SAND2008-8048P

Magnesium Oxide Carbonation Rate Law in Concentrated Brines

AGU 2008 Fall Meeting

December 15, 2008

San Francisco, CA

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Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. This research is funded by WIPP programs administered by the Office of Environmental Management of the U.S Department of Energy.

Waste Isolation Pilot Plant (WIPP)

- The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy deep-geologic repository for defense-related transuranic waste
- It is located in southeast New Mexico at a depth of 655 m in the Salado Formation, a Permian bedded-salt formation

•Waste contains cellulose, plastic and rubber that could microbially degrade to produce CO_2, which would acidify any brine present and dissolve / complex with actinides in the waste

MgO is emplaced with the waste

- Functions as an engineered barrier by consuming CO_2 from possible microbial activity generated by the biodegradation of cellulosic, plastic, and rubber materials, thereby decreasing actinide solubilities
  - MgO reacts with CO_2 and H_2O in brine and water vapor to form hydrous and, eventually, anhydrous Mg carbonates

$$5Mg(OH)_2(s) + 4CO_2 \rightleftharpoons Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O(s)$$

$$Mg(OH)_2(s) + CO_2 \rightleftharpoons MgCO_3(s) + H_2O$$

  - Will keep pH at mildly alkaline range

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

Objective of this study

- **Obtain experimental evidence for the functional form of the CO_2 sequestration rate-law by Mg in concentrated brines under well-mixed laboratory conditions**
  - Sum of a series of first order processes?

$$\frac{dP_{CO2,carbonation}}{dt} = -Ae^{-k_1 t} - Be^{-k_2 t} - ....$$

Previous Work

- Smithson and Bakhski, 1973
  - Measured amount of Mg-carbonate precipitated versus time in a flow-through reactor.
  - Recognized two distinct stages in carbonation reaction

1. Supersaturation of solution with Mg-bicarbonate complex

$$Mg(OH)_2(s) + 2\ CO_2 \leftrightarrow Mg(HCO_3)_2(aq)$$

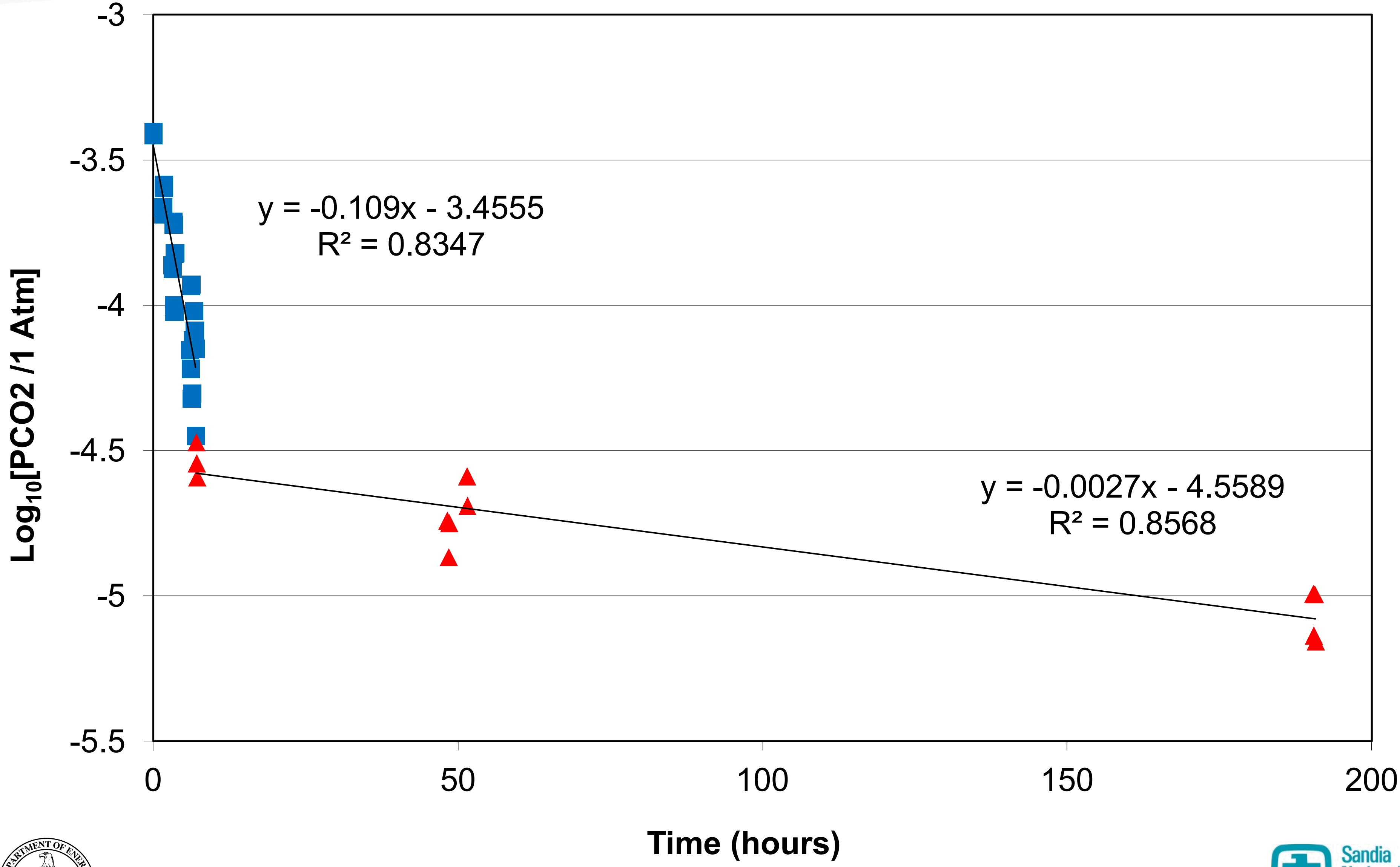
2. Precipitation of magnesium carbonate

$$Mg(HCO_3)_2(aq) \leftrightarrow \text{Mg-Carbonate}(s)$$

Summary of Experimental Method

- Filled HDPE serum bottles with 20mL of 5m NaCl brine and 0.4 g $Mg(OH)_2$
- Bottle headspace was charged with 5% CO_2
- Bottles were then capped with rubber septa and crimped with Al caps
- Bottles were placed on a stir plate and stirred continuously
- Headspace gas-phase CO_2 concentration was monitored versus time by Varian 3900/2100T GC/MS
  - Capable of measuring down to < 1 PPM

Results in De-Ionized H_2O (started at laboratory $P_{CO2} \sim 10^{-3.4}$ Atm)



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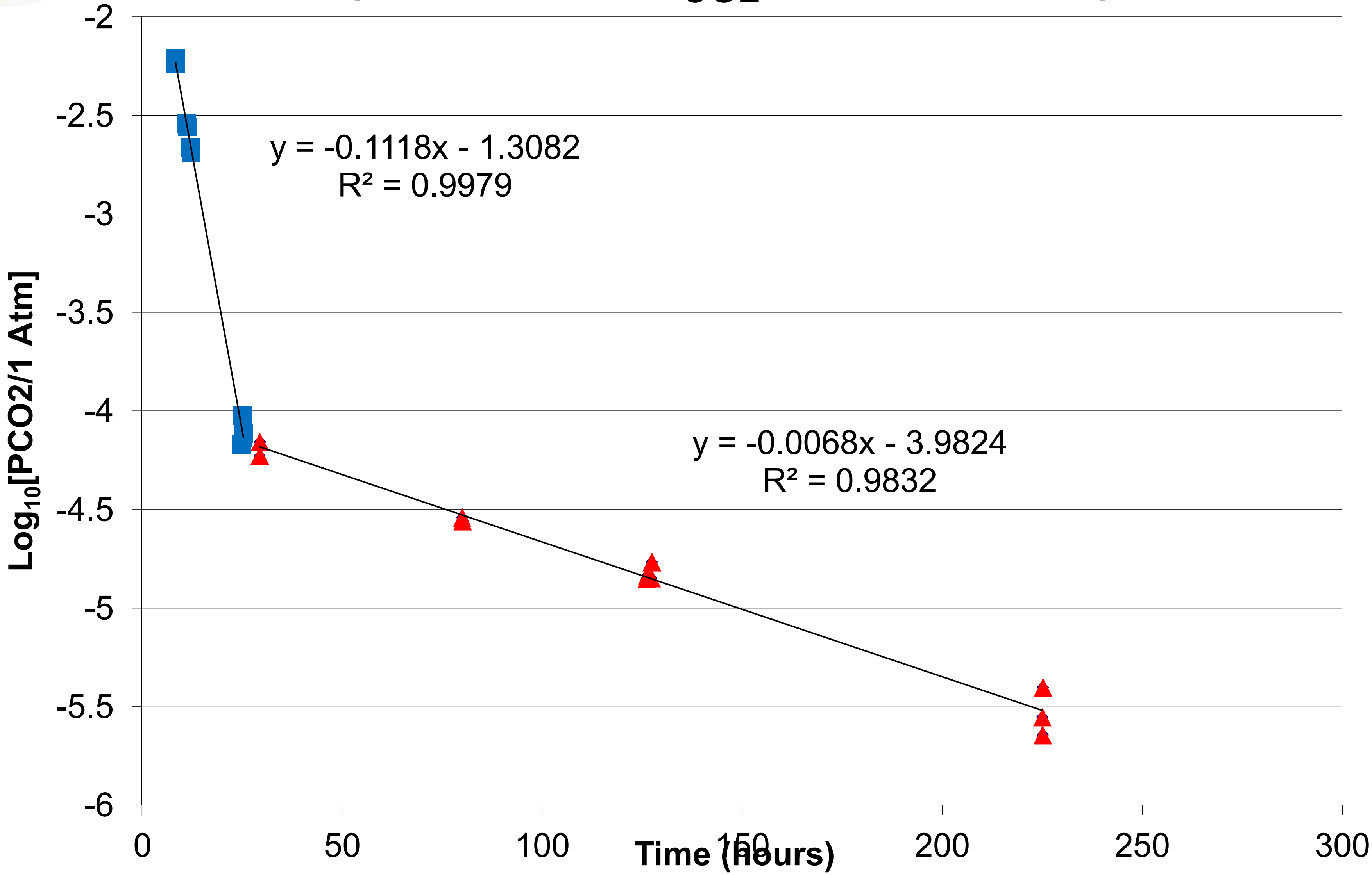
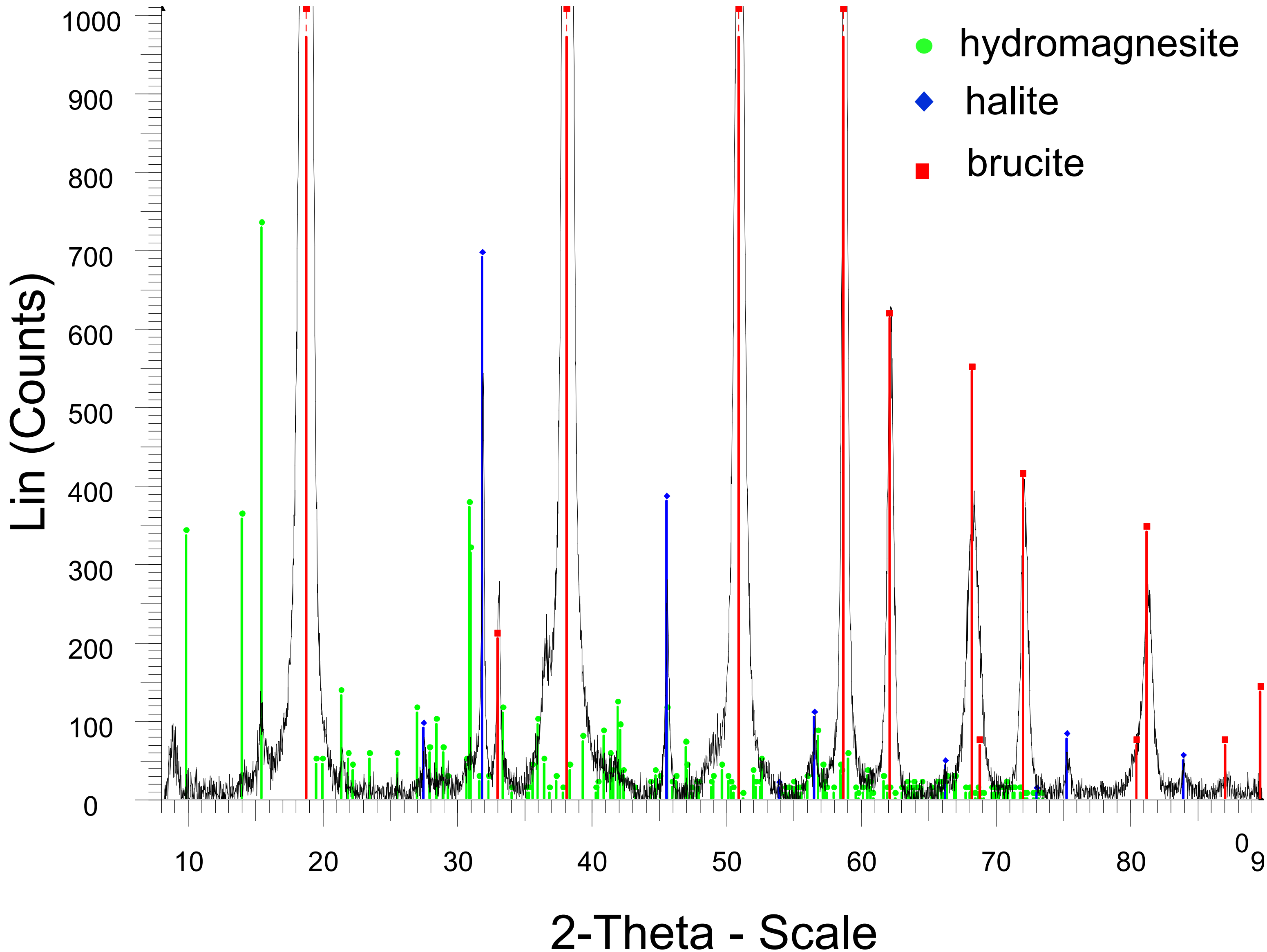
Results in 5m NaCl (started at P_{CO2} ~ $10^{-1.3}$ Atm)



XRD of solids after 2 runs (in 5m NaCl)

(enough CO_2 for 6 mol % of Mg)



Summary of Results

- Directly observed fast and slow timescale behaviors
  - Fast timescale
    - Supersaturation of brine with aqueous carbonate complex

$$Mg(OH)_2\,(s) + 2CO_2(aq) \leftrightarrow Mg(HCO_3)_2(aq)$$

  - Slow timescale
    - Precipitation of carbonate solids from solution and/or phase changes

$$4Mg(HCO_3)_2(aq) + Mg(OH)_2 \leftrightarrow Mg_5(CO_3)_4(OH)_2{\bullet}4H_2O(s) + 4CO_2$$

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Summary of Results Contd.

- **Obtained experimental evidence for the functional form of the carbonation rate law**
  - **Sum of two first-order processes**

$$P_{CO2}(t) = P_i\left((1 - \frac{B}{P_i})e^{-k_{fast}t} + \frac{B}{P_i}e^{-k_{slow}t} \right) + P_{hydromag}$$

- In 5m NaCl brine:
  - k_{fast} = *0.31 ± 0.05 hours*$^{-1}$
  - k_{slow}= *0.01 ± 0.005 hours*$^{-1}$
  - B = $10^{-4.2 \pm 0.2}$ Atm

Future Work

- Repeat methodology on the liquid phase
  - Should observe fast increase in carbonate concentration followed by slow decline that mirrors behavior in gas phase
- Try adding hydromagnesite
- Look at XRD at different times
- Repeat on the analogous Fe^{2+} system
- Tie model obtained here to long-term carbonation experiments underway at SNL

Backup Slides

Why is understanding the Mg carbonation rate law important?

- DOE is required to predict the performance of the repository for 10,000 years into the future
  - Need to be able to model carbonation reaction
  - Understand the kinetics and rate-controlling steps in CO_2 consumption

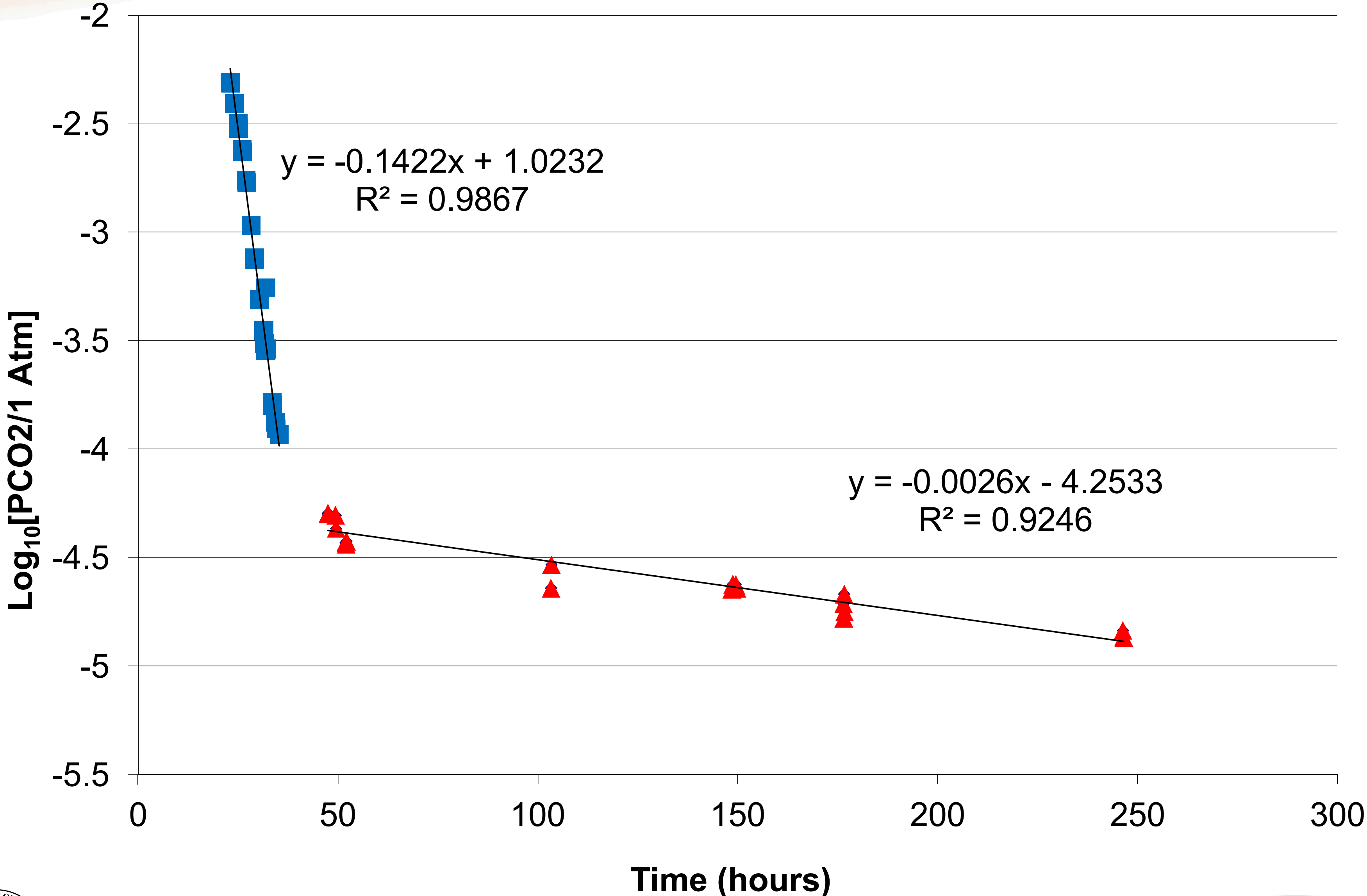
Experimental

- Fisher ACS-grade brucite $Mg(OH)_2$
  - Twice purified to remove carbonate forming cations (other than Mg^{2+})
- Brine: 5m NaCl prepared from DI H_2O and Fisher ACS grade NaCl.
  - Sparged with laboratory air to saturate with CO_2 and precipitate any carbonate forming cations
- 20 mL of Brine (or DI H_2O) + 0.4 g of $Mg(OH)_2$ were placed in 125 mL HDPE serum bottles (Wheaton)
- 5 % CO_2 (Airgas) was bubbled through the serum bottles for 5 minutes at a flow rate of 1 L/min. The bottles were then capped and crimped with rubber septa and aluminum caps

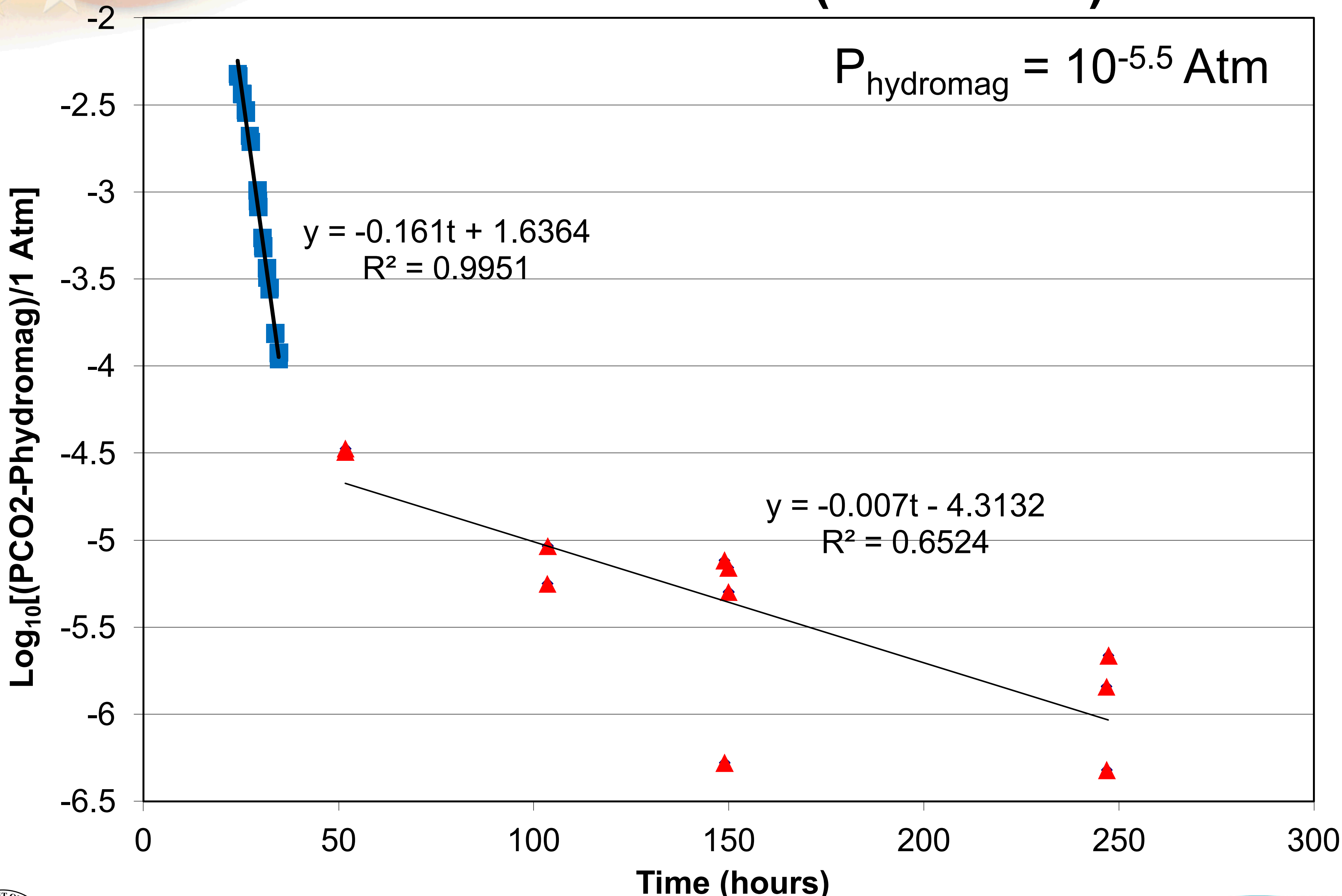
Experimental Contd.

- Bottles were stirred continuously at a high rate on a stir plate
- Temperature was maintained at 25 ± 3 °C
- Blanks containing only brine + 5% CO_2 and blanks containing only 5 % CO_2 were prepared to show that the brine and bottle weren't significant sources of CO_2 sequestration
- CO_2 concentrations in the headspace of the bottles were obtained using a Varian 3900 GC coupled to a Varian 2100T ion-trap MS using a CP-SilicaPlot column
- The experiments were repeated twice on the same bottles, with 4 replicates per run for a total of 8 experiments

Results in 5m NaCl (series 1.1)



Results in 5m NaCl (series 1.2)



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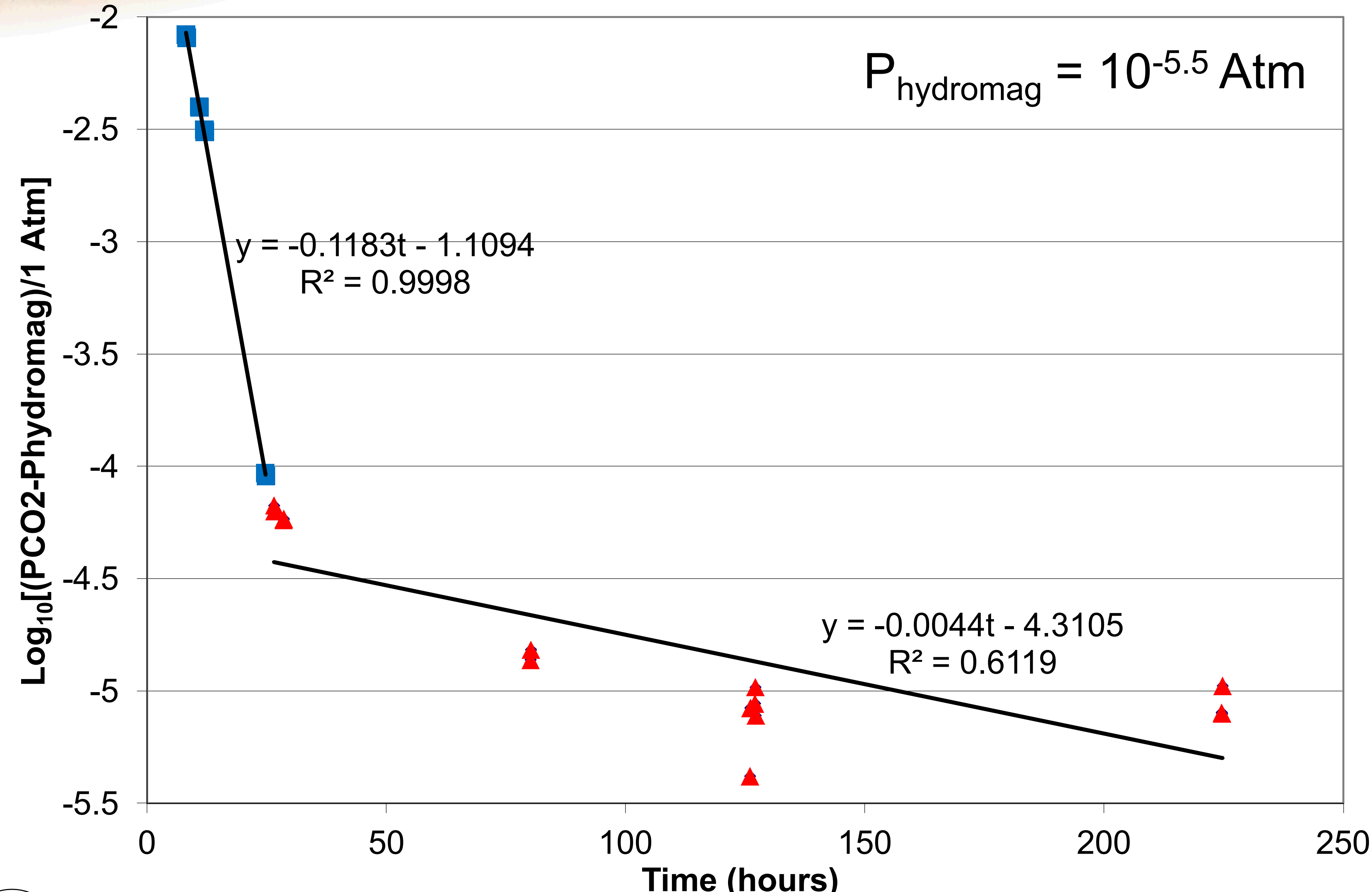
Results in 5m NaCl (series 2.1)



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