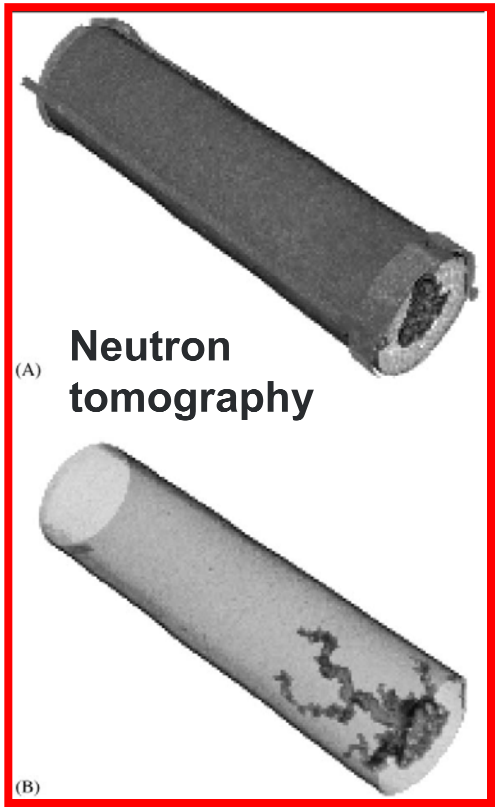
Properties of CO_2-Rich Pore Fluids and Their Effect on Porosity Evolution in EGS Rocks



May 20, 2010

Principal Investigator:
David R. Cole
Oak Ridge National Laboratory

Chemistry, Reservoir and Integrated Models

Project Overview

- Overarching goal: Quantify key parameters critically needed for developing and validating numerical modeling of chemical interactions between EGS reservoir rocks and supercritical CO_2 and CO_2-rich aqueous fluids.
- Timeline
  - Project start date: October 1, 2009
  - Project end date: September 30, 2011
  - Percent complete: 25% (out of 24 months)
  - Budget

    Total funding: $1,000K; DOE share-100%, awardee share- 0%, funding received in FY09-$500K, funding for FY10-$500K
  - Barriers (several – e.g. thermophysical properties at P&T; pore/fracture scale changes; scale up)
  - Partners (no-cost): LBNL (Mack Kennedy; Kevin Knauss)

Objectives and Relevance: General

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Objectives:

- Measure the thermophysical properties of $CO_2 + H_2O$ bulks and pore fluids using novel vibrating tube densimetry
- Characterize pore features in representative geothermal rocks and assess the sorption and wetting behavior of $CO_2 + H_2O$ in key EGS rock samples
- Develop real-time imaging methods (X-rays and neutrons) to observe fluid infiltration and pore evolution in representative EGS rocks

Relevance:

- Mineral-fluid reactions are rate-limited by exchange at a variety of interfaces – minerals surfaces, grain boundaries, pores, fractures
- Interfacial processes can include dissolution-precipitation, recrystallization replacement, surface diffusion, grain boundary diffusion, etc.
- Certain interfacial processes can modify rock strength and pore structure leading to porosity and permeability modifications
- Understanding fluid properties and processes controlling fluid-rock interactions can lead to improved predictions of reservoir performance: reservoir hydrodynamics and local porosity/permeability evolution that impact effective heat mining.

Task 1: Thermophysical Properties of Bulk and Pore Fluids

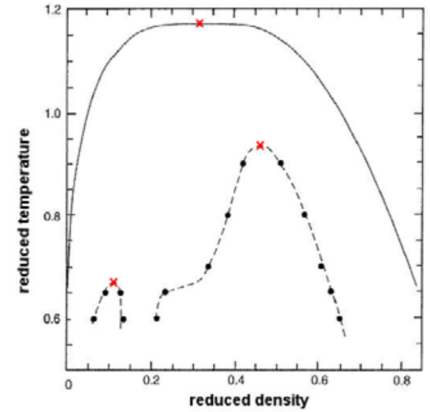
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Goals:

- Provide key thermophysical data on CO_2-rich fluid mixtures – phase boundaries and the densities of coexisting phases at 150 – 250 ºC to 500 bar

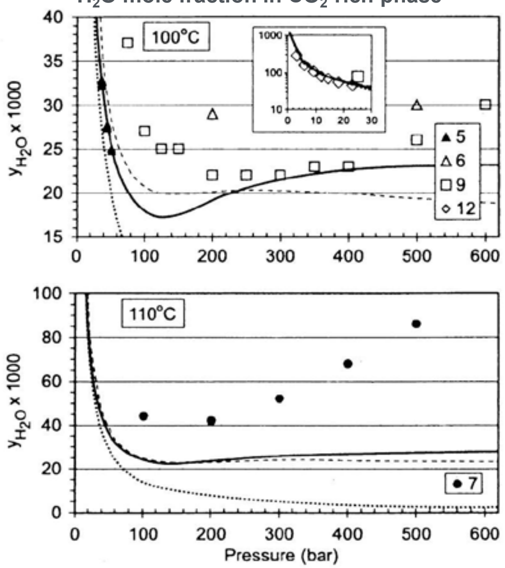
- Explore the effect of pore confinement on fluid-fluid equilibria

Sarkisov *et al.*, 1998
from Gelb *et al.*, 1999



GC Monte Carlo simulation of the coexistence curve of methane confined in silica aerogel compared with the bulk fluid.

H_2O mole fraction in CO_2-rich phase



The solubilities of water in the CO_2-rich phase show significant uncertainty at elevated temperature.

Spycher *et al.*, 2003

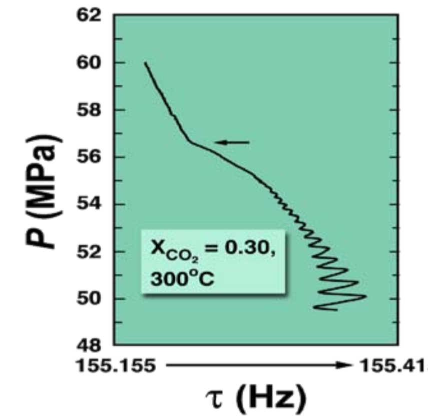
Relevance:

- Reactivity, solubility, and transport of minerals depend on the properties of multicomponent fluids in a wide range of *T* and *P* conditions.

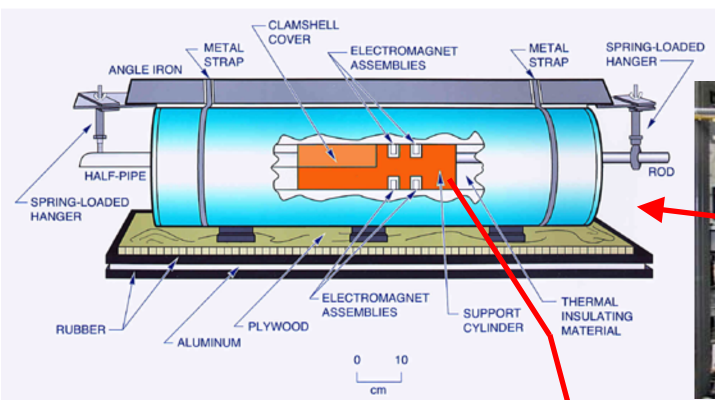
- However, existing *PVTx* data are inadequate for reliable numerical modeling of the evolution of EGS systems. Serious gaps and discrepancies exist even for the essential binary CO_2 + H_2O.

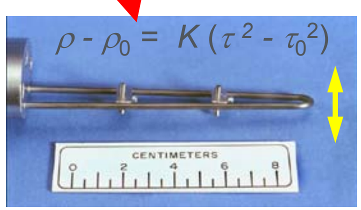
Task 1: Approach – Vibrating Tube Densimetry of Mixed Fluids

- Custom-built flow vibrating tube densimeters (VTD) have been used at ORNL to rapidly and accurately determine densities and phase diagrams of fluid mixtures to 400 ºC and 1000 bar.
- Direct measurement of the density of the fluid confined in a porous solid by VTD has never been tried before.

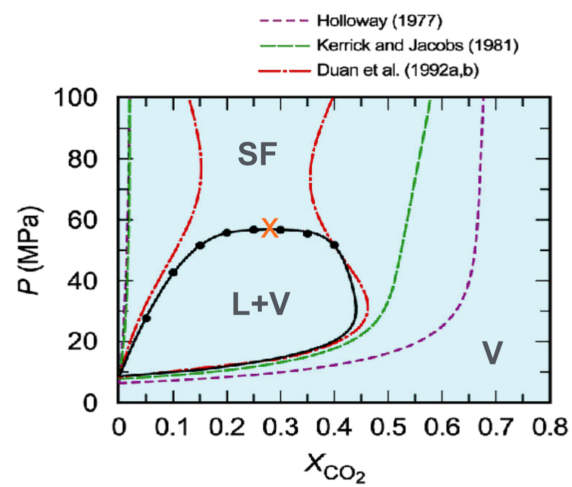


The principle of phase boundary detection (Blencoe *et. al.*, 2001)





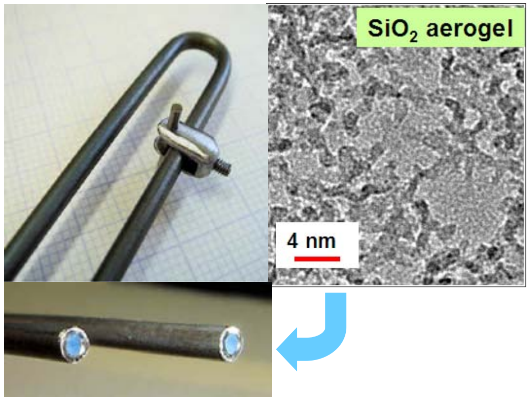
ORNL high-temperature VTD operating to 400 ºC and 1000 bar. The density is proportional to the square of the vibration period.



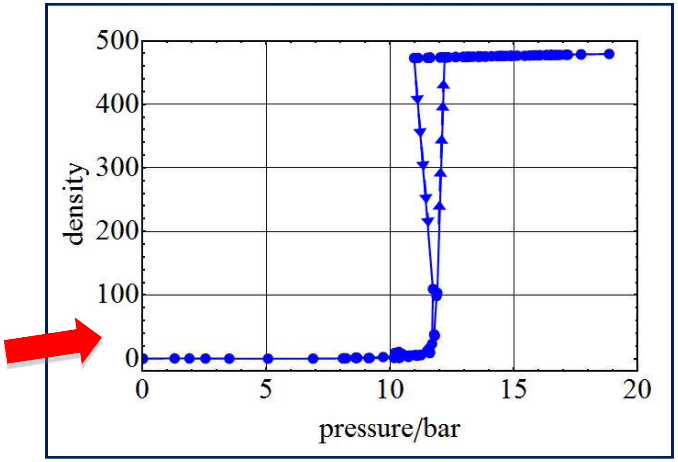
Calculated H_2O+CO_2 phase diagrams show large discrepancies between widely used numerical models reflecting earlier experimental data.

Task 1: Progress, Expected Outcomes and Accomplishments

- Two vibrating tube densimeters (VTD) operating to 400 ºC are being modified and updated: one for flow measurements on bulk fluids, and another for novel measurements of density of pore-confined working fluids.
- Silica aerogel (density 0.2 g/cm^3; ~4 nm pore size) was synthesized inside Hastelloy U-tubes (leveraged from BES LBNL EFRC). Initial tests with propane (an "inert" adsorbate) at 35 ºC confirmed mechanical stability of the solid phase and sensitive detection of vapor condensation into the pores through the density (frequency) signal. Some indications of metastability of the pore phase were observed.
- The proof-of-principle density measurements in the vicinity of the critical point of propane (97 ºC) will be followed by the same solid saturated with CO_2 and then bulk supercritical H_2O + CO_2 fluids to temperatures 150ºC and above.



Vibrating tube filled with the prototype porous solid - SiO_2 aerogel with 95% porosity; 0.1 and 0.2 g/cc

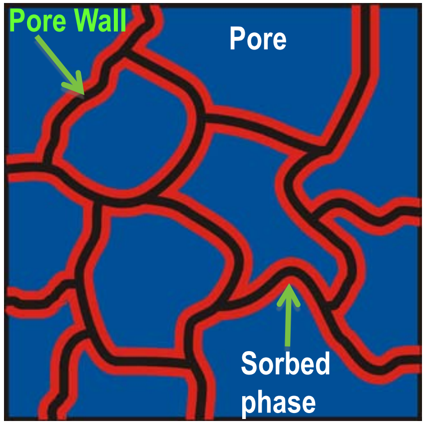


Density as a function of pressure showing pore condensation of propane at 35 ºC.

Task 2: Characterization of Rock Pores and Adsorbed Fluids

- Goals:
  - Probe the pore-scale features encountered in subsurface EGS environments and how these may change after water-rock reactions
  - Assess the impact of pore-scale confinement on the properties of CO_2-rich fluids such as sorption and wetting at relevant EGS temperature and pressure conditions

- Relevance:
  - Pore scale features in EGS rocks and their evolution during reaction with CO_2-bearing working fluids control:
    a) fluid-accessible pore volume
    b) fluid flow dynamics
    c) selective fluid retention by capillary forces
    d) chemical reactivity at the fluid-mineral interface



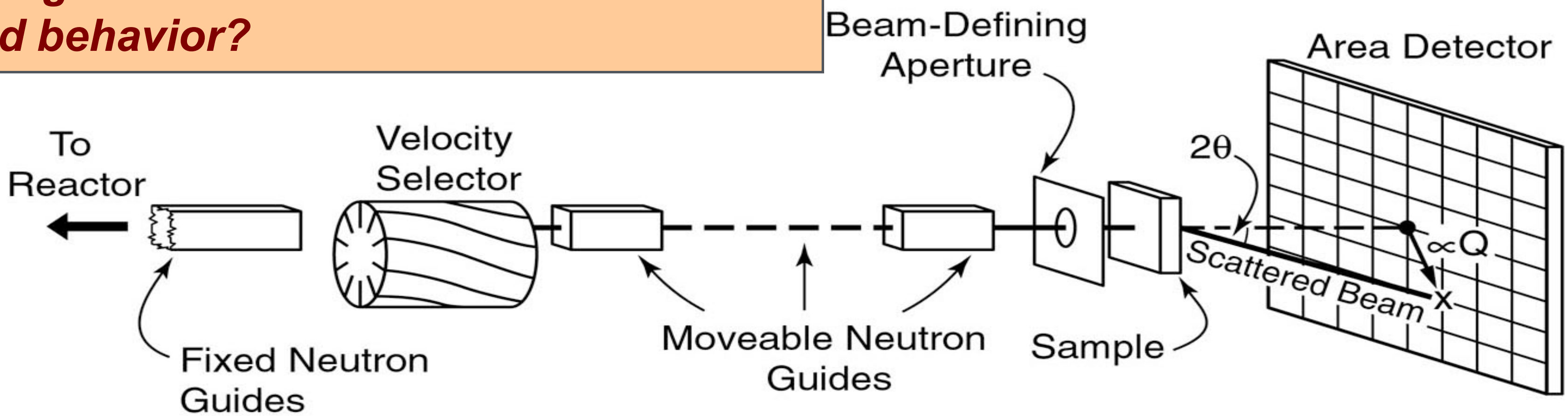
- Objectives:
  - Determine total porosity, pore surface area, pore number, fractal (surface roughness) features
  - Obtain fluid densities and volumes of CO_2-rich supercritical fluids using new neutron-based Adsorbed Phase Model (APM)

Task 2: Approach – Neutron Scattering and Electron Microscopy

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

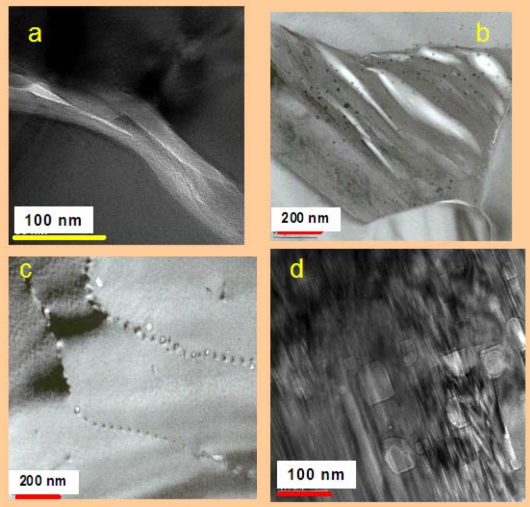
How does pore micro-structure develop during reaction and how does this affect fluid behavior?

Complements BET; Hg porosimetry



- **SANS: structures on length scales 5 – 2000 Å (micro- & mesoscopic)**
- **Combination with WANS, USANS, BSE, SALS: lengths 1 Å – ~1 mm**
- **High penetration depth, H/D contrast variation (assess connected vs unconnected pores); use differences in SLD**
- **Systems:**
  - **Clays, zeolites, reaction zones, grain boundaries, nano-composites**
  - **Fluids, mixtures in bulk and in pores**
  - **Polymers, biopolymers in bulk and at interfaces**

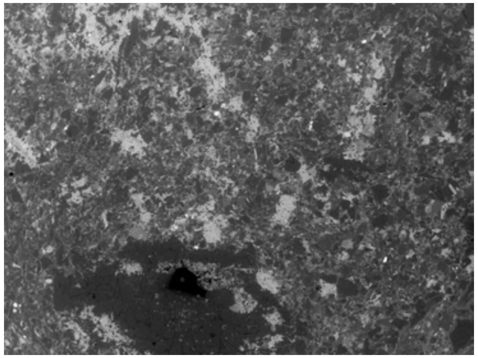
TEM images



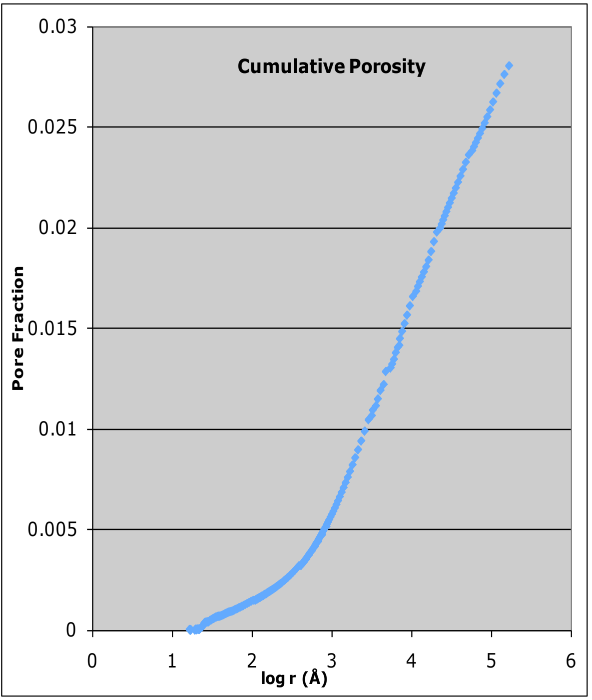
Task 2: Progress, Expected Outcomes and Accomplishments

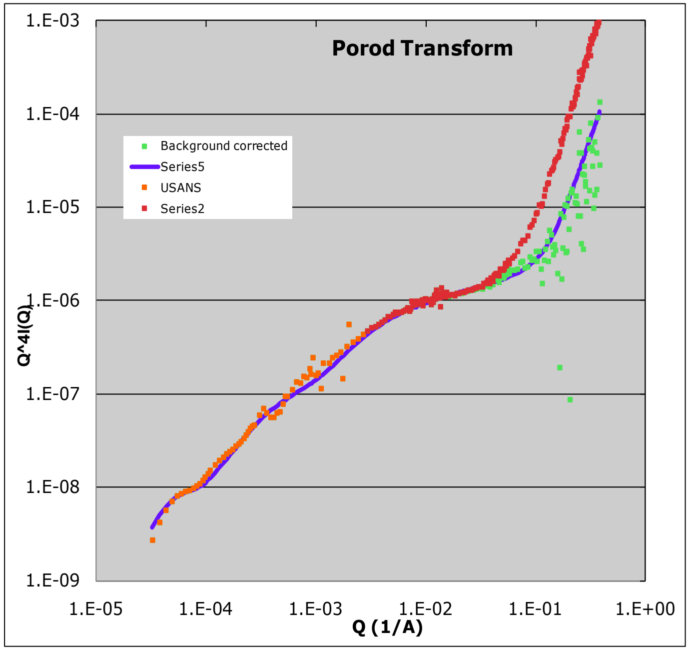
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

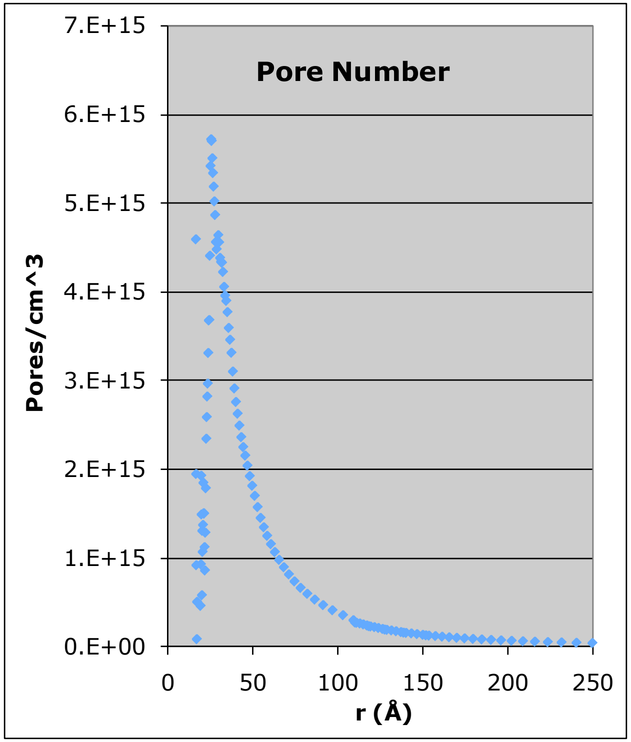
- Initiated SANS, USANS, BSE characterization of rocks from: Los Alamos (Fenton Hill), N Mex; Geyser, CA; Long Valley, CA; Awibengkok, Indonesia
- Plan to examine natural and experimental rocks from Desert Peak, NV; Raft River, ID; Yellowstone, WY
- Features: Pore size, pore size distribution, pore number, fractality



Back Scatter Electron Image





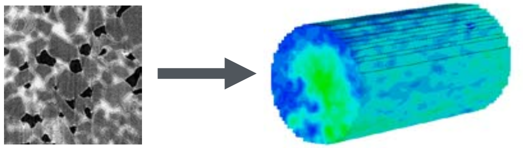


Specific surface area: 1.59 m^2/g

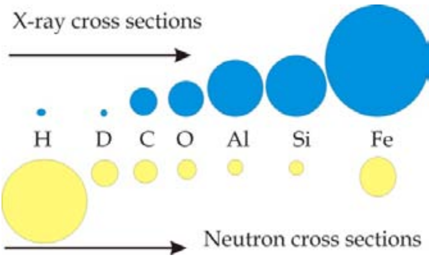
NW Geysers – Prati State 12 (1909 m)

Task 3: In Situ Imaging of Fluid-Rock Interactions

- **Goals:**
  - Real-time imaging of CO_2-rich fluids to characterize the progression of infiltration and dissolution fronts at pore to core scales

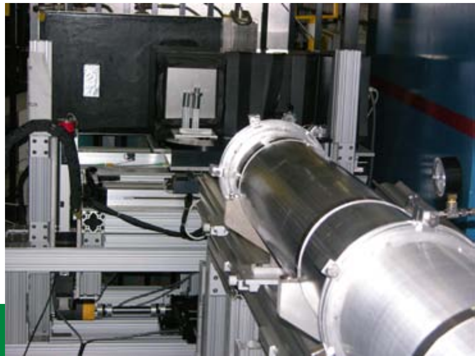


- **Relevance:**
  - Understanding of how CO_2-rich fluids infiltrate and how dissolution-precipitation fronts propagate are crucial to the development of predictive reactive transport model under EGS conditions



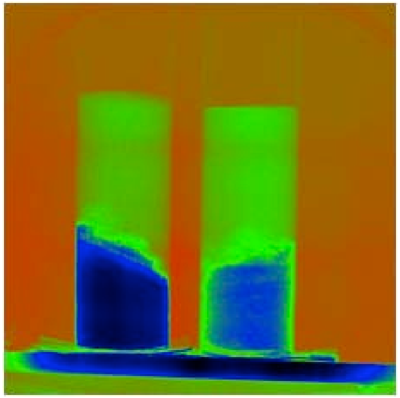
- **Approach:**
  - Novel neutron and X-ray imaging techniques (radiography-tomography)
    - Neutron and X-ray are complementary
  - Advanced new neutron Imaging instrument at ORNL HFIR (CG-1)
    - CCD camera: 8x8 cm with 50 μm resolution / 1 frame per second spatial resolution
  - X-ray CT instruments (Xradia) at ORNL
    - 1x1 mm w/0.6 μm or 5x5 mm w/3 μm resolution

ORNL HFIR/CG-1

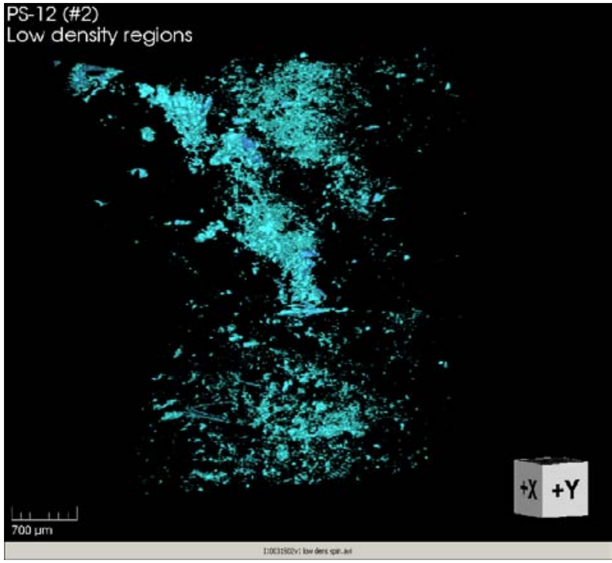


Characterize basic physical features (textures, surface area, porosity) and mineralogy of select geothermal reservoir rocks

- Design custom Al-alloy reactor for neutron tomography: P-T range (<200 bar, <200^{o}C)
- Acquired first neutron radiographs of partially water-saturated porous material from new ORNL/HFIR beamline
    - Sand with normal water (left) shows stronger contrast relative to heavy water (right).
- Acquired 3-D X-ray micro-tomography images of porosity distribution in geothermal (Geysers rocks, Fenton Hill, Awibengkok, Long Valley)
    - Heterogeneous distribution of porosity can be clearly seen



Neutron radiography of water in sediment column



3D images of porosity in Geysers rock (PS-12)

Project Management/Coordination

Geothermal HQ

Tom King, Director
Energy, Efficiency and Electricity Technologies Program

reporting

Penny Humphreys
Program Management Coord.
Geothermal Technologies

Dave Cole
Project PI

Biweekly mtgs.
Monthly reports
Quarterly reports
Purchasing

Chemical Sciences Division

Operational Support

ESH&Q Operations
Monty Ross (CSD)
Kennie Edwards (MSTD)
Janet Wagner (Quality)

Education and Outreach
Greg Gruzalski

Human Resources
David Lett
Cindy Spence

Finance Officer
Brenda Johnson

Procurement
Linda Woods

Technology Transfer
Alex DeTrana

Task 1
Thermophysical Properties
Mirek Gruszkiewicz

Task 2
Rock Pores & Sorbed Fluids
Gernot Rother

Task 3
Xray/Neutron In Situ Imaging
Juske Horita

Milestones/Deliverables/Schedule

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Task 1: Milestones

- Tests completed for fluid behavior in confined pores using static VTD (09/30/2010)
- Complete upgrades and testing of high-temperature, high Pressure flow VTD (12/31/2010)
- Measure fluid phase behavior and densities for H_2O+CO_2 between 150 and 250^oC (09/30/2011)

Deliverables

- Thermophysical data on a confined fluid in a porous matrix (12/31/2010)
- Thermophysical data on H_2O+CO_2 binary fluids between 150 and 250^oC (09/30/2011)

Task 2: Milestones

- Characterize mineralogy and chemistry of representative geothermal rocks (09/30/2010)
- Determine pore features of geothermal rocks using neutron scattering (12/31/2010)
- Determine CO_2 fluid behavior in representative rock matrix at reservoir conditions (09/30/2011)

Deliverables

- Pore structure and pore distribution in representative geothermal rocks (12/31/2010)
- Sorption properties and densities of sorbed working fluid in a geothermal rock (09/30/2011)

Task 3: Milestones

- Characterize representative geothermal rocks with X-ray micro-CT tomography (09/30/2010)
- Design and construct high-pressure, high-temperature cell for neutron tomography (12/31/2010)
- Complete neutron imaging of a working fluid in a representative rock matirx (09/30/2011)

Deliverables

- A high-pressure, high-temperature cell for in situ imaging of rock-fluid interaction (12/31/2010)
- Neutron tomographic images of a working fluid in a geothermal rock (09/30/2011)

Summary

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

- Program management team in place; reporting protocols established
- Project nearly on target with respect to spending (within ~10%)
- All three tasks moving forward on schedule to meet milestones and deliverables
- Accomplishment Highlights:

  - Initial thermophysical tests made on fluid in porous matrix

  - Upgrades to flow VTD well underway and on schedule

  - Mineralogy and petrochemisty of geothermal rocks nears completion

  - SANS/USANS/BSE results obtained on rocks from four areas; detailed analysis in progress

  - Preliminary characterizations yield pore size distribution, pore number, specific surface areas, fractal dimensions

  - X-ray micro-CT tomography images obtained on all rock samples; image analysis underway

  - Testing of neutron tomography beam line and sample holder initiated