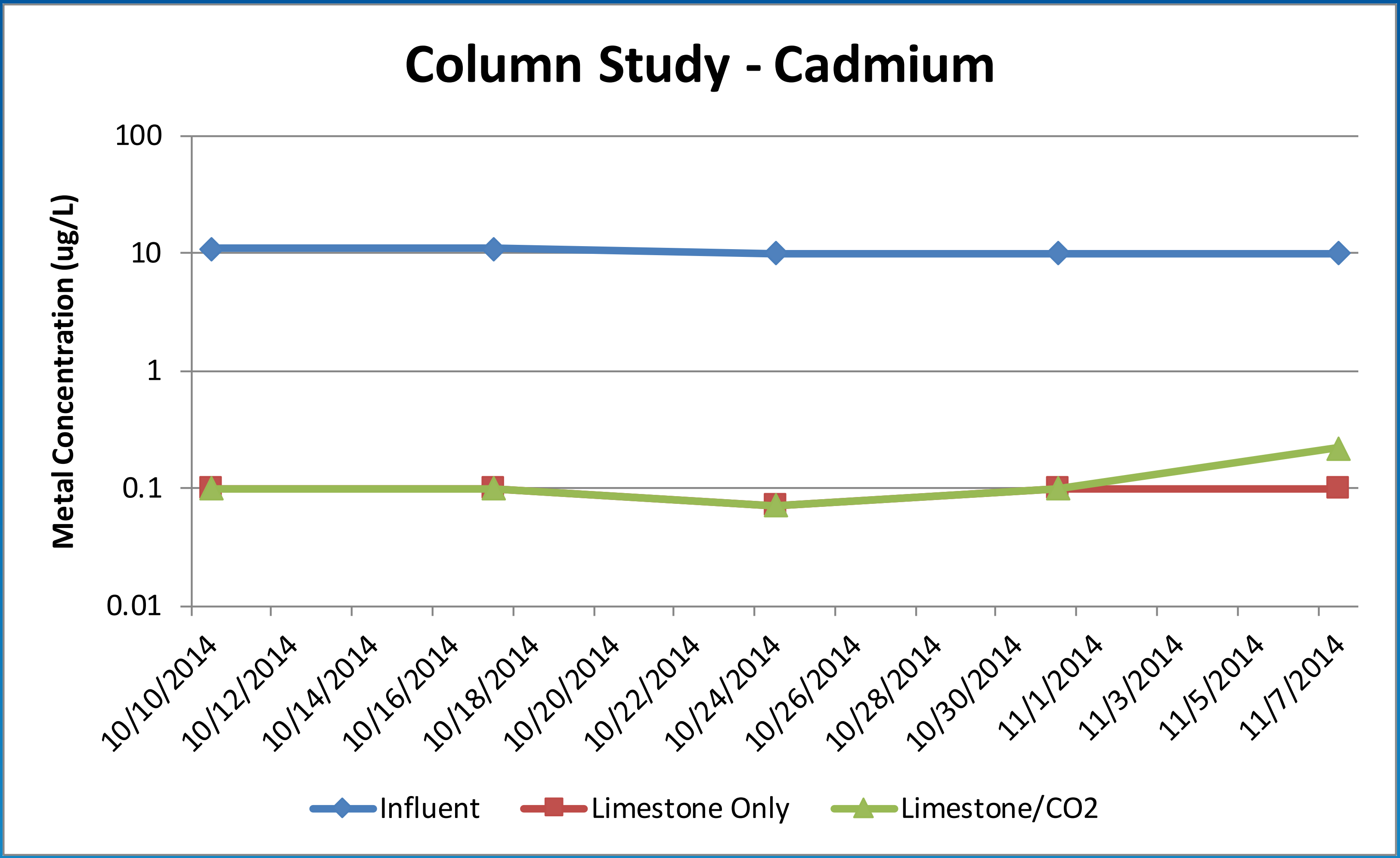
CDM Smith

Column Study Design

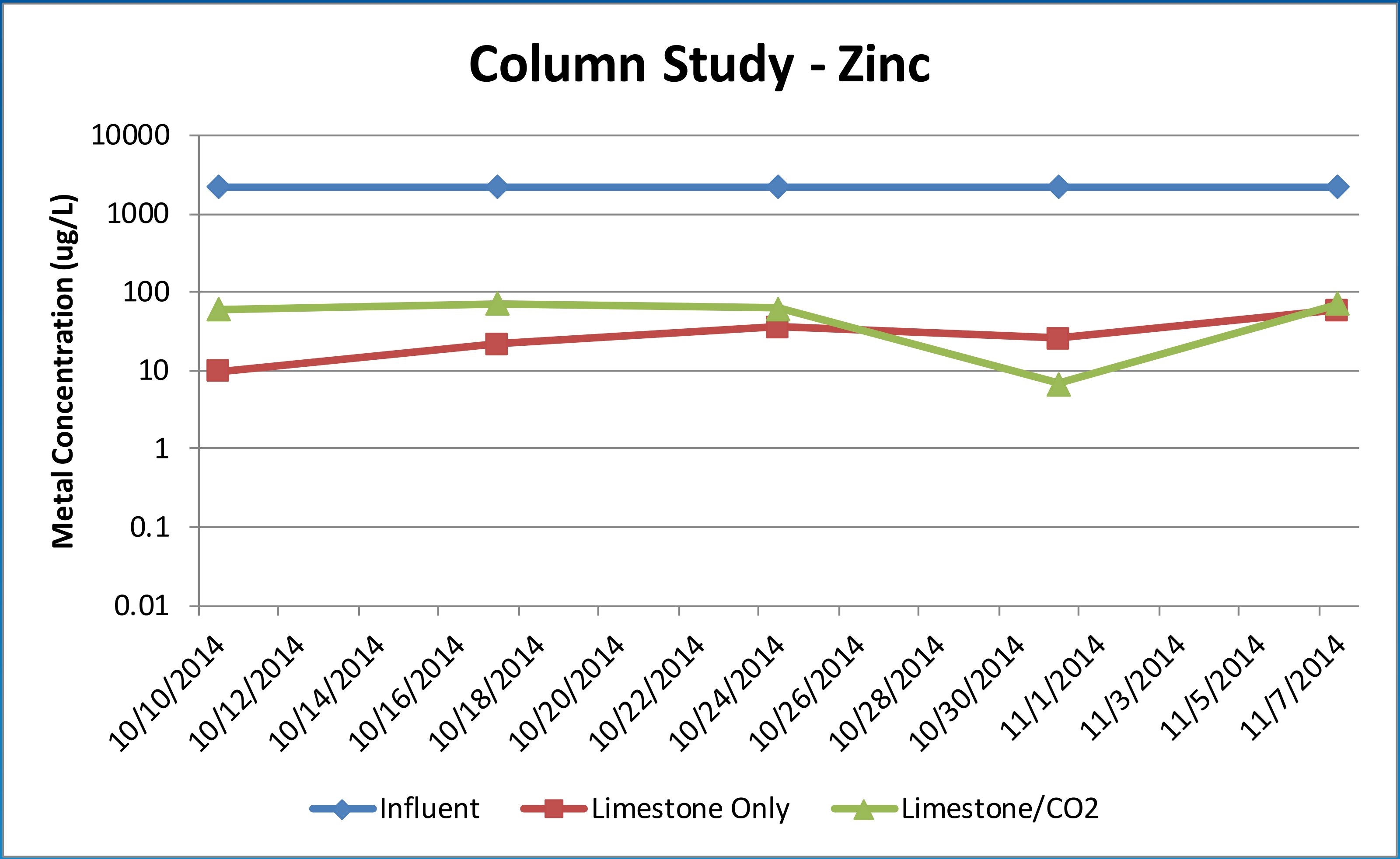
- Columns were upflow
- Limestone only (control)
- Limestone w/ CO2 acidification (pretreatment)
- Operated 8 weeks, at a retention time of 15 hours
- Carbon dioxide stripping same as for the batch tests
- Samples were collected for analysis both before and after CO_2 stripping.



Column Study Results - Cadmium

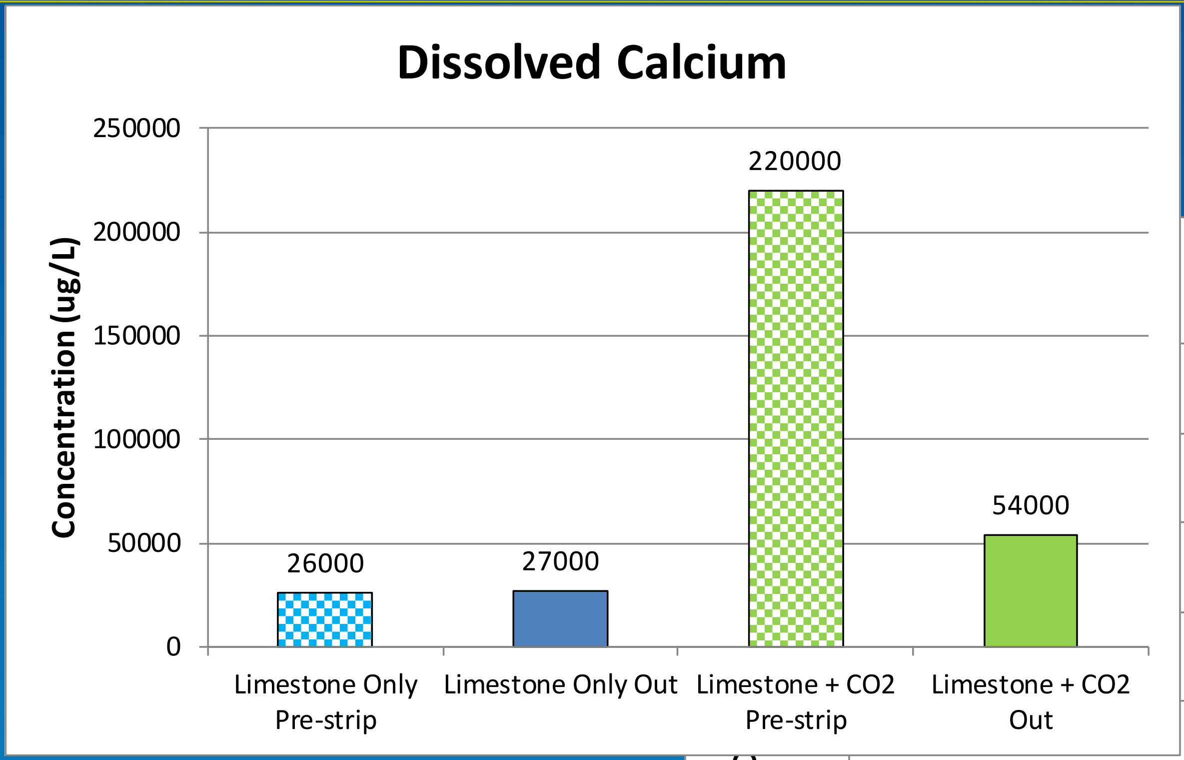


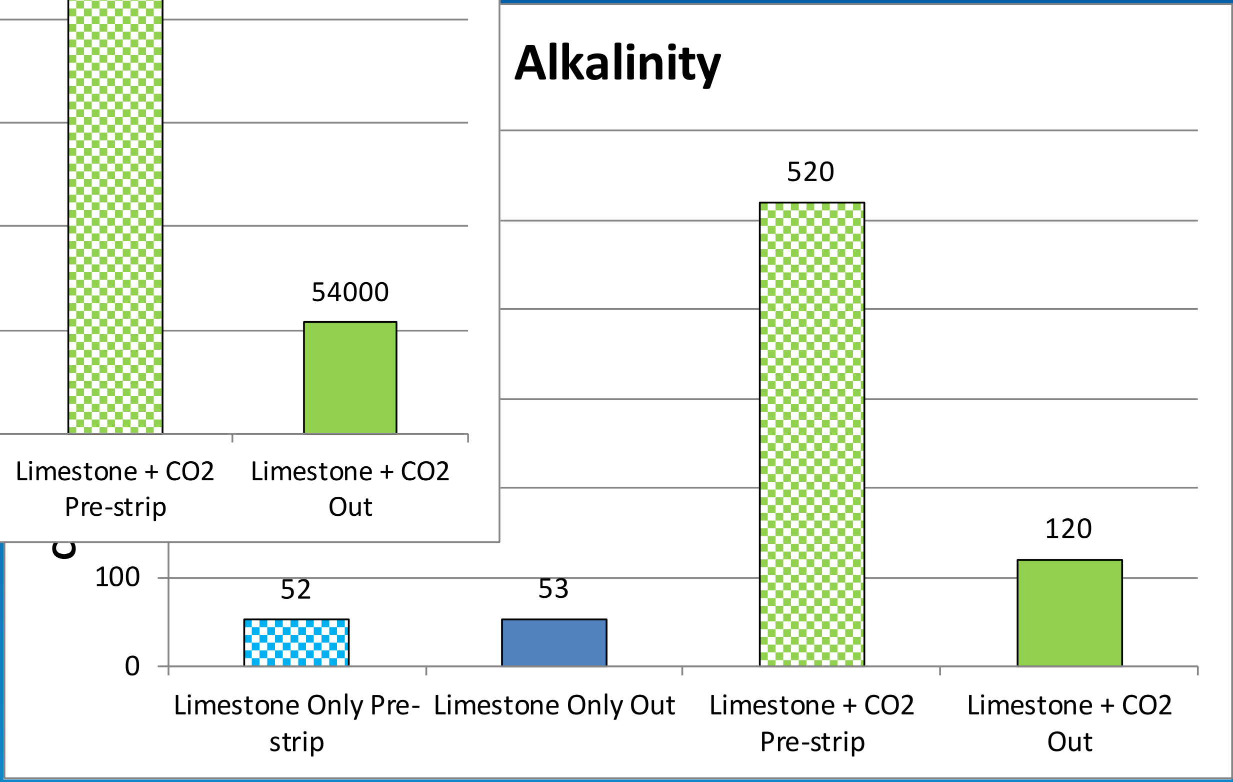
Column Study Results - Zinc



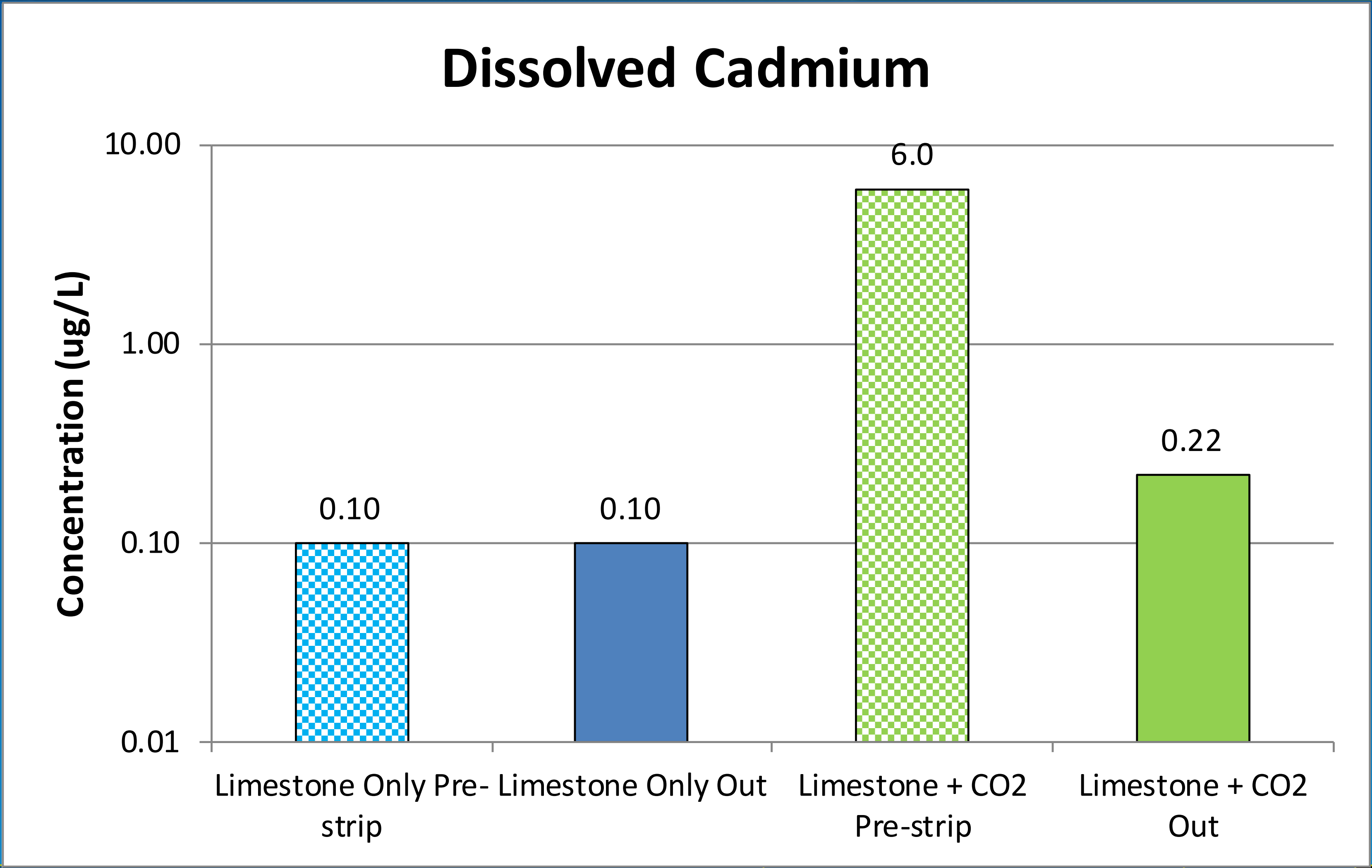
CDM Smith

Column Study Results



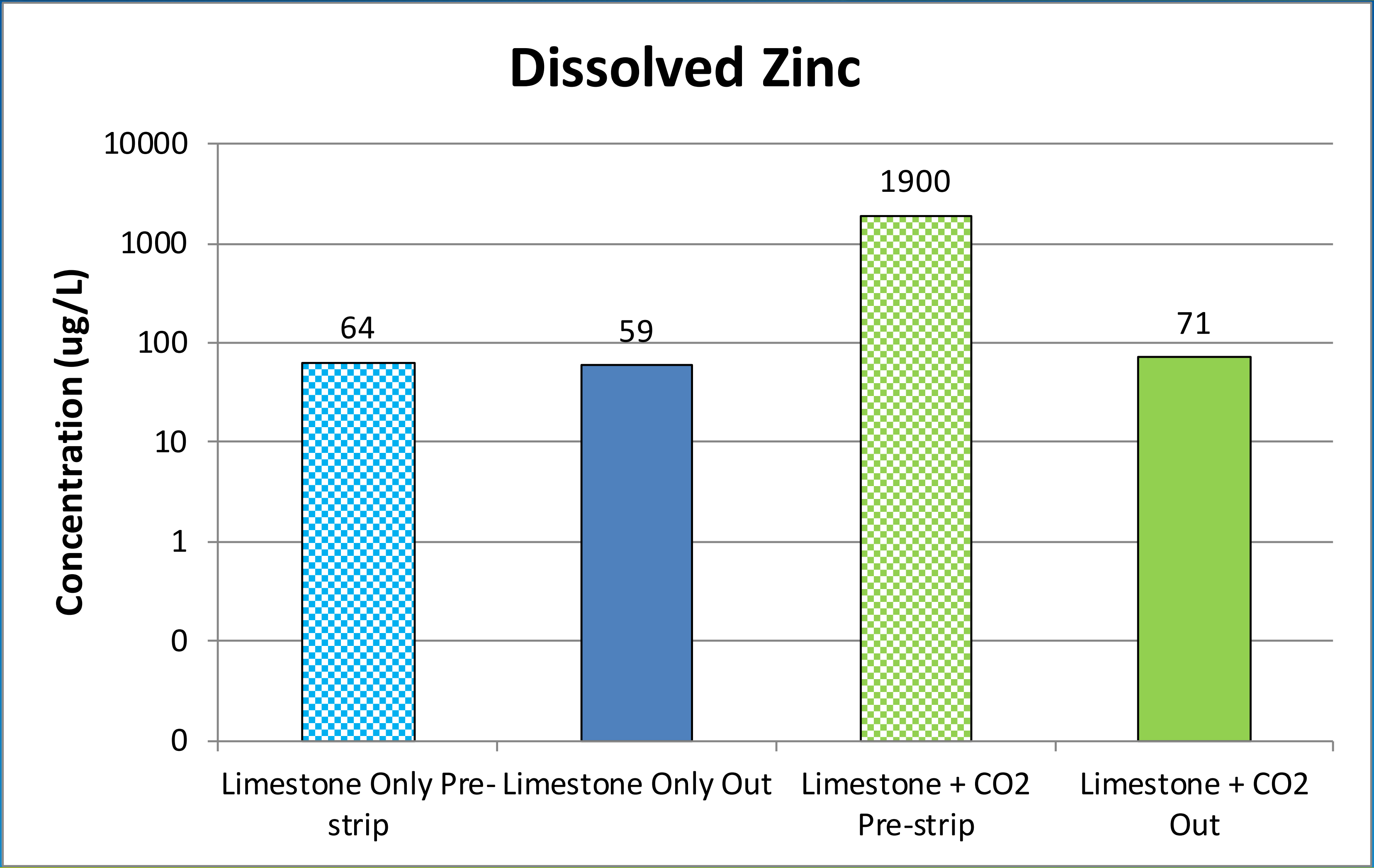


Column Study Results



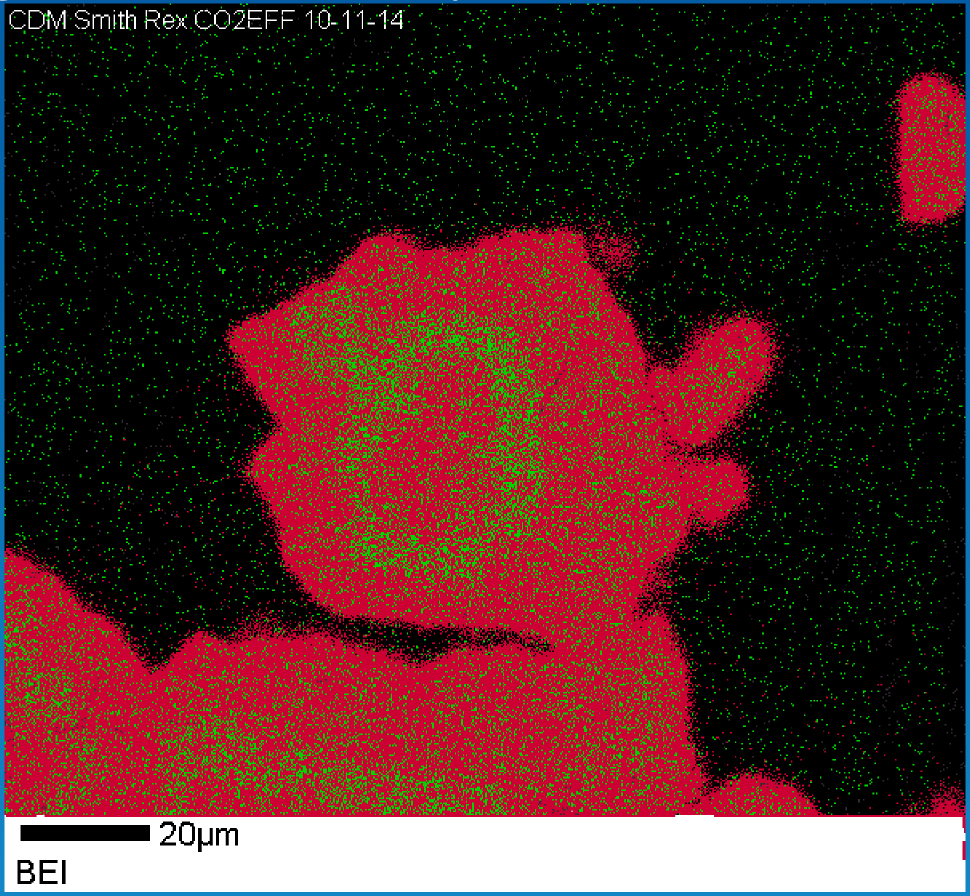
CDM Smith

Column Study Results



Sparging Vessel Precipitate Analysis

A sample of the calcite precipitate from the sparging vessel was analyzed using an electron microprobe



Other Observations – Limestone Only Column

- The influent water used in the column test was undersaturated with respect to calcite, but not enough to react within the calcite present in the limestone.
- Only 30 mg/L calcite dissolved during the column test.
- Essentially no calcite was re-precipitated during CO_2 stripping.
- Little or no metals were removed during the stripping process.

Other Observations – Limestone Plus CO_2 Column

- The effluent from the limestone (pre-stripping) was saturated with respect to calcite.
- Approximately 515 mg/L calcite dissolved during the column test.
- Approximately 80% of the dissolved calcite was re-precipitated during CO_2 stripping.
- A significant fraction of the Pb in the column effluent was within the suspended fraction, but not as much as for the limestone only column.
- Most of the Cd and Zn were removed during the CO_2 stripping process

Conclusions

- Zinc and cadmium removal to over 90% and 99%, respectively.
- Simple limestone bed and open aeration field application
- Low cost if CO_2 addition is not required.
- Pre-treatment with CO_2 can very likely be avoided by collecting the water at the underground discharge point.
- Applicable for low sulfate and low iron/aluminum MIWs

CDM Smith

Questions?