Characterization of Gas Shale Pore Systems by Analyzing Low Pressure Nitrogen Adsorption

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September 2012
Objective

- Quantitative analysis of the gas shale pore systems in Perth and Canning basins.
- Determining the shale samples with the higher potential for methane sorption.

Limitation:

- High heterogeneity of the potential gas shale layers
- Small sample size

“Our results only will show nature and variability in pore structure”
Gas Adsorption

- Can measure only open pores
- Pore size > 1 nm
- Can determine PSD
- Micro & Mesopores

Used Techniques for Porosity Analysis

- Mercury Porosimetry
- Helium Porosimetry
Used Techniques for Porosity Analysis

- Similar to gas adsorption
- Can measure only open pores
- Pore size > 3 nm
- Can determine PSD
- Meso & Macropores
Used Techniques for Porosity Analysis

- Gas Adsorption
  - Can measure only open pores
  - Easy & Established technique

Mercury Porosimetry

Helium Porosimetry
Theory: Porosity Measurement

Specific Surface Area = \( \frac{\text{Total Surface Area, } m^2}{\text{Mass of the sample, gr}} \times \frac{m^2}{\text{gr}} \)

Porosity = \( \frac{\text{Pore Volume}}{\text{Bulk Volume}} \times 100 \)

or

Specific Pore Volume = \( \frac{\text{Total Pore Volume, } cm^3}{\text{Mass of the sample, gr}} \times \frac{cm^3}{\text{gr}} \)
Theory: Size of Pores (IUPAC Standard)

- **Micropores**: 2 nm
- **Mesopores**: 50 nm
- **Macropores**:
Theory: Adsorption Process

1. Diffusion to adsorbent surface
2. Migration into pores of adsorbent
3. Monolayer builds up of adsorbate
Theory: Isotherm

- Isotherm is a measure of the volume of gas adsorbed at a constant temperature as a function of gas pressure.
Theory: Hysteresis

- Hysteresis: Dependence of a system to its history.
- Hysteresis gives information regarding pore shapes.
Theory: Hysteresis

- **Type A**: Cylindrical
- **Type B**: Slits
- **Type C**: Funnel shaped
- **Type D**: Bottle neck

![Graphs showing hysteresis for different types](image)
Steps for Measurement

1. Sample Preparation
   - Crushing shale samples
   - Sieve analysis
     - Proper samples: less than 250 µm
   - Heating shale samples for 8 hours at 110°C under vacuum condition

2. Adsorption Analysis

3. Interpretation
Interpretation

<table>
<thead>
<tr>
<th>Points</th>
<th>$P/P_0$</th>
<th>Volume adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Weight of sample

Results

- Pore shape
- Pore size & distribution
- Specific surface area
- Pore volume
# Results

## Perth Samples

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>He Porosity (%pu)</th>
<th>TOC Content (wt%)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (°C)</th>
<th>BET Surface Area (m&lt;sup&gt;2&lt;/sup&gt;/gr)</th>
<th>Total Pore Vol. (cm&lt;sup&gt;3&lt;/sup&gt;/100gr) at maximum pressure</th>
<th>Micropore Vol. (cm&lt;sup&gt;3&lt;/sup&gt;/100gr)</th>
<th>Mesopore Vol. (cm&lt;sup&gt;3&lt;/sup&gt;/100gr)</th>
<th>Macropore Vol. (cm&lt;sup&gt;3&lt;/sup&gt;/100gr)</th>
<th>Adsorption Average pore width (4V/A)(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS2-S1</td>
<td>2.783</td>
<td>3.03</td>
<td>459</td>
<td>5.4255</td>
<td>1.538</td>
<td>0.0590</td>
<td>0.9435</td>
<td>0.0985</td>
<td>11.3238</td>
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<tr>
<td>AS2-S2</td>
<td>2.894</td>
<td>1.36</td>
<td>466</td>
<td>2.3393</td>
<td>0.994</td>
<td>0.0090</td>
<td>0.7154</td>
<td>0.1218</td>
<td>16.9967</td>
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<tr>
<td>AS2-S4</td>
<td>4.150</td>
<td>---</td>
<td>---</td>
<td>7.5669</td>
<td>1.669</td>
<td>0.0085</td>
<td>0.186</td>
<td>0.0222</td>
<td>8.8242</td>
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<tr>
<td>AS2-S6</td>
<td>2.920</td>
<td>---</td>
<td>---</td>
<td>4.2824</td>
<td>1.193</td>
<td>0.0011</td>
<td>0.788</td>
<td>0.0458</td>
<td>11.1421</td>
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<tr>
<td>RB2-S1</td>
<td>3.075</td>
<td>2.99</td>
<td>484</td>
<td>5.2341</td>
<td>1.137</td>
<td>0.0514</td>
<td>0.4805</td>
<td>0.0206</td>
<td>8.3896</td>
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<td>RB2-S2</td>
<td>---</td>
<td>2.545</td>
<td>481.5</td>
<td>9.7799</td>
<td>1.574</td>
<td>0.0905</td>
<td>0.5105</td>
<td>0.0147</td>
<td>6.3023</td>
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<tr>
<td>RB2-S3</td>
<td>2.55</td>
<td>1.43</td>
<td>509</td>
<td>12.0305</td>
<td>1.8796</td>
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<tr>
<td>RB2-S4</td>
<td>1.45</td>
<td>2.415</td>
<td>507.5</td>
<td>7.9625</td>
<td>1.3136</td>
<td>0.1727</td>
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<tr>
<td>RB2-S5</td>
<td>3.65</td>
<td>2.46</td>
<td>507</td>
<td>5.752</td>
<td>1.0914</td>
<td>0.1078</td>
<td>0.4638</td>
<td>0.0284</td>
<td>7.59</td>
</tr>
</tbody>
</table>

## Canning Samples

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>He Porosity (%pu)</th>
<th>BET Surface Area (m&lt;sup&gt;2&lt;/sup&gt;/gr)</th>
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<th>Micropore Vol. (cm&lt;sup&gt;3&lt;/sup&gt;/100gr)</th>
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<th>Adsorption Average pore width (4V/A)(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW1</td>
<td>4.497</td>
<td>16.0617</td>
<td>2.990</td>
<td>0.0809</td>
<td>1.4536</td>
<td>0.0389</td>
<td>7.1974</td>
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<tr>
<td>ML1</td>
<td>5.033</td>
<td>11.6597</td>
<td>3.127</td>
<td>0.0330</td>
<td>2.1866</td>
<td>0.2031</td>
<td>10.7288</td>
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<tr>
<td>PE1</td>
<td>1.102</td>
<td>16.3690</td>
<td>1.959</td>
<td>0.3834</td>
<td>0.7623</td>
<td>0.0107</td>
<td>4.7888</td>
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<tr>
<td>S1-DD1</td>
<td>0.745</td>
<td>13.7106</td>
<td>1.193</td>
<td>0.1462</td>
<td>0.9654</td>
<td>0.0056</td>
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<td>S2-DD1</td>
<td>5.374</td>
<td>5.7666</td>
<td>1.3632</td>
<td>0.0180</td>
<td>0.7613</td>
<td>0.0449</td>
<td>9.4561</td>
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<tr>
<td>WL1</td>
<td>3.598</td>
<td>15.3800</td>
<td>2.2603</td>
<td>0.3159</td>
<td>0.9517</td>
<td>0.0492</td>
<td>5.8786</td>
</tr>
</tbody>
</table>
Results

Perth Samples

AS2-S1

AS2-S2

AS2-S4

AS2-S6

RB2-S1

RB2-S2

RB2-S3

RB2-S4

RB2-S5

Type B

P/P₀

Slits
Canning Samples

GW1

ML1

PE1

S1-DD1

S2-DD1

WL1

Type B

$\frac{\rho}{\rho_0}$

Slits
Pore Size Distribution (PSD)

Perth samples

AS2:
Avg. SA ≈ 5 m²/gr

RB2:
Avg. SA ≈ 8.2 m²/gr
Pore Size Distribution (PSD)

Canning samples-Goldwyer Formation

Goldwyer Formation: Avg. SA ≈ 13.16 m²/gr
Pore Size Distribution (PSD)-MICP vs. Gas Adsorption

AS2-S1

AS2-S4

RB2-S1

RB2-S2

Micropore
Mesopore
Macropore

Incremental PV(%)pu

Pore width(nm)

Incremental PV(%)pu

Pore width(nm)

Incremental PV(%)pu

Pore width(nm)

Incremental PV(%)pu

Pore width(nm)
Pore Size Distribution (PSD)-MICP vs. Gas Adsorption

1. Different sample preparation
2. Compressibility of grains at high mercury intrusion pressure
Conclusions

Pore Size vs. Pore Volume:

1. All samples show an increase in Micropore vol. and decrease in Macropore vol. with decreasing pore diameter.
Conclusions

**Pore Size vs. Surface Area:**

- Avg. Pore Diameter
- Micropore Vol.
- Macropore Vol.
- Surface Area

2. Micropore Vol. has an important role on adsorbed gas storage.
Conclusions

**GA results vs. He porosity:**

3. Micropore vol. has not any positive effect on free gas storage.
Conclusions

Perth Samples

4. TOC content is not a controlling factor for high SA.

5. Perth samples with higher thermal maturity has a higher potential for gas adsorption.
High Pressure Volumetric Adsorption Measurement
Thank you for Your Attention