Assessing ultramicropores of shales by CO$_2$ adsorption at 273K

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Acknowledgements: This material is based upon work supported by the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) under Grant Number DEFE0023223. This project is managed and administered by the Colorado School of Mines OCLASSH and funded by DOE/NELT and cost-sharing partners. We acknowledge Fluids & OCLASSH consortium for support.
Motivation

• Storage mechanisms in unconventional:
  – Adsorption can account for 80% of estimated GIP in shales (Ambrose et al. 2012)
  – Observed storage capacity in standard clays in reservoir condition increases with BET specific surface area (SSA) (Busch et al. 2008)
Motivation

• Seismic & electrical properties are affected by fluid saturation
  – Shales have large surface area
  – Increased rock – fluid interactions

• Problems: (Saidian et al. 2016)
  – CEC sensitive to clay content & type
  – N2 – SSA is not as sensitive

(Saidian et al. 2016)
Objectives

• Perform CO$_2$ adsorption at 273 K to characterize nanopores of shales
  – Study ultramicropores of shales (0.2 -1.4 nm)
  – Compare or compliment N$_2$ at 77 K results (.7 nm - 50nm)
  – Kinetic diameter of CO$_2$ is smaller than N$_2$
Adsorption mechanism

Video modified from Quantachrome
IUPAC Definitions

• Ultramicropores
  – Pore diameter ≤1 nm

• Micropores
  – Pore diameter ≤2 nm

• Mesopores
  – Pore diameter 2-50 nm

• Macropores
  – Pore diameter ≥50 nm

* IUPAC (Thommes et al. 2014)

TEM resolution : 0.2 nm
   (Curtis, 1989)

CO₂ : < 1.4 nm
   IUPAC (Thommes et al. 2014)

SEM resolution : 2 nm
   (Shao et al. 2017)

N₂ range : 0.7 – 50 nm
   IUPAC (Thommes et al. 2014)

NMR : > 2 nm
   (Klobes & Meyer 2014)

MICP: > 3 nm (400 MPa)
   (Rouquerol et al. 2014)
Adsorption mechanism

Adsorbed amount at **constant temperature** and **volume** is a function of

**Pressure**, **pore structures (geometry, size)** & **materials**

*(composition, gas used)*

(IUPAC 2015)
Inversion methods

• **Macroscopic** thermodynamics based method
  – **BJH**, t-plot, BET
  – Most widely used

• **Microscopic** thermodynamics/ statistical mechanics based methods
  – Most recent development due to advances in computational methods
  – **DFT**, molecular simulation
  – recommended for nano-scale phenomena
Materials

- SWy-2*: Na-rich montmorillonite
- ISCz-1*: Illite smectite
- IMt-1*: Illite
- Utica 2.7% TOC, 53.3% clay, Carbonate 12%, QFPP 32%
- Niobrara 3% TOC, 35% clay, Carbonate 32%, QFPP 30%

* from The Clay Mineral Society
Isotherms of SWy-2

**N₂ at 77 K**

**CO₂ at 273 K**
Isotherms of SWy-2

**N$_2$ at 77 K**

$P_{\text{max}} = 1 \text{ atm}$  
$P_0 = 1 \text{ atm}$

**CO$_2$ at 273 K**

$P_{\text{max}} = 1 \text{ atm}$  
$P_0 = 2600 \text{ atm}$
PSD of SWy-2 Nitrogen

Left graph:
- ΔV/Δr [cc/g/Å]
- Halfpore width, r [Å]
- Log-log scale

Right graph:
- Cumulative surface [m²/g]
- Halfpore width, r [Å]
- Log-log scale

The graphs show the pore size distribution and cumulative surface area for SWy-2 Nitrogen, with the pore size plotted on a log scale and the corresponding volume or surface area plotted on another log scale.
PSD of SWy-2 N₂ CO₂
PSD of Niobrara

- CO₂ adsorption at 273 K
- N₂ adsorption at 77 K

Graphs showing the cumulative surface area and half-pore width distributions.
Summary

The diagram illustrates the surface area (m²/g) for five samples: SWy-2, ISCz-1, IMt-1, Nio, and U. The surface area is broken down into three components:

1. **μN₂**: Micropores from Nitrogen
2. **μCO₂**: Micropores from CO₂
3. **mesoN₂**: Mesopores from Nitrogen

Each sample shows a different distribution of these components, indicating the varied microporous nature of these materials. The legend at the bottom of the diagram labels the colors used for each component.
Summary

Fraction from total surface area (%)

Mineralogy by weight (%)

Nio U

m Hurt (\%)

U Hurt (\%)

\( \mu_{\text{N}_2} \)

\( \text{micropore from Nitrogen} \)

\( \mu_{\text{CO}_2} \)

\( \text{additional micropores from CO}_2 \)

\( \mu_{\text{N}_2} \)

\( \text{mesopores from Nitrogen} \)

\( \text{Carb.} \)

\( \text{clay} \)

\( \text{TOC} \)

\( \text{QFPP} \)

\( \text{carbonate} \)

\( \text{TOC} \)

\( \text{clay} \)

\( \text{QFPP} \)

\( \text{meso} \)

\( \text{meso} \)

\( \text{Add.} \)

\( \text{Add.} \)

\( \mu_{\text{CO}_2} \)

\( \mu_{\text{CO}_2} \)

\( \text{Add.} \)

\( \text{Add.} \)

\( \text{micropore from Nitrogen} \)

\( \text{additional micropores from CO}_2 \)

\( \text{mesopores from Nitrogen} \)

\( \text{Carb.} \)

\( \text{clay} \)

\( \text{TOC} \)

\( \text{QFPP} \)

\( \text{carbonate} \)

\( \text{TOC} \)

\( \text{clay} \)

\( \text{QFPP} \)
Learnings

• Would’ve missed large surface area if one only measure $N_2$ adsorption
• Mineralogy controls pore size distribution
• Clay types may contribute to different pore size distribution
Future works

• Further investigation of micropore region
  – Low temperature, pressure CO$_2$ adsorption
    • Samples with varying TOC and clay content

• Mineralogy – PSD relationship
  – Fluid coverage?
Thank you!

Questions?