Effects of long-term CO$_2$ storage in coal on the physical and chemical properties of coal

Tshifhiwa Maphala and Nicola Wagner
Contents

- South African context – emissions + reduction strategy
- Atlas on geological storage of carbon dioxide in south Africa - highlights
- Storage in coals: Effects of carbon dioxide storage in coal on the coal structure and properties
“Dark continent”
South Africa’s energy mix - Coal is still King

- Approximately 90% of primary energy is derived from fossil fuels [coal, oil and gas] - (Cloete, 2010)
- Coal contributes about 65.9% total energy supply - (Cloete, 2010)
- 500(Mt/a) CO₂ emissions
- Ranked 13th in the world-total GHG emissions
- A higher emissions intensity (emissions/GDP) than China, India and Brazil
Two Scenarios:
Growth without Constraints and Required by Science

Gap: difference between where emissions might go (GWC – RBS, emissions in 2050) and where they need to go.

Gap is 1300 Mt CO2-eq in 2050. More than three times 2003 annual emissions.
South Africa’s GHG emission reductions strategy – peak, plateau and decline

[Graph showing emissions trend and constraints]

Mt CO₂-equiv

- 1800
- 1600
- 1400
- 1200
- 1000
- 800
- 600
- 400
- 200
- 0


Growth without Constraints
Required by Science

a
b

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SA’s GHG emission reduction strategy

- Carbon Capture and Storage (CCS) is key to SA’s greenhouse gases reduction strategy.

- Provides a bridge between current trend and future carbon-free renewables future.
Storage ready emissions

- 2010 total stationary point emissions 500(Mt/a)
- About 8% of direct emissions are sequestration ready
  - *Does not necessarily require capturing*

<table>
<thead>
<tr>
<th>Type of emissions</th>
<th>CO₂ emitted(Mt/a)</th>
<th>CO₂ concentration(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sequestration ready</td>
<td>35</td>
<td>90-98</td>
</tr>
<tr>
<td>Requires capturing</td>
<td>465</td>
<td>10 – 15</td>
</tr>
</tbody>
</table>
CCS roadmap for South Africa

- CCS Potential 2004 - Completed
- Carbon Atlas 2010 - completed
- Test injection 2016 - 10s thousands tonnes
- Demo plant 2020 - 100s thousands tonnes
- Commercial 2025 - millions tonnes
Contents

- South Africa's Greenhouse gases emissions and mitigation strategies
- Atlas on geological storage of carbon dioxide in South Africa - highlights
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SA potential storage capacity

ATLAS

on

geological storage of carbon dioxide in South Africa
# South Africa Storage Capacity

Source: South Africa Carbon Storage Atlas, 2010

<table>
<thead>
<tr>
<th>Geological Formation</th>
<th>Basin</th>
<th>Storage Capacity (GtCO₂)</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saline</td>
<td>Outeniqua basin</td>
<td>48</td>
<td>Offshore</td>
</tr>
<tr>
<td>Saline</td>
<td>Orange basin</td>
<td>56</td>
<td>Offshore</td>
</tr>
<tr>
<td>Saline</td>
<td>Durban/Zululand</td>
<td>42</td>
<td>Offshore</td>
</tr>
<tr>
<td>Saline</td>
<td>Zululand</td>
<td>0.46</td>
<td>Onshore</td>
</tr>
<tr>
<td>Saline</td>
<td>Algoa</td>
<td>0.40</td>
<td>Onshore</td>
</tr>
<tr>
<td>Coalfield</td>
<td>Different</td>
<td>1.2</td>
<td>Onshore</td>
</tr>
</tbody>
</table>
SA’s coal seam storage capacity

Good source-sink match
Summary

- South Africa is one the world’s major global emitters of CO₂
- CCS to play an important role in emissions reduction
- CTL plants produce a highly concentrated CO₂ stream
- Onshore storage is very important
- Onshore storage capacity-coalfields have the highest capacity
Contents

- South Africa's Greenhouse gases emissions and Mitigation strategies
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Carbon Dioxide storage in coal seams (1)

Diagram showing carbon dioxide storage in coal seams.
**CO$_2$ storage in coal seams (2)**

- Few concerns with CO$_2$ storage in coal seams:
  - Stability of the sequestrated CO$_2$
  - Sterilisation of the coal seams
  - Swelling of coal on CO$_2$ injection
  - Definition on “unminable”

- Lack of understanding of CO$_2$-coal interactions

- CO$_2$-coal interactions are very complex and are not easily predictable or modeled

- Understanding CO$_2$-coal interactions important for long term CO$_2$ migration simulations in coal seams (monitoring?)
### Storage mechanisms and coal structure and properties

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Weak interactions (van der Waals and/or dispersion forces) with sorbent surface molecules</td>
<td>- Very strong interactions with sorbent (chemical reactions?)</td>
</tr>
<tr>
<td>- Reversible desorption</td>
<td>- Irreversible desorption</td>
</tr>
<tr>
<td>- No coal structural changes</td>
<td>- Induces coal structural changes (plasticization, swelling properties)</td>
</tr>
</tbody>
</table>

- Adsorption
  - Weak interactions (van der Waals and/or dispersion forces) with sorbent surface molecules
  - Reversible desorption
  - No coal structural changes

- Absorption
  - Very strong interactions with sorbent (chemical reactions?)
  - Irreversible desorption
  - Induces coal structural changes (plasticization, swelling properties)
Aim:

To study, fundamentally, the **physical and chemical properties changes** of coal upon **long term** CO₂ storage under **subcritical conditions** and **supercritical conditions**

- Results obtained under subcritical conditions are presented in this presentation (below 72.9bar and 31.1°C)
Sampling and sample preparation

- Waterberg coalfield
  - Vitrinite rich and inertinite rich samples

- Density separated
  - Little or no effect on physical and chemical properties

- Particle size
  - -150μm

- Air dried

- Some samples were demineralised for structural analysis purposes
Methodology

Pre-adsorption coal structure characterisation:
- Petrographic analyses
- BET
- He pycnometry
- FTIR
- XRD
- 13C NMR
- High pressure CO2 adsorption isotherms measurements (sorption behaviour)

Adsorption Experiment:
- Long-term CO2 adsorption (up to 6 months)
  - 15, 30, 45 bar
  - 14 days
  - 42 bar
  - 6 months

Post-adsorption coal structure characterisation:
- Petrographic analyses
- BET
- He pycnometer
- FTIR
- XRD
- High pressure CO2 adsorption isotherms measurements (sorption behaviour)

Field samples study:
- Raw sample analysis
- post-storage sample analysis
- Compare with laboratory results
Results

NON DEMINERALISED
## Selected results - Sample properties

<table>
<thead>
<tr>
<th></th>
<th>Coal A</th>
<th>Coal B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vitrinite (mmf)</strong></td>
<td>91.8</td>
<td>11.2</td>
</tr>
<tr>
<td><strong>Inertinite (mmf)</strong></td>
<td>4.4</td>
<td>80.2</td>
</tr>
<tr>
<td><strong>Moisture (adb)</strong></td>
<td>3.8</td>
<td>3.0</td>
</tr>
<tr>
<td><strong>Ash (adb)</strong></td>
<td>4.9</td>
<td>10.4</td>
</tr>
<tr>
<td><strong>Carbon Content (adb)</strong></td>
<td>55.7</td>
<td>63.2</td>
</tr>
</tbody>
</table>
Selected results: Pre-sorption properties

- Coal A - Vitrinite rich
- Coal B - Inertinite rich

- Micropore Volume (cm³ g⁻¹)
- Specific BET Surface (m² g⁻¹)
Low pressure sorption behaviour

AdSORBED VOLUME (cm³ g⁻¹) vs. RELATIVE PRESSURE P/P₀

- Coal A (green line)
- Coal B (red line)
Selected results: XRD-Vitrinite coal(A)
Selected results: XRD-Inertinite coal (B)
Physical changes - Surface area

![Bar chart showing BET (m²/g) for Vitrinite rich and Inertinite rich samples after untreated and CO₂ 42bar 6mon treatments.](chart.png)
Physical structure changes-pore size distribution

- Vitri_untreat_nondemin
- Vitri_nondemin_CO2_42bar_6mon
Physical structure changes-pore size distribution

Pore Width (Å)

dV/dw (cm³/g·Å)

- Inert_untreated_nondemin
- Inertinite_CO2_6mon_42bar_Nondemin
Sorption behaviour– High Pressure Volumetric Adsorption System
High pressure sorption behaviour (Langmuir)

Quantity adsorbed (kgCO₂/tonCoal) vs Relative pressure $P/P₀$.

Inert_untreat_nondemin
Vitri_untreat_nondemin
Sorption behaviour: Vitrinite rich coal (A)

![Graph showing sorption behaviour with quantity adsorbed (kg CO2/ton coal) on the y-axis and relative pressure (P/P₀) on the x-axis. Two lines are plotted: one for Vitri_untreat_nondemin and another for Vitri_CO2_6mons.](image)
Sorption behaviour: Coal B – Inertinite rich

![Graph showing the sorption behaviour of Coal B with Inertinite rich. The x-axis represents the Relative Pressure P/P₀, and the y-axis represents the Quantity adsorbed (kg CO₂/ton Coal). The graph compares two conditions: Inert_untreat_nondemin and Inert_CO2_6mons.](image-url)
Results

DEMINERALISED
Structural changes - XRD

Inert_untreated
Inert-CO2_6 months_42bar
Inert_CO2_14days_45bar
Summary and future work

Summary

Different maceral rich coals show different behaviour on \( \text{CO}_2 \) sorption

Vitrinite rich coals show more pronounced structural changes than inertinit

Future work

Comparisons with field samples

Chemical structural changes

Blank runs-inert atmosphere
Acknowledgements

- Dr Nicola Wagner (Wits University)
- Dr Dirk Prinz (RWTH Aachen University, Germany)
- Gregory Okolo (North West University, Potchefstroom Campus)
- Chemvak (Pretoria) – High Pressure VAS
- JAD systems (Johanneburg) – NI and Labview
- Coal and Carbon Research Group (Wits University)