Interaction between CO_2-rich brine and marly shale under supercritical CO_2 conditions

G. DÁVILA[1], L. LUQUOT[1], J. M. SOLER[1] AND J. CAMA[1*]

[1]Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Jordi Girona 18-26, Barcelona 08034, Catalonia, Spain (*correspondence: jordi.cama@idaea.csic.es)

Geological CO_2 sequestration at a pilot-plant scale is going to be performed at Hontomin (Spain). The reservoir rocks are mainly fractured limestones and the caprock is made up of marly shales, with an average composition (wt%) of 56% calcite, 21% quartz, 17% illite, 3% clinochlore and albite and trace amounts of pyrite, gypsum and anhydrite. An experimental study was performed to (1) evaluate mineral dissolution/precipitation processes as a sulfate- and CO_2-rich brine circulates through an open fracture and (2) to quantify the effects these processes may exert on fracture permeability.

Percolation experiments under CO_2 supercritical conditions (p_total = 15 MPa, pCO_2= 8 MPa, T = 60°C) were performed using two synthetic CO_2-rich brines (sulfate-free and sulfate-rich) that circulated at constant flow rates (0.2, 1 and 60 mL/h) through artificially fractured shale cores (7.5 mm in diameter and 18 mm in length).

The pH of the injected solution was acidic (~3). In the case of the sulfate-free solution the interaction mainly promoted the dissolution of calcite. Permeabilities remained almost constant. At flow rates 0.2 and 1 mL/h, fracture permeability ($k_{initial}$ ~$1x10^{-12}$ m^2) decreased slightly ($k_{final}/k_{initial}$ = 0.8). Under the highest flow rate (60 mL/h), permeability ($k_{initial}$ = $17x10^{-12}$ m^2) increased slightly ($k_{final}/k_{initial}$ = 1.2). In the experiments with sulfate-rich solution (synthetic Hontomin groundwater), calcite dissolution and gypsum/anhydrite precipitation were the dominant processes. At the lower flow rates rates (0.2-1 mL/h), the fracture permeabilities ($k_{initial}$ 1-$20x10^{-12}$ m^2) decreased remarkably ($k_{final}/k_{initial}$ ≤ 0.03), as expected from the precipitation of sulfates. However, at the highest flow rate (60 mL/h) the permeability ($k_{initial}$ = $22x10^{-12}$ m^2) increased significantly ($k_{final}/k_{initial}$ = 4), showing a dominant dissolution effect under those fast-flow conditions.

The Chicago Instrument for Laser Ionization: progress and promise

A. M. DAVIS[1,2,3]*, T. STEPHAN[1,2], M. J. PELLIN[1,2,3,4], D. ROST[1,2], M. R. SAVINA[1,4], R. TRAPPITSCH[1,2] AND N. LIU[1,2]

[1]Chicago Center for Cosmochemistry
[2]Dept. of Geophysical Sciences, Univ. of Chicago, Chicago, IL 60637 (*correspondence: a-davis@uchicago.edu)
[3]Enrico Fermi Inst., Univ. of Chicago, Chicago, IL 60637
[4]Materials Science Div., Argonne National Laboratory, Argonne, IL 60439

Current state-of-the-art secondary ion mass spectrometers (SIMS) have reached lateral resolution of 50–100 nm and useful yields of a few percent or less. CHILI (the CHicago Instrument for Laser Ionization), a resonance ionization mass spectrometry (RIMS) nanobeam instrument, is designed for isotopic and chemical analysis at the few-nm scale with a useful yield of ~40%. CHILI is equipped with a COBRA-FIB high resolution liquid metal ion gun for sputtering samples and an e^-CLIPSE Plus field emission electron gun for imaging samples, both at the few-nm scale. Both Orsay Physics guns are installed and tested. A built-in optical microscope is installed and demonstrates a diffraction-limited resolution of <1 μm. It will be used for overview imaging and for laser ablation (with a Photonics Inc. 351 nm Nd:YLF laser) of larger samples. A piezoelectric stage capable of reproducible nm-scale motions and equipped with a sample holder that will accept a wide variety of sample mounts is operational. The flight tube for the time-of-flight mass spectrometer is mounted vertically above the sample chamber, under vacuum and leak-free. Resonance ionization will be done with six Ti:sapphire tunable solid state lasers of our own design pumped with three Photonics 527 nm 40W Nd:YLF lasers, which will allow isotopic analysis of two to three elements simultaneously. The pump and tunable lasers have been shown to meet specifications, but are awaiting completion of a beam combiner to introduce all tuned laser beams on a single line through the sample chamber.

CHILI will have broad applications in geochemistry and cosmochemistry. Its strengths will be in isotopic and chemical analysis at lateral resolutions and concentrations beyond the current state-of-the-art. Among the applications currently planned are isotopic analyses of material returned to Earth by spacecraft: Stardust–cometary and contemporary interstellar dust; Genesis–solar wind; Hayabusa–asteroidal material. Also well-suited to CHILI's capabilities are presolar grains, which inform us about stellar nucleosynthesis, and refractory inclusions and chondrules, useful for early solar system chronology.

www.minersoc.org
DOI: 10.1180/minmag.2013.077.5.4