Pacific Northwest
NATIONAL LABORATORY
*Proudly Operated by* Battelle *Since 1965*

# Evaluating and predicting impacts of $CO_2$ intrusion into a confined sandstone aquifer


**NIK QAFOKU, AMANDA LAWTER, HONGBO SHAO, GUOHUI WANG AND CHRIS BROWN**

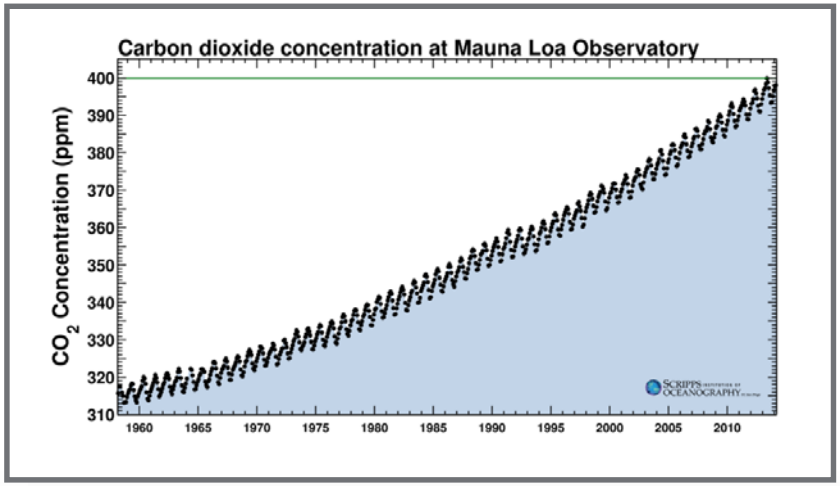
**Geosciences Group, Earth Sciences Division**
**Pacific Northwest National Laboratory**
**Richland, WA**

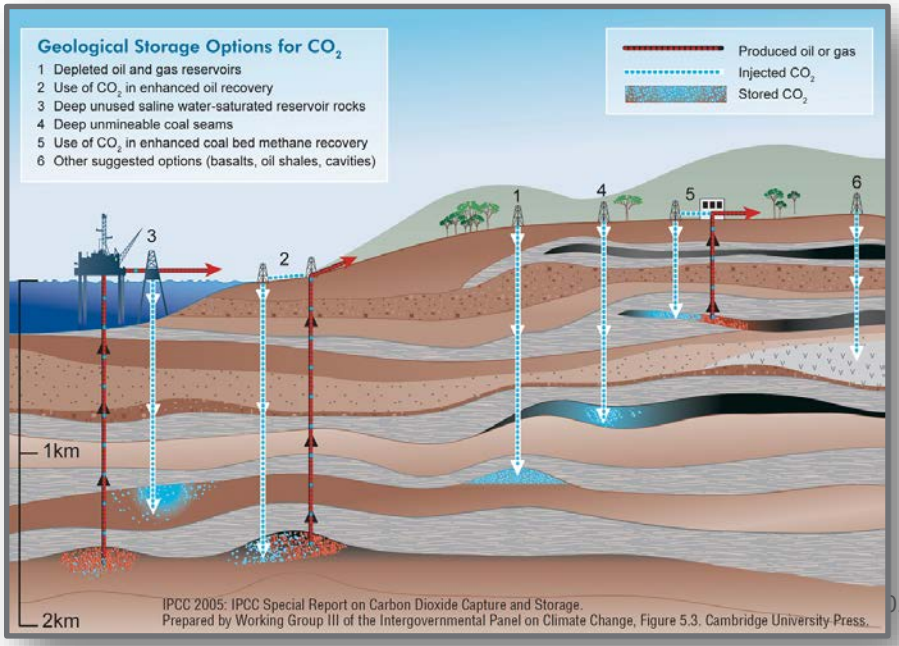

***International Conference on Greenhouse Gas Technologies***
***October 6, 2014***

# Carbon Storage: the Overall Concept

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by* Battelle *Since 1965*

- Geologic carbon sequestration is considered feasible option for controlling increasing atmospheric $CO_2$ (http://keelingcurve.ucsd.edu)
- Suitable formations include:
  - un-mineable coal seams,
  - exploited oil and gas reservoirs,
  - deep (often saline) non-potable aquifers
- Understanding potential impact on near-surface geochemistry (e.g. vadose zone, capillary fringe, potable aquifers and aquitards) is therefore crucial



# Conventional Thinking



$$CO_{2(g)} + H_2O \leftrightarrow H_2CO_{3(aq)} \leftrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

Primary reaction driver

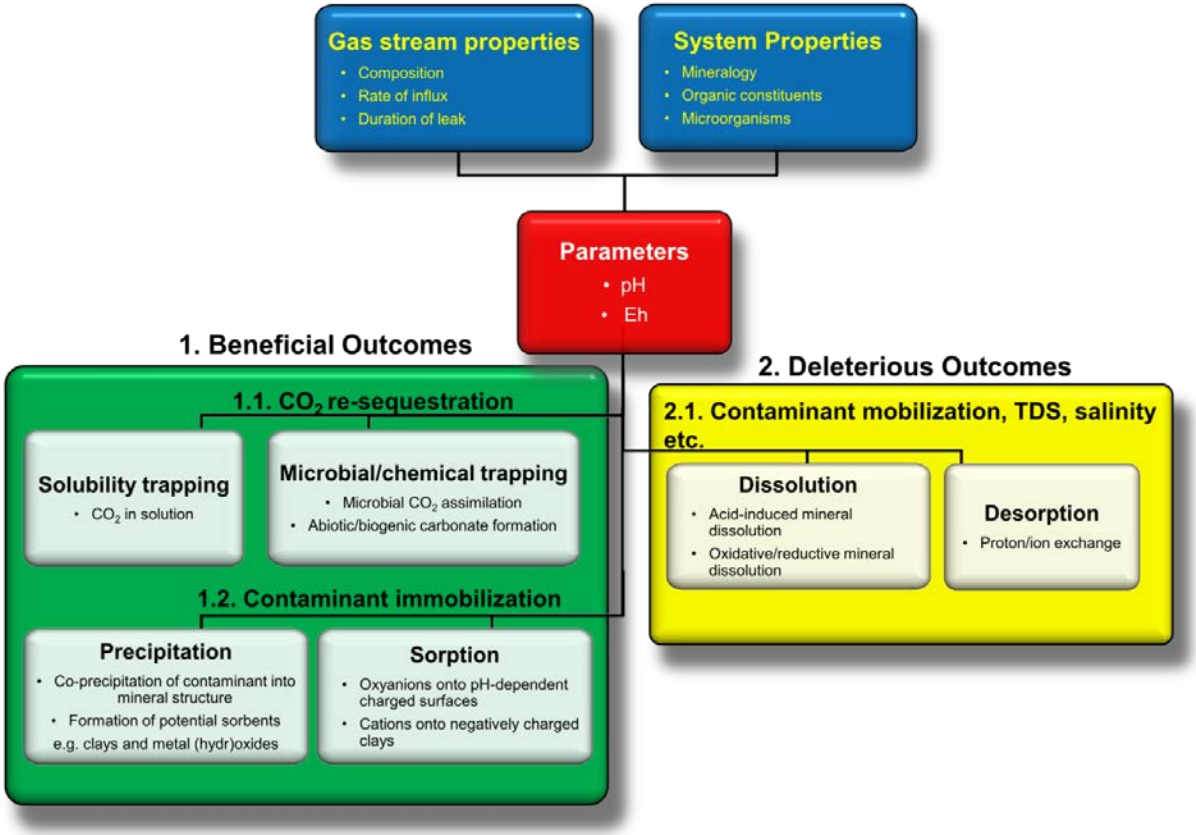
Increase in $H^+$ activity → Decrease in pH → Enhanced mineral weathering/dissolution

SI>>1 → Precipitation of neophases

SI<1 → Release of contaminants, increase TDS etc.

# Literature Review and Working Hypotheses



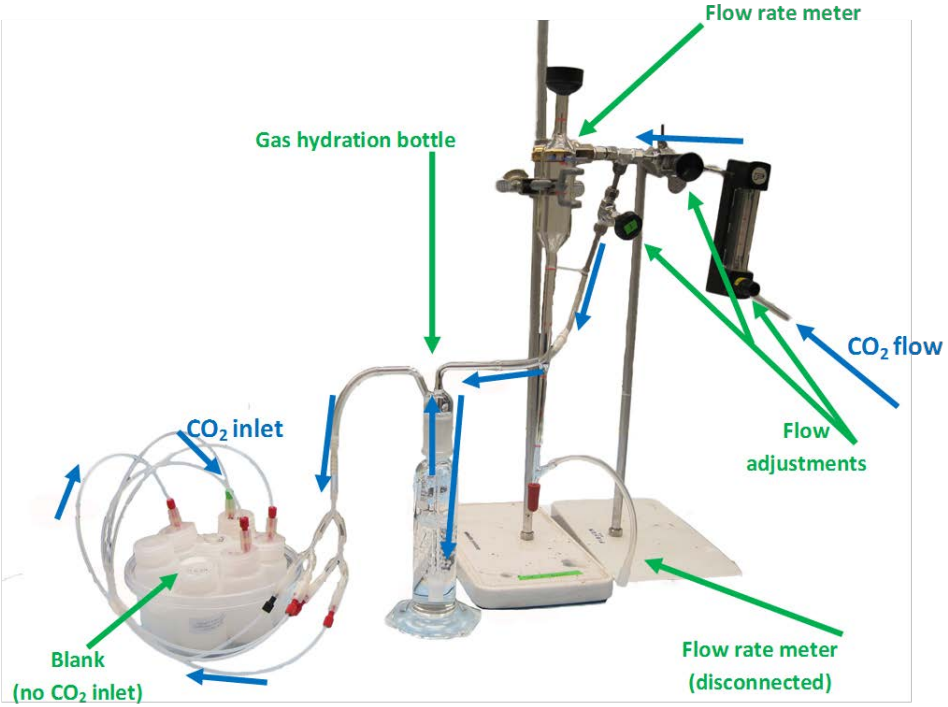



**The geochemical impact of $CO_2$ migration, from deep geologic storage, into near surface environments will be driven by the characteristics of the intruding gas stream, properties of the impacted system, and subsequent effects on not only system pH but also Eh.**

Harvey et al., 2013, ES&T, 47(1):23-36 DOI: 10.1021/es3029457

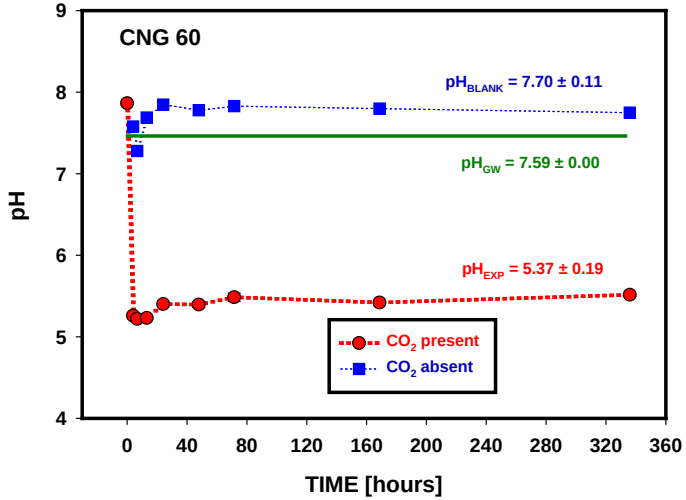
# Batch and Column Experiments

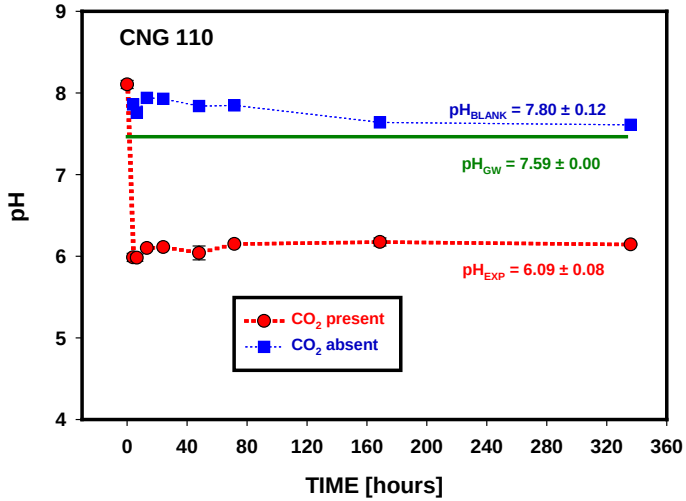


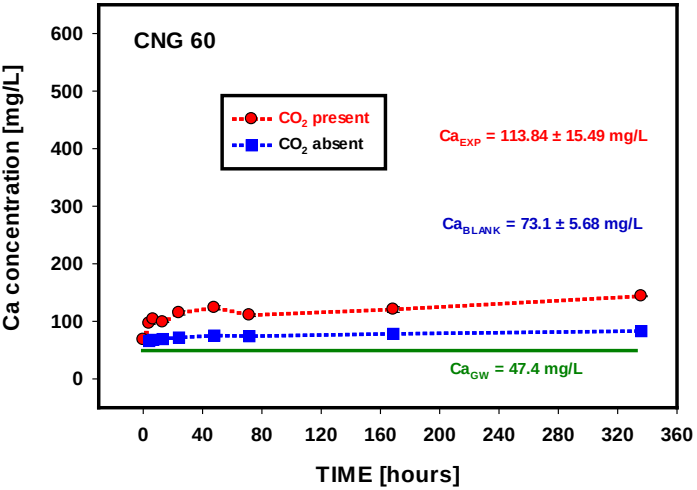


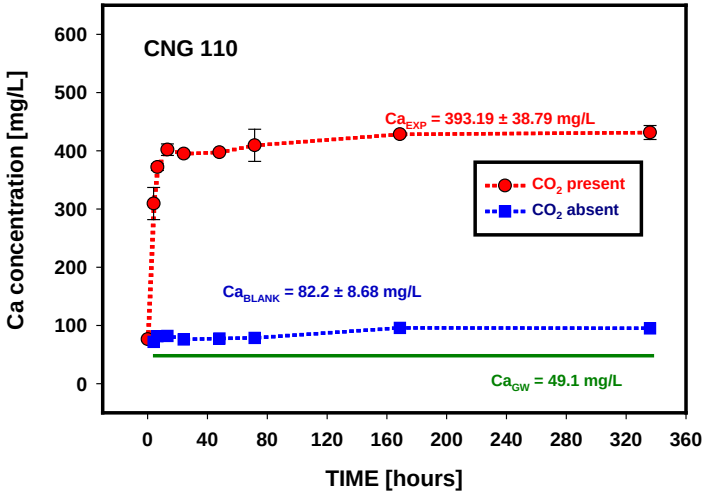
- Conducted at room temperature and atmospheric pressure
- Batch experiments simulate sudden, fast, and short-lived releases of the $CO_2$ gas as would occur in the case of well failure during injection
- Column experiments simulate slow, gradual leakage as would occur in the case of undetected faults

# Batch experiment results: The effect of injected $CO_2$



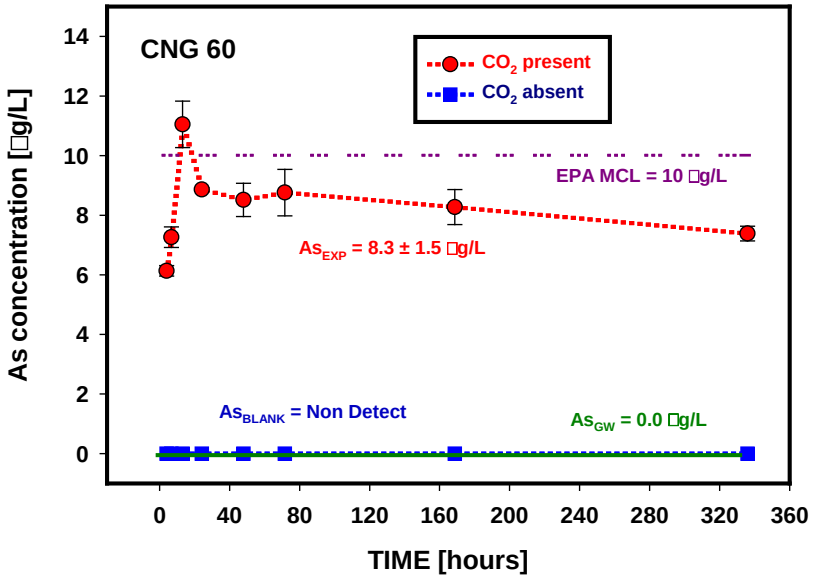




- Well: CNG
- Depth: 60' and 110'
- SGW: Kansas High Plains
- Gas: $CO_2$

**QXRD results:**

- CNG 60 silt contains 59% quartz, 23% albite, 12% microcline, 3.6% mica, 0.9% kaolinite
- CNG 110 silt contains 23% quartz, 35% calcite, 11% albite, 3.9% microcline, 1.2% mica, 1.9% kaolinite

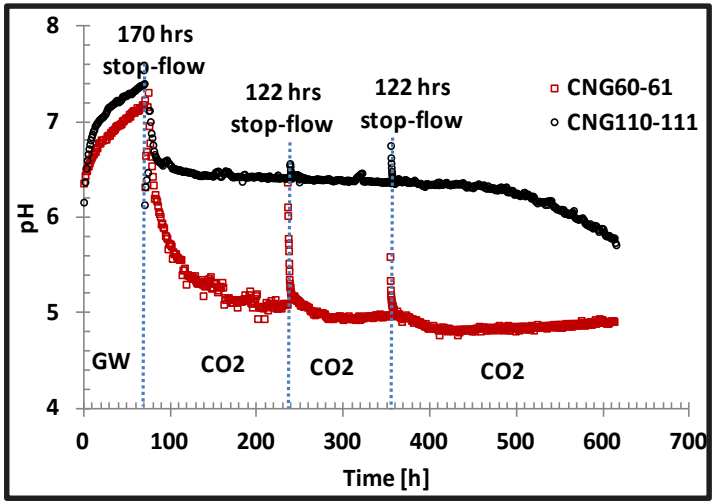
# Batch experiment results: The effect of $CO_2$ on As mobility

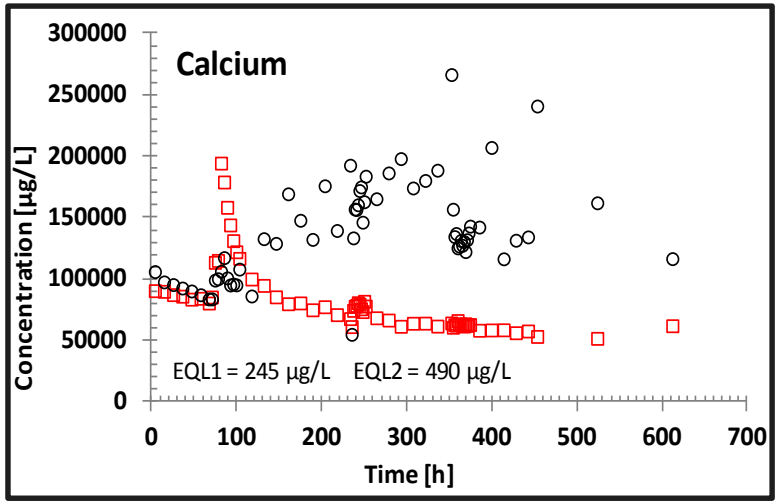



- Well: CNG
- Depth: 60'
- SGW: Kansas High Plains
- Gas: $CO_2$

- Arsenic was not detected in CNG 110 batch experiment, and was only above detection limits periodically in the column experiment
- A greater number of trace elements was consistently released in CNG 60 compared to CNG 110

# Column experiment results: The effect of injected $CO_2$

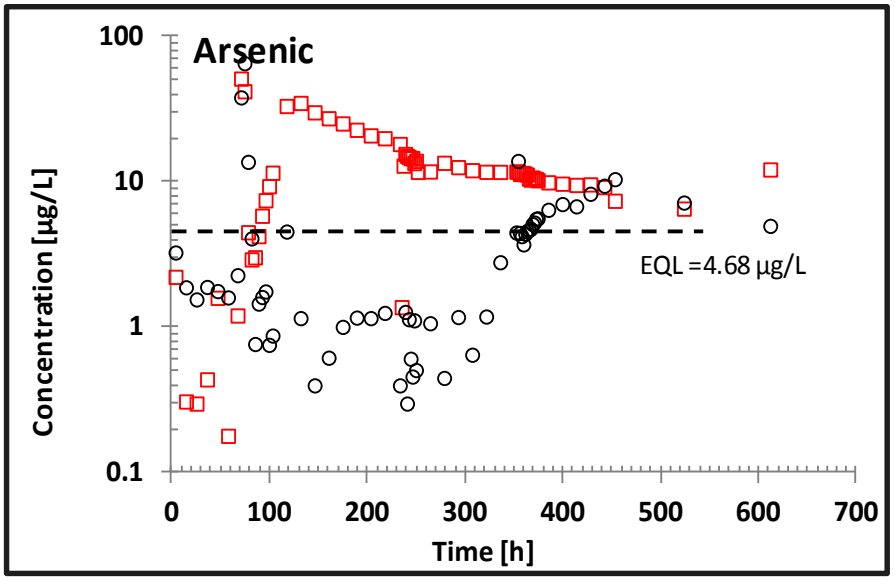



- Well: CNG
- Depth: 60' and 110'
- SGW: Kansas High Plains
- Gas: $CO_2$

- The pH measured in the columns is similar to the pH measured in the respective batch experiments
- The Ca concentration in CNG 60 did not change significantly during stop-flow events, likely indicating that cation exchange reaction (not dissolution) was controlling Ca concentrations in this sediment

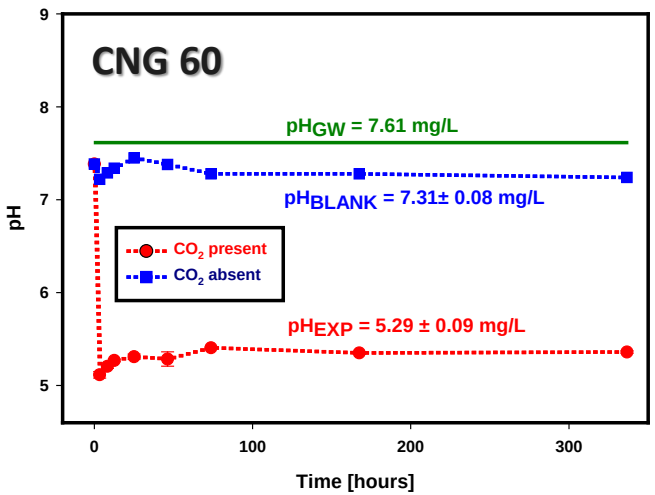
# Column experiment results: The effect of $CO_2$ on As mobility

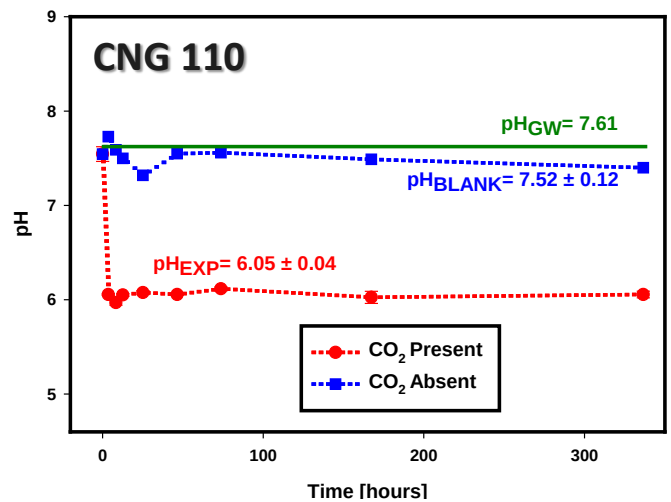



- Well: CNG
- Depth: 60' and 110'
- SGW: Kansas High Plains
- Gas: $CO_2$
- As MCL = 10 µg/L

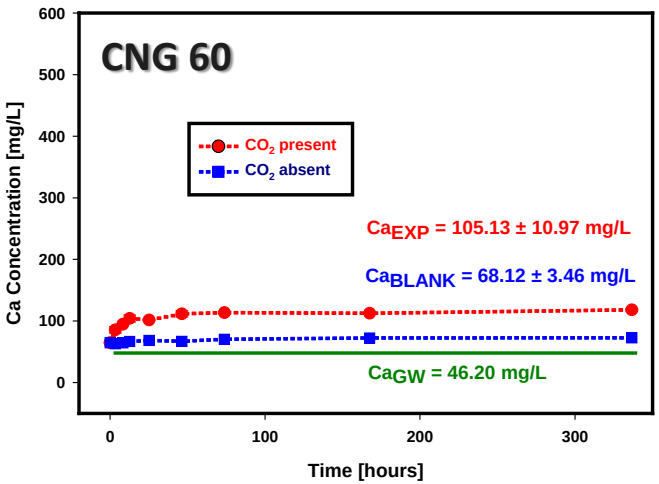
- Arsenic was not detected in CNG 110 batch experiment, and was only above detection limits periodically in the column experiment
- A greater number of trace elements was consistently released in CNG 60 compared to CNG 110

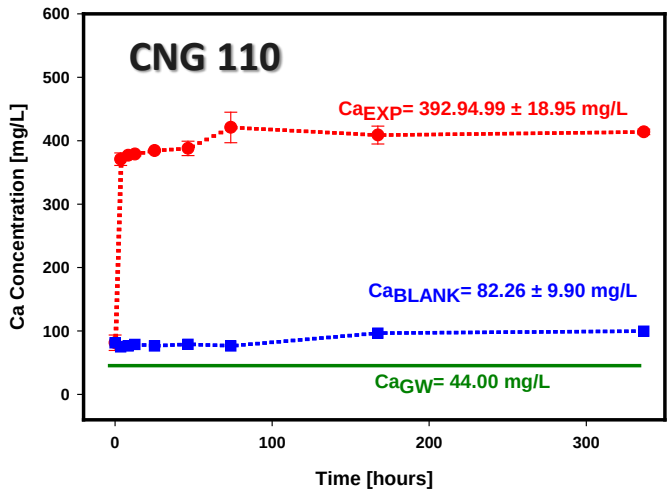
# Batch experiment results: $CO_2$ and As-spiked SGW



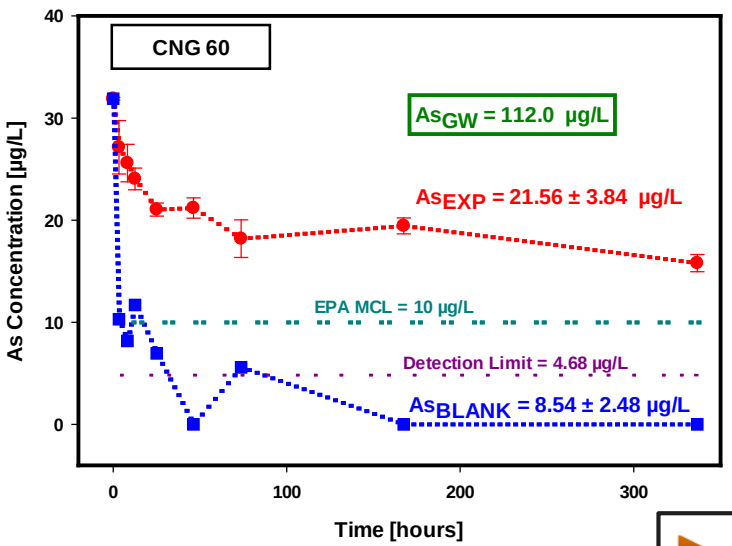

- SGW: Kansas High Plains spiked with As and Cd
- Gas: $CO_2$

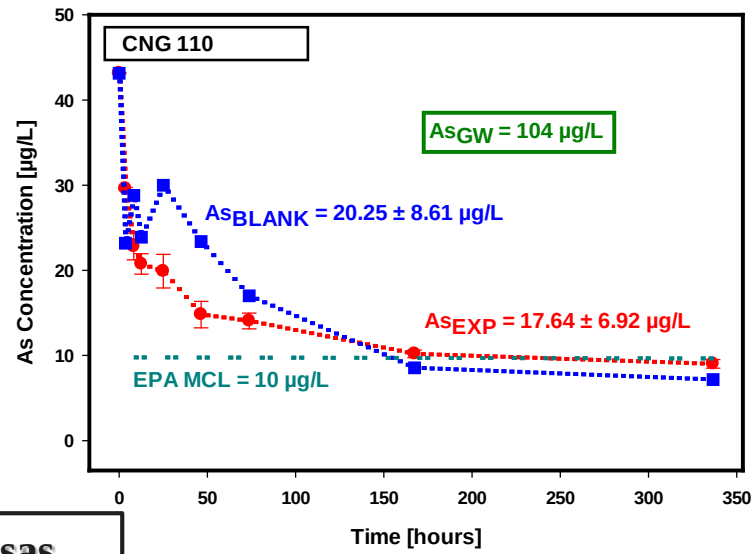



- Again, pH of CNG 110 does not decrease as much as CNG 60, due to buffering capability of calcite

# Batch experiment results: $CO_2$ and As-spiked SGW



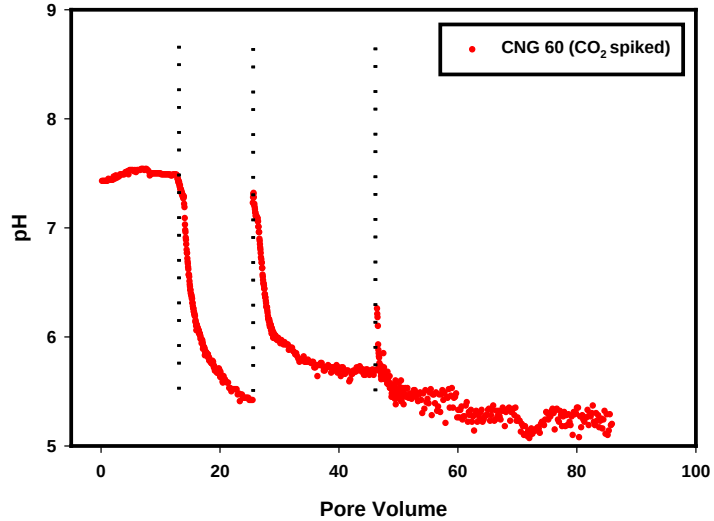



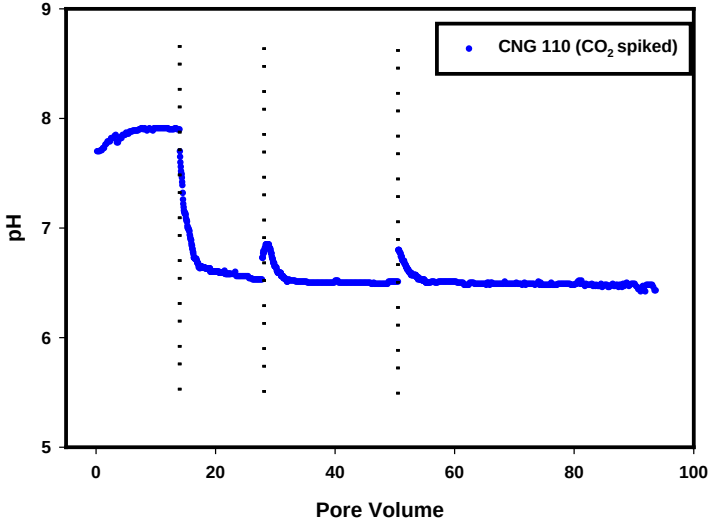

- SGW: Kansas High Plains spiked with As
- Gas: $CO_2$

- Batch and column experiments were run with an As spike added to the SGW
- The SGW was spiked with 114 ppb As representing the maximum concentration expected at the leakage point based on model results
- Liquid phase As concentrations were significantly lower than the initial concentration

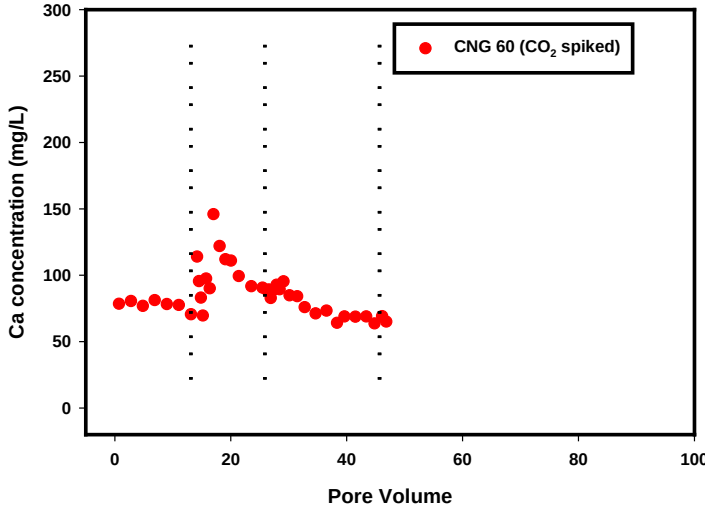
# Column experiment results: $CO_2$ and As-spiked SGW

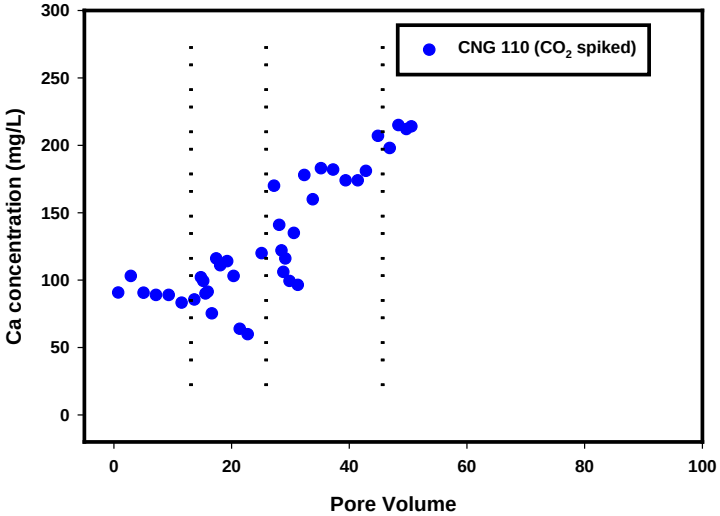
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965




- SGW: Kansas High Plains spiked with As and Cd
- Gas: $CO_2$

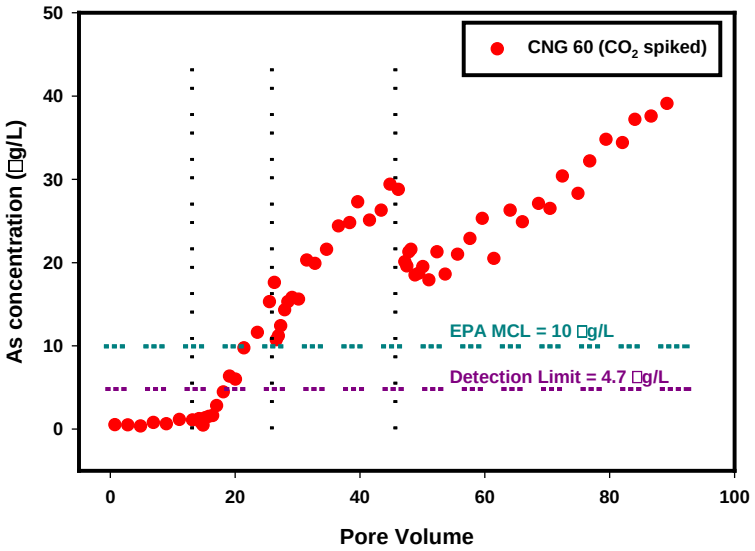


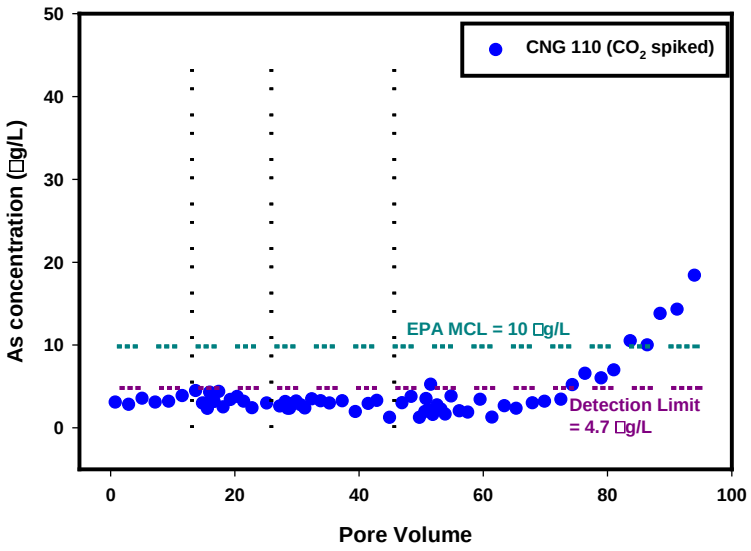




- A large difference is again shown between the sediments' ability to buffer against pH changes

# Column experiment results: $CO_2$ and As-spiked SGW

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



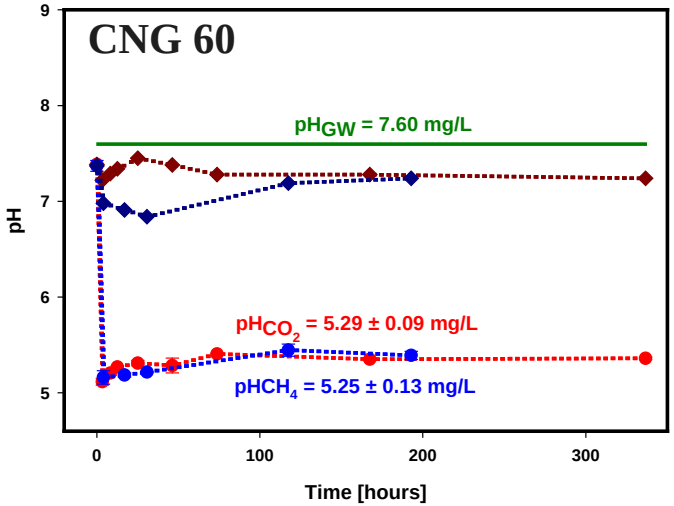



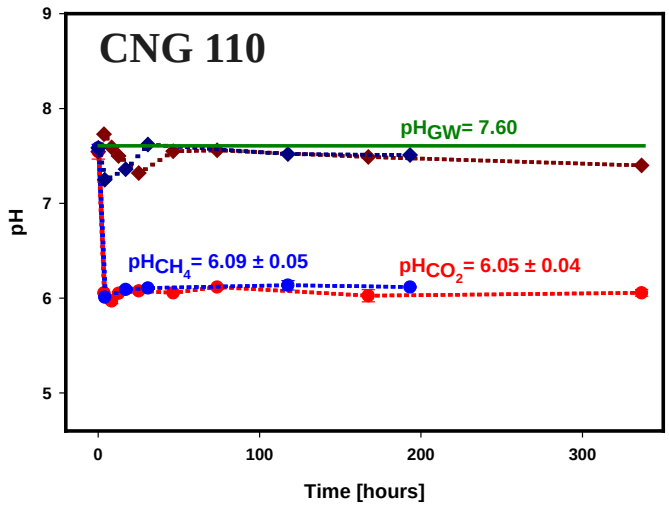

- SGW: Kansas High Plains with As spike
- Gas: $CO_2$

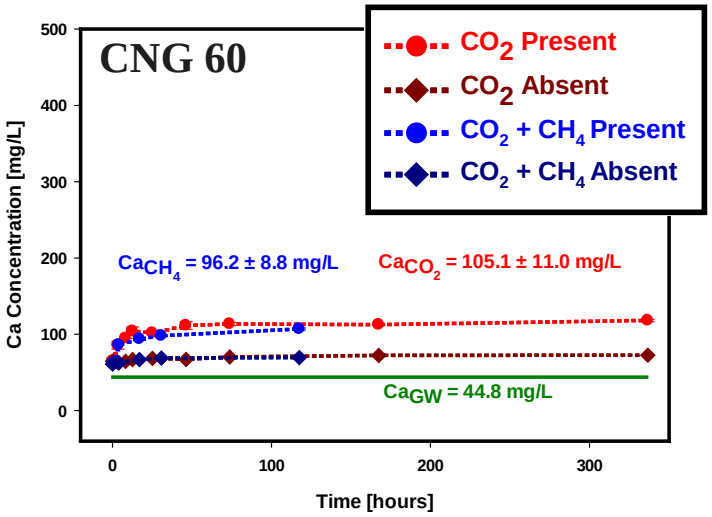
- Greater amounts of As are detected in CNG 60
- The detection limit is approximately 5 µg/L, making most of the CNG 110 effluent As data "non-detectable"

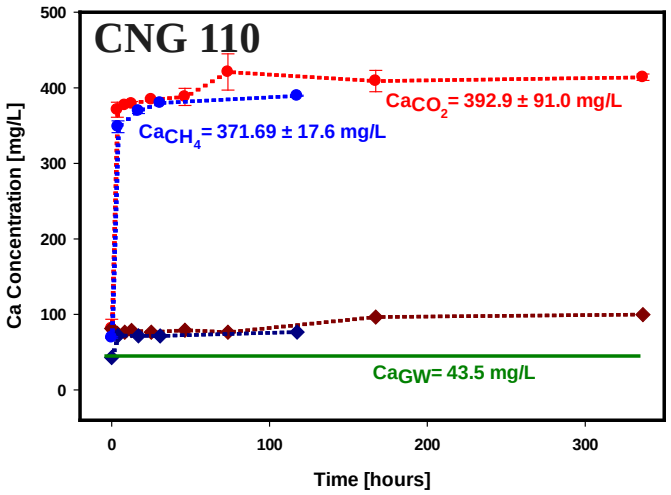
# Batch experiment results: $CO_2$ / $CH_4$ and As-spiked SGW

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



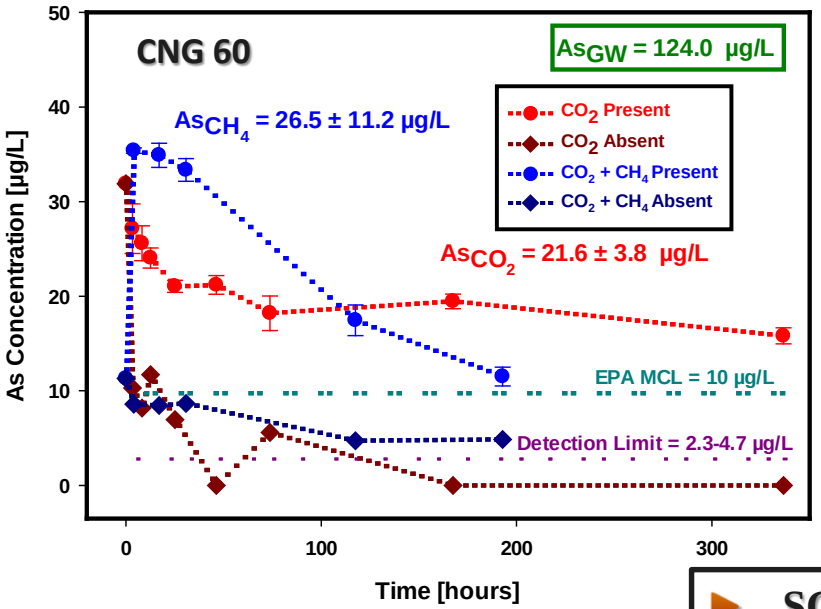



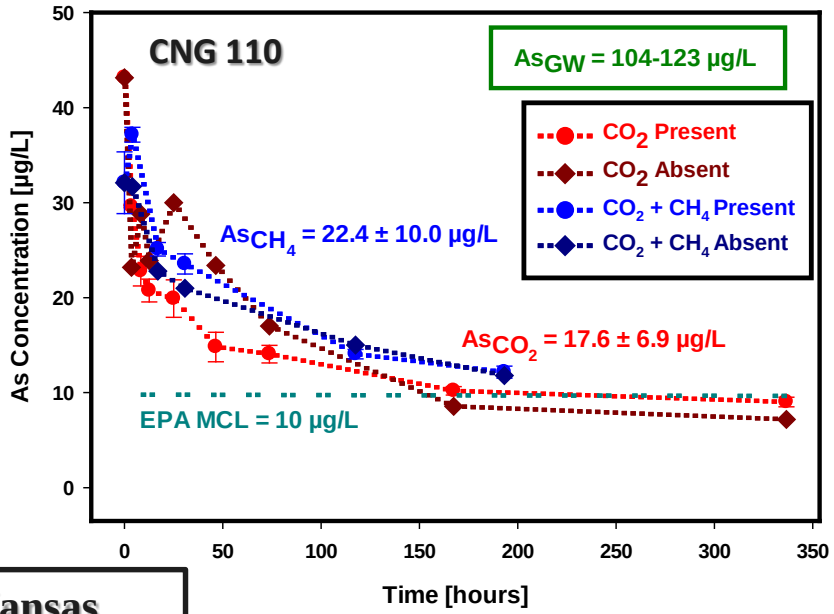




- SGW: Kansas High Plains with As/Cd spike
- Gas: $CO_2$ + $CH_4$

- Conducted the same experiments, with 1% $CH_4$ mixed with $CO_2$
- Can be present as an injected impurity, a native gas, or as a product of methanogenesis

# Batch experiment results: $CO_2$ / $CH_4$ and As-spiked SGW



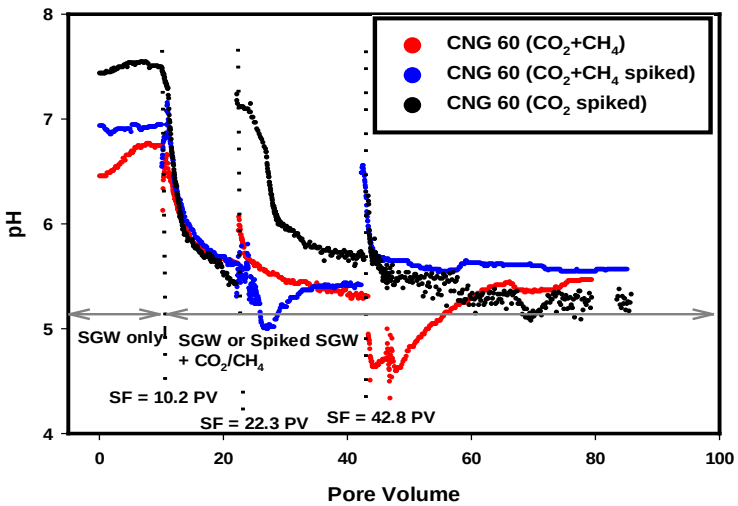



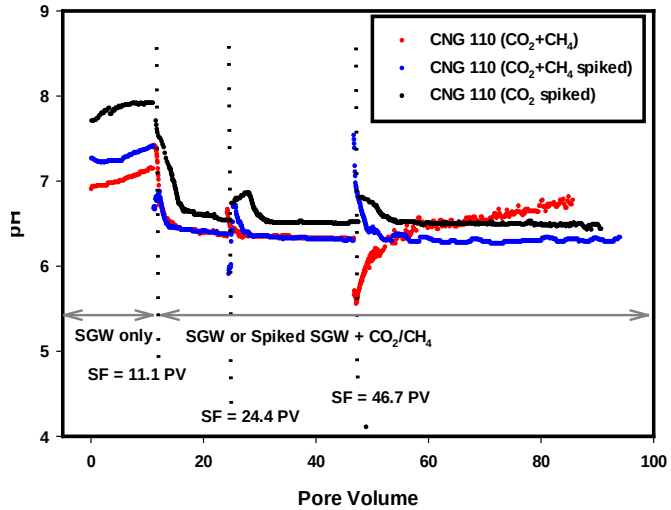

- SGW: Kansas High Plains with As/Cd spike
- Gas: $CO_2$ + $CH_4$

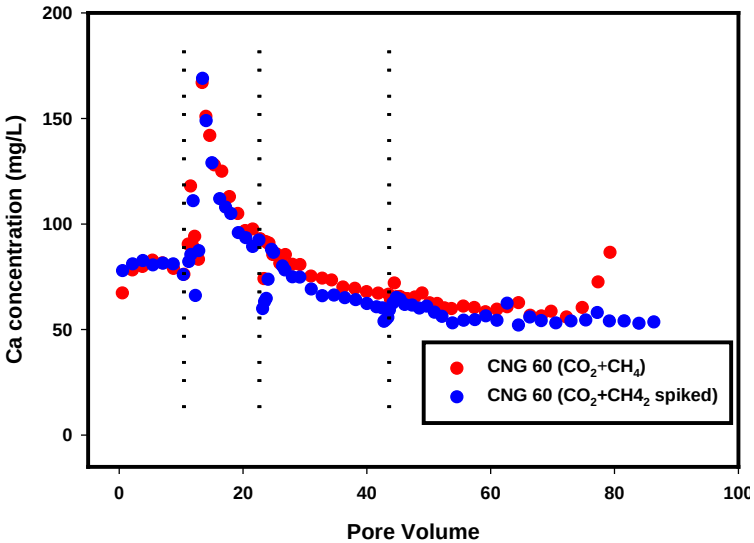
- As concentration decrease with time is greater with $CH_4$ present in CNG 60
- Trends are similar with or without $CH_4$ in sediment CNG 110
- As concentration after equilibration is more than 50% less than the As spike

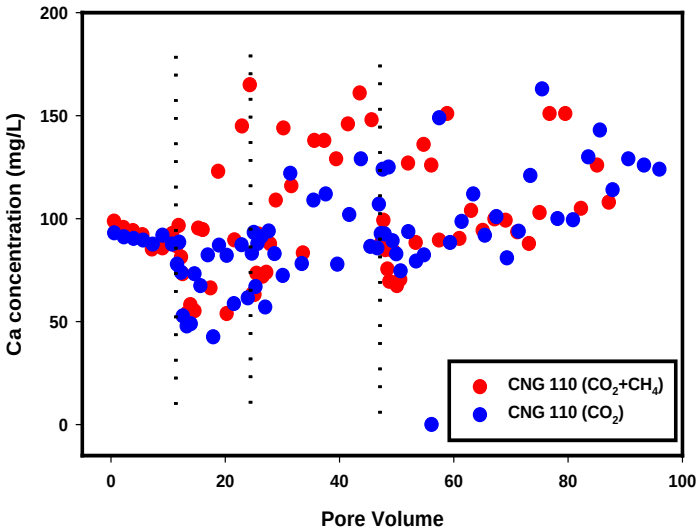
# Column experiment results: $CO_2$ / $CH_4$ and As-spiked SGW

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



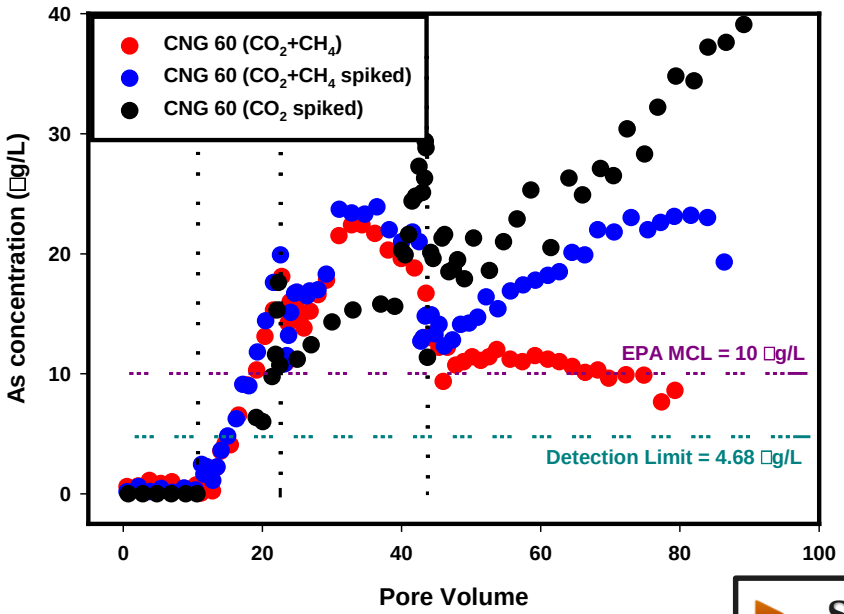



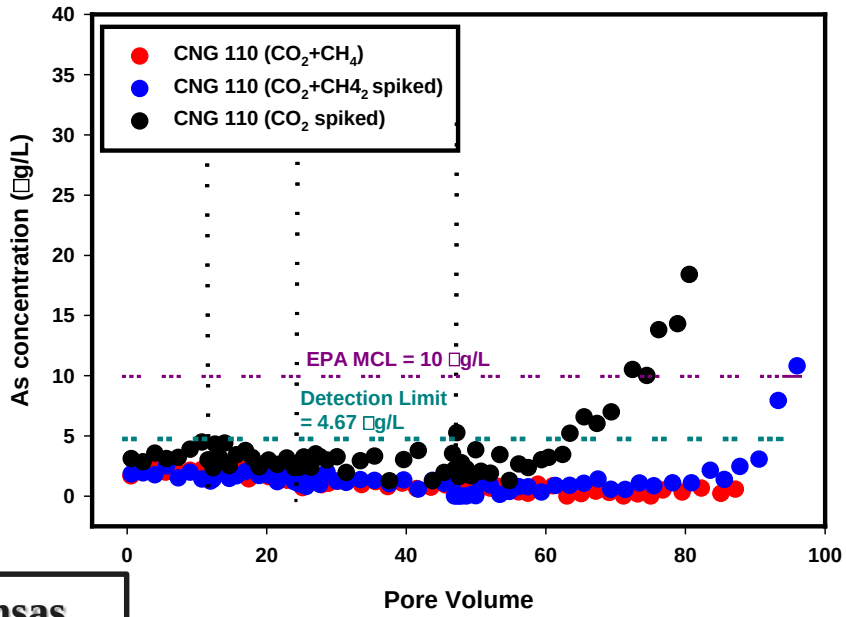




- SGW: Kansas High Plains with As/Cd spike
- Gas: $CO_2$ + $CH_4$

- pH values for SGW and spiked SGW columns are generally similar (up to 3rd SF)
- Ca patterns vary greatly between the sediments

# Column experiment results: $CO_2$ / $CH_4$ and As-spiked SGW

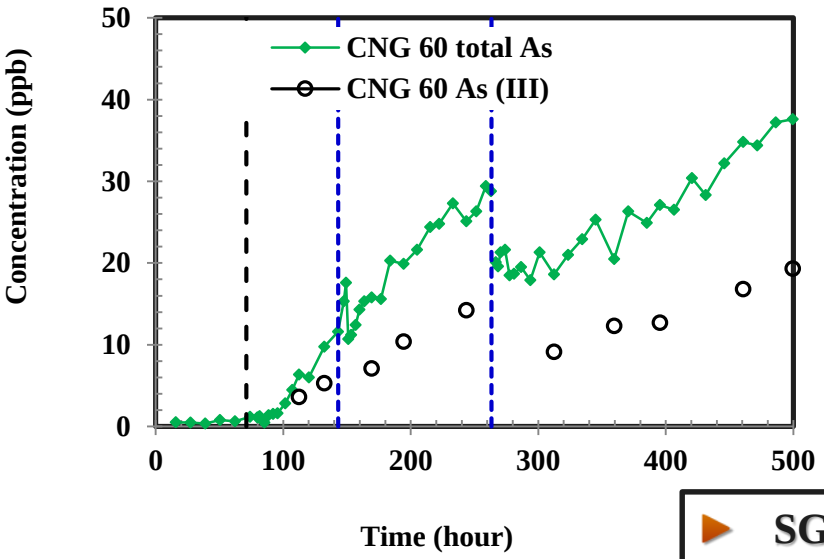


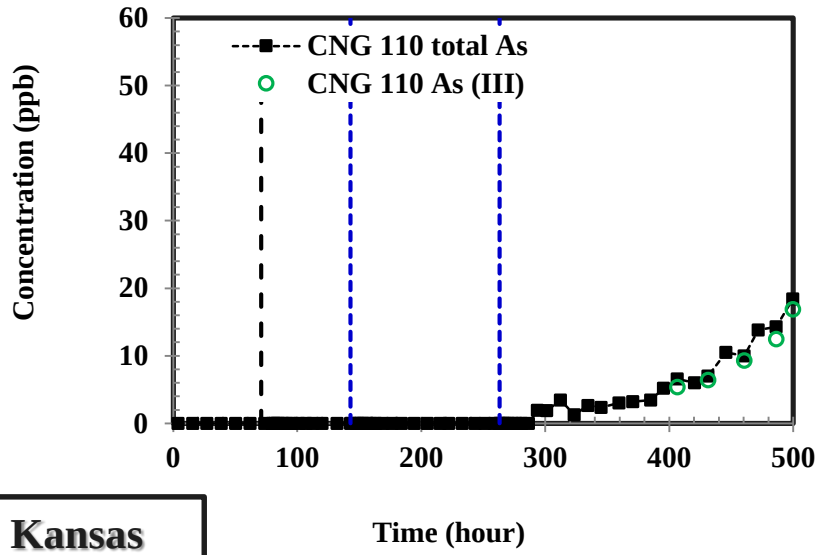




- SGW: Kansas High Plains with As/Cd spike
- Gas: $CO_2$ + $CH_4$

- As remained under the detection limit for CNG 110 until the end
- The similar As trends in CNG 60 columns suggest the source of effluent As is from the sediment, not the spike, until after the 3rd stop flow

# Column experiment results: $CO_2$ and As speciation




- SGW: Kansas High Plains with As/Cd spike
- Gas: $CO_2$

- As(V) was used in the As-spiked SGW, but column effluent contains As(III) as well as As(V)
- Possible sources of As(III) include reduction of As(V) to As(III), desorption of As(III)/adsorption of As(V), or dissolution of an As(III)-bearing phase

# Batch experiment results: CO2 / CH4 and As-spiked SGW

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

| Sample (8 day sampling) | units | As (III) | Total As | As (V) | MDL | % As (III) |
|---|---|---|---|---|---|---|
| CNG 60 As (III) Sample A | ug/L | 4.04 | 12.2 | 8.16 | 2.34 | 33.1 |
| CNG 60 As (III) Sample B | ug/L | 1.9 | 10.8 | 8.9 | 2.34 | 17.6 |
| CNG 60 As (III) Sample BLK | ug/L | 3.02 | 4.86 | 1.84 | 2.34 | 62.1 |
| As (III) SGW Sample | ug/L | 9.04 | 115 | 105.96 | 2.34 | 7.9 |
| CNG 110 As (III) Sample A | ug/L | 1.52 | 12.6 | 11.08 | 3.34 | 12.1 |
| CNG 110 As (III) Sample B | ug/L | 2.03 | 11.7 | 9.67 | 4.34 | 17.4 |
| CNG 110 As (III) Sample BLK | ug/L | 3.54 | 11.8 | 8.26 | 5.34 | 30.0 |
| Non-detect | | | | | | |

- As (III) Speciation results: As (III) and Total As were measured for the 8 day $CO_2/CH_4$ samples.
- As (V) was determined by subtracting As (III) concentrations from the total As concentration.
- Blanks represent samples with As-spiked SGW and aquifer sediment, but no gas injection.

# Conclusive Remarks



- As behavior and the source of As(III):
  - As(V) reduction to As(III)
  - As(V) adsorption/ As(III) desorption
  - As(III) –bearing phase dissolution

- The ternary system As(V), As(III) and calcite

# Conclusive Remarks

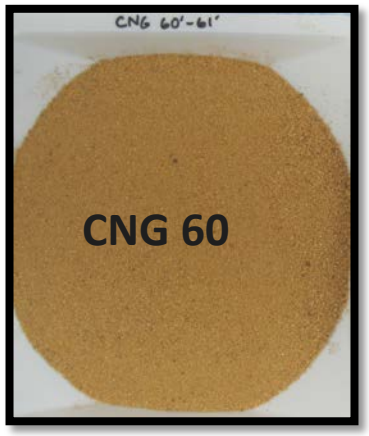


- **Batch tests conducted under constant $CO_2$ gas exposure:**
  - **pH decreases by about 1.5 units in CNG 110 and 2.5 units in CNG 60.**
  - **Concentrations of Ca, Ba, Sr, Mg, Na, K, S, Sn and Mn increase significantly.**
  - **Aqueous Si concentrations increase significantly in the materials that are abundant in montmorillonite and quartz.**
  - **Al and Fe are occasionally present in the aqueous phase suggesting aqueous phase mediated transformation of Al/Fe-bearing solid phases.**
  - **Low concentrations of trace elements (µg/L) are also present irregularly in the aqueous phase, such as Cu = 9.15; Mo = 2.74; Cs = 1.2; Pb = 7.94; Cr = 3.06; and Cd = 7.6.**

- **Column experiments:**
  - **pH decreases fast immediately after the gas-saturated groundwater is injected.**
  - **Effluent Ca concentrations are controlled by dissolution, precipitation, adsorption, desorption.**
  - **Dissolution of a Si-bearing phase(s) (silicate or phyllosilicate) is controlling the aqueous Si concentration.**
  - **The column effluent concentrations of Sb, Ba, Mg, Si, Ag, Na, Sr, Sn, and S are above detection limits in both columns (in addition to Ca).**
  - **Trace elements are rarely observed, and when present, were found at low concentrations (e.g., Cs = 0.5 µg/L, Mo = 11 µg/L and Hg = 30 µg/L).**

# Extra slides

- Sediment from High Plains Aquifer
  - CNG 58'-61' ("CNG 60")
  - CNG 109'-111' ("CNG 110")
- Synthetic Groundwater (SGW)
  - Based on USGS data for High Plains Aquifer
  - Spiked with 114 ppb As and 28 ppb Cd, representing maximum expected amount in brines
  - pH adjusted to 7.60
- 5 g:15 mL for batch experiments

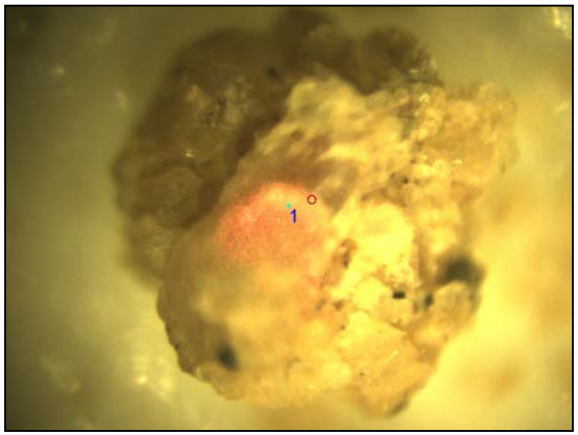



| High Plains Synthetic Groundwater | |
|---|---|
| Chemical Used | Amount per 1L |
| $CaCO_3$ | 0.1201g |
| $MgCO_3$ | 0.0691g |
| $Na_2SO_4$ | 0.0568g |
| NaCl | 0.0269g |
| 2% $HNO_3$ | 15.03ml |
| 1M KOH | 1.23ml |

# Extra Slides

# Extra slides

- 8M Nitric Acid extractions
  - As is present in the sediment prior to the experiment
- Laser ablation was also conducted, confirms As in both sediments



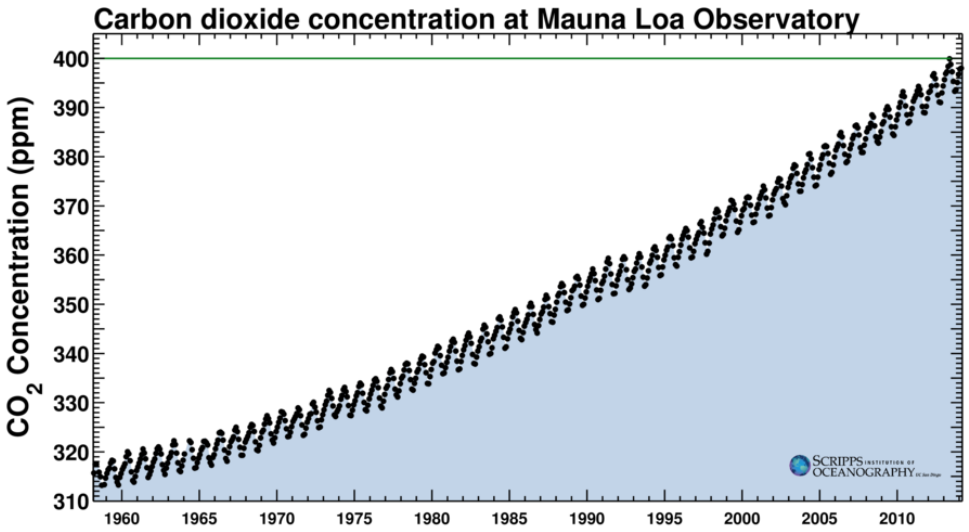

| | | CNG 60 | | CNG 110 | |
|---|---|---|---|---|---|
| | | Average | Standard Deviation | Average | Standard Deviation |
| | UNITS | | | | |
| Aluminum | ug/g | 2.48E+03 | 2.12E+01 | 2.22E+03 | 8.63E+02 |
| Arsenic 75 | ug/g | 1.59E+00 | 1.56E-01 | 9.64E-01 | 5.66E-03 |
| Barium | ug/g | 2.37E+01 | | 6.74E+01 | |
| Cadmium 111 | ug/g | ND | | ND | |
| Calcium | ug/g | 2.26E+03 | 3.54E+01 | 9.42E+03 | 4.36E+03 |
| Cesium 133 | ug/g | 3.48E-01 | 2.62E-02 | 3.19E-01 | 7.78E-03 |
| Chromium 53 | ug/g | 3.21E+00 | 3.46E-01 | 2.68E+00 | 7.07E-03 |
| Iron | ug/g | 4.36E+03 | 4.95E+01 | 3.32E+03 | 1.09E+03 |
| Lead 208 | ug/g | 2.38E+00 | 2.40E-01 | 1.49E+00 | 2.83E-02 |
| Magnesium | ug/g | 8.33E+02 | 1.20E+01 | 1.23E+03 | 5.79E+02 |
| Manganese | ug/g | 4.49E+01 | 9.19E-01 | 8.86E+01 | 6.28E+01 |
| Phosphorus | ug/g | 5.07E+02 | 1.13E+01 | 1.62E+02 | 4.74E+01 |
| Potassium | ug/g | 6.79E+02 | 3.54E+00 | 4.13E+02 | 1.22E+02 |
| Strontium | ug/g | ND | | 2.49E+01 | |

# The Argument: Climate change

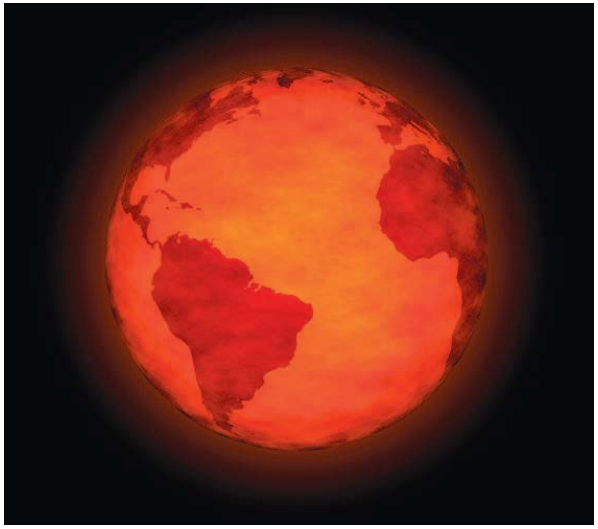
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Rising global temperatures attributed to rising atmospheric $CO_2$

**The Keeling Curve**

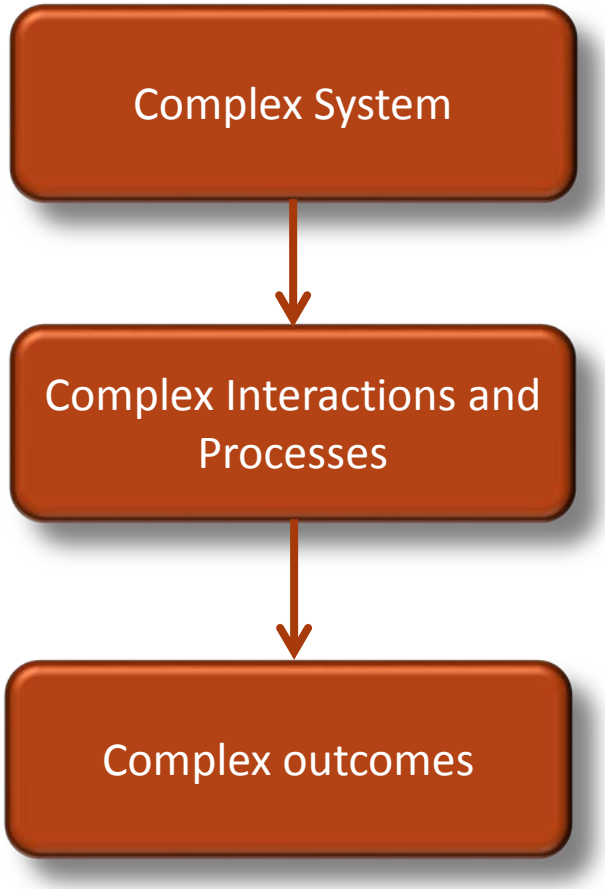



**http://keelingcurve.ucsd.edu/**



**www.sciencemag.com**

# Could it be that simple?
# No! Not in heterogeneous subsurface media

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Initiated a systematic program of study to:
  - Develop a methodical understanding of how CO2 leakage is likely to influence pertinent geochemical reactions (e.g. dissolution/precipitation, sorption/desorption and redox)
  - Identify prevailing environmental conditions that would dictate one geochemical outcome over another
- Results would provide useful information to support site selection, risk assessment, policy-making and public education efforts associated with GCS