Subcritical injection of CO$_2$-saturated water through a siliceous sandstone from the Northern of Spain

by

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Context

The "Energy City Foundation", CIUDEN, was established as a legal public state foundation by Resolution of the Spanish Council of Ministers on May, 12th, 2006. Its purpose is to "strengthen economic and social the Bierzo region" by means of activities related to energy and environment.

The “Energy & Environment” program includes activities related with the construction of pilot plant for testing technologies of CO₂ capture and the commissioning of a field laboratory where a pilot injection project will be developed in 2013.
Purpose and Aims

- The experiment described is the first in a series of tests of increasing complexity.
- Its main purpose was monitoring physical and chemical parameters simultaneously for long experiments at the real pressure conditions by the injection of CO$_2$.
- Because its preliminary nature and demonstration purpose, we opted for a low-sophistication approach, keeping automation in a minimum.
- The experimental device allows the …
  - continuous monitoring pore pressure, flow of water or gas, permeability,
  - continuous monitoring of temperature, pH and specific conductance of the pore fluid
  - measurement of the instantaneous concentration of selected relevant chemical constituents via ion chromatography (ANIONS: F, Cl, Br, NO$_3$, NO$_2$, SO$_4$, PO$_4$) and ICP-MS (CATIONS: Na, K, Ca, Mg, Al, SiO$_2$, Ba)
  - measurement of P waves and S$_1$ and S$_2$ waves.
Sample Preparation

Rock block slicing  Drilling the rock block  Core sampling (plugs)

Plug facing  Dimensional verification
Experimental Device

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Equipment (I)

Gas mass flow meter (Agilent Technologies)

Low P microelectrode array (Microelectrodes Inc.)
Equipment (& II)

Injection platens w. sonic velocity transducers

High P fluid carbonation vessel (disassembled)

Data acquisition system & Electronics

Ion chromatograph, ICP-MS,…
Samples come from a relatively complex, folded & thrusted Southern flank. They are representative of one of the potential reservoirs in the Hontomin zone.
Tested Sample

- Sandstone from the Arcera Formation (Malm-Berriasian)

- Sample I.D.: A 1.3
- Diameter: 38.3 mm (~ 1.5 in)
- Height: 74.55 mm (~ 3 in)
- $\phi_{\text{mean}}$: 8.25 % (7.3 % in the tested sample)
- Mineralogy (% volume - DRX):
  - Quartz: ~80.2 %
  - Muscovite: ~8 %
  - Microcline: ~3.2 %
  - Fe oxides: ~8 %
  - Clay minerals: ~0.08 %
  - Calcite: ~0.44 % (estimated from LOI-FRX)

- High permeability (~500 mD – 500/1000 mD; Levosen, 1967)
- Poor reservoir rock ($\phi$~8 % – 5/10 %; Levosen, 1967)

Description of the Experiment

Continuous subcritical injection of CO$_2$-saturated water (4 MPa) in a siliciclastic core plug during several weeks.

- Ambient temperature (~22 ºC)
- 10 MPa confining pressure
- 15 MPa axial pressure
- 4 MPa pore pressure
- The sample is dry at the beginning

Experimental stages:

- N$_2$ injection and determination of gas and liquid permeability. Determination of reference direct and shear velocities ($V_P$ & $V_S$)
- Flooding with distilled water in order to saturate the sample. Periodic measurement of $V_P$, $V_S$
  - Start recording chemical parameters (T, pH, CE$_{25}$)
  - In & out flow recording
- Flooding with CO$_2$-saturated distilled water. Periodic measurement of $V_P$, $V_S$
- Dismantling
Experimental Conditions

\[ \sigma_1 = 15 \text{ MPa} \]
\[ \sigma'_1 = 11 \text{ MPa} \]
\[ \sigma_3 = 10 \text{ MPa} \]
\[ \sigma_1 - \sigma_3 = 5 \text{ MPa} \]

\[ \sigma_F = 4 \text{ MPa} \]

C.P. 7.38 MPa
31.1 °C
At 22 °C and 4 MPa, the theoretical CO₂ content of the experimental fluid is 2 % (molar).

This proportion corresponds to a dissolved CO₂ concentration of 1.39 mol/kg H₂O (~61.1 g CO₂/kg H₂O).

The initial pH is netly acidic, with a theoretical value of ~3.2.

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**Figures adapted from Akinfiev & Diamond (2010) (top) and Li & Duan (2007) (left)**


- Li, D. & Duan, Z. (2007) The speciation equilibrium coupling with phase equilibrium in the H₂O-CO₂-NaCl system from 0 to 250 °C, from 0 to 1000 bar, and from 0 to 5 molality of NaCl. Chemical Geology 244, 730-751
Results

Nearly 500 pore volumes circulated through the sample during the experiment.

In the H₂O-only injection phase, a slight permeability increase is observed (A): Dissolution of readily soluble salts present in the sample.

When the core starts to be flooded with the CO₂-saturated fluid, the permeability first drops slightly (B). After approx. 100 PV, it suddenly increases (C).

In the final part of the experiment, permeability rises again.

From the beginning to the end of the experiment, the permeability increased by a 3-fold factor.
Results

The continuous monitoring of pH & CE$_{25}$ proved to be challenging: Bubbling & CO$_2$ unmixing in the flow-thru electrode.

The results look consistent, with a "steady" pH value at room conditions close to 5.5
Results

- CE_{25} shows an interesting evolution.
- A) Washout of readily soluble salts (H_{2}O-only flooding stage);
  B) Sudden increase due to the arrival of CO_{2}^{-}-saturated water and dissolution of carbonates;
  C) CE_{25} decrease as carbonate become exhausted;
  D) Steady background CE_{25} associated to the less significant contribution of solutes through the dissolution of silicates.
Results

Those constituents closely related with the dissolution of salt minerals display a pattern consistent with that observed in CE\textsubscript{25}.

Steady concentrations develop when salts have been washed out. Ca & Mg are exceptions.

The amount of equivalent NaCl dissolved is estimated to be ~64 mg, which is consistent with an EC\textsubscript{25} of ~120.
The 2nd stage of the experiment (flooding with CO$_2$-saturated water) illustrates different elemental behaviors:

- Constituents with constant concentrations: A
- Elements highly +correlated with Ca (dissolution of carbonates or silicates with higher solubilities): B
- Elements highly -correlated with Ca (likely source are silicates): C
- Silica shows a moderate +correlation with Ca
Results

- **Ca & Mg** display a mirror pattern and readily respond to the arrival of the acidic fluid. It is likely its release by a common mineral source: magnesian calcite.
- The release of both elements is governed by a **CO-DISSOLUTION** process:
  - There is a lineal relationship between the concentrations of both elements.
  - Assuming that the dissolution of carbonate is congruent, its theoretical stoichiometry would be $\text{Ca}_{0.67}\text{Mg}_{0.33}\text{CO}_3$.
Results

Ca (& Mg) displays a complex pattern:
- Following the washout stage (A), the concentration suddenly rises upon arrival of the acidic fluid (B).
- Then, the concentration decreases with time (C).
  - Is carbonate being progressively exhausted?
- The increase in permeability does not follow immediately to the increase in Ca concentration (D).
- The rise in permeability occurs when Ca concentration starts to decline abruptly.
- The last part of the experiment likely reflects silicate-dominated processes.

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Assuming that the change in the concentrations of Ca & Mg are directly related with the dissolution of carbonates, a mass balance can be assessed.

- The increase in permeability would be with the exhaustion of accessible carbonates.
- The reason why permeability increases is not straightforward: In addition to rock reactivity, mechanical processes (derived from the dissolution of sandstone cement, local grain collapse, microcracking) cannot be ruled out.
Assuming that the change in the concentrations of Ca & Mg are directly related with the dissolution of carbonates, it is possible to compute how much carbonate would have been dissolved throughout the experiment:

- ~0.02 cm³ of calcite would have been dissolved.
- According with the initial carbonate content (~0.44 %) and the dimensions of the sample, the volume of calcite at the beginning of the experiment was ~0.38 cm³.
- The amount of calcite dissolved is ~5 % of that present in the rock at the beginning of the test.
- We conjecture that not all the carbonate was accesible to the reactive fluid.
- Porosity evolved from ~7.323 to ~7.345 %, that is, an increase of ~0.25 %.
Results

Sonic velocities clearly identify the different experimental stages:
- The $V_P$ velocity increases when flooding with the CO$_2$-saturated occurs (A). However, in this stage, the velocity is not constant (B) and, on average, decreases (C). That suggests structural damage of the sample (microcracking?)
- Shear velocities decrease with the CO$_2$-saturated fluid flooding (D).
- However, $V_{S1}$ & $V_{S2}$ become equal at the final stage of the experiment what would be consistent with the conjectured microcracking.
Conclusions

- The experimental arrangement has proved to be able to perform tests of several months of duration.
- The multi-stage approach developed allowed us to better constrain and interpret the experimental data obtained.
- Highly reactive phases present in the sample in small amounts appear to govern the physico-chemical evolution of the system as well as the hydrodynamics.
- A 3-fold increase in permeability has been observed to occur after 1 & ½ months of continuous injection of CO$_2$-saturated water.
- The observed decoupling in the evolution of porosity and permeability suggest that the sample might have been damaged (microcracks) during the experiment. This is supported by sonic velocities.
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