UTILISING RED MUD AS AN OXYGEN CARRIER AND CATALYST FOR CHEMICAL LOOPING GASIFICATION TO PRODUCE HYDROGEN-RICH SYNGAS

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Clean Coal and CCS

- About 30 researchers
- 7 active projects sponsored by DOE and industrial consortia
- 10-18 peer reviewed publications, annually
- 5-10 proposal submitted, annually
CLC Principle

- In-situ oxygen separation instead of stand alone air separation units
- Generate high purity CO\textsubscript{2} stream at the fuel reactor exhaust

**Slow Gasification**

**Catalyst-Oxygen Carrier**

- Oxygen & heat carrier (Reactivity, oxygen transport) capacity
- Production cost
- Stability, agglomeration, sintering, attrition
Why Red Mud – The Properties

Physical Characteristics

Particle size: **80% particles <10μm**
Concentration: **50-65%**
pH: 12-13.5 (need neutralization)

Chemical Composition (Dry)

- **Fe₂O₃**: 30%-60%
- **Al₂O₃**: 10%-20%
- **SiO₂**: 3%-50%
- **TiO₂**: 2%-25%
- **Na₂O**: 2%-10%
- **CaO**: 2%-8%

Active composition
Support
Bonding

Direct Granulation (spray dry method)
Calcination
Cost-effective OC

No mechanical grinding & slurry preparation needed
No additive needed
The Effectiveness of Red Mud

**Graphs and Figures:***

- **Graph 1:** Comparison of reduction rate (%/min) over cycle number for different oxygen carriers.
  - Reference OC (FeO/AlO = 50/50)
  - RM OC (calcinated at 1100°C)

- **Graph 2:** RCOC conversion over time for different oxygen carriers.
  - Fe-Al OC
  - Fe-Al-Ce OC
  - Red mud OC
  - Ilmenite OC

- **Graph 3:** Test conditions for EKY Char Gasification with Sand:
  1. Mass of OCs or sand: 300 g
  2. Temperature: 950°C
  3. Mass of EKY coal char: 2 g
  4. Steam concentration in reduction: 50 vol%

- **Graph 4:** Conditions for CLC with Char (Steam Gasification Agent - 50 vol%):
  1. Bed material: Red Mud OC or Sand (215 g)
  2. Solid fuel: 2 g PRB char
  3. Temperature: 950°C

- **Graph 5:** Instantaneous rate of conversion (g/g/s) for different processes:
  - Char Combustion
  - Char Pyrolysis
  - Steam Gasification of Char (50 vol% water vapor)
  - CLC with Char (Steam Gasification Agent - 50 vol%)
  - Solid (Char) - Solid (OC) Contact Reaction (N2 Fluidizing Gas)
  - Red Mud OC Reduction by 20 vol% CO

- **Tables:**
  - Reduction Rate (%/min) over cycle number for different oxygen carriers.
  - EKY Char Gasification with Sand results.

- **Images:**
  - SEM images of red mud at different scales (5μm and 1μm).
RM Cyclic Performance

**Gas concentration**

Conditions:
1. Bed material: SRM 100g
2. Solid fuel: 2.4 g WKY700
3. Temperature: 950 °C
4. Fluidizing agent: 50 vol% Water Vapor

**Carbon conversion**

Conditions:
1. Bed material: SRM 100g
2. Solid fuel: 2.4 WKY(700)
3. Temperature: 950 °C
4. Fluidizing agent: 50 vol% Water Vapor

- Porous structure well maintained after 20 cycles
- No agglomeration detected

**Fresh**

**Post run**

**PSD**
Catalytic Function for In-situ WGS

Gas residence time: 6s (973 K)
Inlet gas: 10% CO + 30% Steam

\[
\log J_{eq} = -2.4198 + 0.0003855T + \frac{2180.6}{T}
\]
Trial Run

Raw Material -> Fire in Kiln -> Clinker -> Crush Sieve -> OC Product
Calcine Temp. in Rotary Kiln

<table>
<thead>
<tr>
<th>Temperature</th>
<th>1200°C</th>
<th>1250°C</th>
<th>1300°C</th>
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</thead>
<tbody>
<tr>
<td>Strength (N)</td>
<td>1.60</td>
<td>2.76</td>
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<tr>
<td>Bulk Density (kg/m³)</td>
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<td>1493.4</td>
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<td>pH</td>
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Crystal Phase Formation

<table>
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</tr>
<tr>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td></td>
<td>Fe₃(Al₀.₂Fe₁.₈)(SiO₄)₃</td>
</tr>
<tr>
<td></td>
<td>Fe₃Al₂(SiO₄)₃</td>
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</tbody>
</table>

**Almandine**

- Very hard
- Dark red
- Melting point: 1250°C

Reactivity with CO and Char

950°C, 20% CO

OC 50 g
EKY Char 0.2 g
950°C, 50 vol.% WV

OC Conversion

Char Conversion

Time (min)
# Grindability Comparison

**OPC**

<table>
<thead>
<tr>
<th>Grind Time (min)</th>
<th>&lt;125 um (g)</th>
<th>125-500 um (g)</th>
<th>&gt;500 um (g)</th>
<th>Total Before Sieve (g)</th>
<th>Total After Sieve (g)</th>
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**RM**

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<th>Total Before Sieve (g)</th>
<th>Total After Sieve (g)</th>
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# Fuel Flexibility

## Proximate Analysis

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<th>FC</th>
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<td>PRB</td>
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<td>EKY</td>
<td>15.92</td>
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<td>4.33</td>
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## Ultimate Analysis

<table>
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<tr>
<th>Coal Char</th>
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<th>H</th>
<th>O</th>
<th>N</th>
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<tbody>
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<td>1.38</td>
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</table>

- Red mud demonstrated stable performance on different types of coal chars
- Gasification rate: PRB > WKY > EKY
Conclusions

- Red mud is proven to be an effective oxygen carrier and catalyst for the CLG process. Stable reactivity is observed within 20 cycles. It also shows a good fuel selectivity.
- Gasification rate of char can be enhanced approximately by 1.5-3 times in the bed of red mud.
- Fabrication of red mud oxygen carriers via rotary kiln proves an effective and cost-efficient method.
- RM produced by rotary kiln displays a similar reactivity to RM synthesized by traditional freezing granulation method.
- The cost of RM produced by rotary kiln is estimated to be approximately $113/ton.
Acknowledgements

- **DOE/NETL**
  - Steven Markovich

- **CMRG**
  - Duke Energy
  - LG&E and KU Energy
  - EPRI

- **CAER**
  - Jacob Blake
  - Zhen Fan
  - Liang Kong
  - Heather Nikolic
  - Lisa Richburg
  - Steve Summers
  - Amanda Warriner
  - Jimin Zeng