Small Business Innovation Research (SBIR/STTR)
Phase II
Department of Energy

Methodology for Attrition Evaluation of Oxygen Carriers in Chemical Looping Systems
(DE-SC0011984)

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This project addresses two critical elements of chemical looping combustion: oxygen carrier (OC) attrition propensity and reactivity

- Loss due to attrition of the OC → minimized to make technology cost-effective
- OC selected - reactive to reduced species (CO, H\textsubscript{2} and HC’s)
- Other objectives: identification of reaction mechanisms, material morphology changes

Approach

- Modification of ASTM D5757 for determining attrition characteristics of powdered catalysts to include high temperature and reacting (cyclic oxidation/reduction) conditions
Attrition in CLC systems

- Several regions of high attrition
  - Jet/bubbling/freeboard regions (1a,b,c)
  - Riser (2)
  - Cyclone (3)
  - Standpipe (4)

Main regions of concern\(^1, 2, 3\)

- Cyclone
- Jet

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PROJECT GOALS

➢ Phase II

1. Attrition performance investigation - several oxygen carriers

2. Determine attrition performance as function of temperature, jet velocity, cyclone inlet velocity, gas composition, test duration

3. Gather reactivity metrics/attrition data

4. Develop new equipment/methodology for evaluation of attrition through cyclonic/impaction mechanisms

5. Develop knowledge database; formulate strategies for commercial test service offering
Jet attrition

- “High velocity jets” in reducer/oxidizer (30-50 m/s)
- Source of attrition
  - \textit{Attrition: oxidizer > reducer} due to re-oxidation requirement
  - Unit should account for temperature/reactions on attrition
  - \textit{Higher jet velocity in test unit} (100-500 m/s); speed up attrition process
Cyclonic attrition

- Cyclone necessary for material transport
- Source of attrition
- Cyclone separating devices accelerate particles to wall
- Particles impact/shear against walls
- Test unit built to mimic impact and shear forces
OXYGEN CARRIER EVALUATION UNIT

Hot Flow Test Unit

- Filters
- Settling Chamber
- Reactor
- Reactor Heater
- Laser Gas Analyzer

Mass Flow Controllers
Electrical Controls
**UNIQUE REACTOR ATTRIBUTES**

- **Reactor interchangeable**
  - Fast removal/installation of jet/cyclone unit
  - Cyclone unit: custom *draft tube guides particles to wall*
  - Jet attrition unit: custom distributor plate (not shown)
Jet and cyclonic attrition testing reactors

- **Cyclic oxidation/reduction** 25-40 cycles at 800 – 970 °C
- Typical cycle: 8 min redox reactions, 2 min purge between redox
- Reduction gases: CO (*and or* H₂), H₂O and N₂
- Oxidizing gases: O₂ diluted by N₂
- Sample size \( \geq 30 \text{ g} \text{ jet attrition}; \geq 70 \text{ g} \text{ cyclonic attrition} \)
- *Jet velocity* 280 ~ 500 m/s at temperature
- *Cyclone inlet velocity* 5-20 m/s at temperature
Jet and cyclonic attrition data gathering/analysis

- **Attrition rate** vs time (and # of cycles)
- Attrition rate – expressed in **% of initial mass charged per hour**
- Exit gas concentration (online laser gas analyzer)
- **Reactivity** – each redox cycle (CO/H₂)
- Reactivity – expressed as **% conversion for each given cycle**
- **Particle size distribution** pre and post test

![Graph of attrition rate vs time](image1)

![Graph of gas concentration](image2)

![Graph of particle size distribution](image3)

**Sample 1.8, 970°C**  **Sample 1.9, 820°C**  **Sample 1.10, 895°C**
Key outcomes

- Predictive jet attrition model proposed
- Attrition rate predictions strongly affected by jet velocity
- Identified new applications for test unit

Attrition not captured by ASTM D5757
RESULTS - JET ATTRITION

- Reactivity (SEM cross-sectional analyses: Post-run ilmenite samples)
  - Material structure less defined at 10% vs 30% fuels cases
  - *Outer FeₙOᵧ-layer* more pronounced at 30% fuel conc.
  - *Enhanced availability of FeₙOᵧ* in outside layer → higher fuel conversion
  - *Reduced attrition* at higher fuel concentrations (agglomeration)
  - *O₂ carrying capacity* = 3.0% for 30% fuels vs 1.6% for 10% fuels (via TGA)
  - Tests indicated *importance* of fuel composition on attrition of OC
Rate of attrition expression

- Proposed attrition model $A_j \propto \left(\frac{E_k g}{m_b}\right)^n$
- Defining $k_j =$ jet attrition constant, we obtain an equality

![Graph depicting the relationship between attrition rate and kinetic energy of moving fluid per mass of bed material, with equations for different materials: Manganese ore, Calcium manganite, Ilmenite (Coarse), Ilmenite (Fine), Red Mud. The equations for each trend line are given, along with their respective R² values.](image)
## Rate of attrition expression

- Model results compared to 10 kW\textsubscript{th} unit (Berguerand & Lyngfelt (2008b))
- Attrition rate (model): 2.0E-02 - 3.4E-02 wt-%/hr
- Attrition rate (experimental): 2.02E-02 wt-%/hr
- Differences - Attributable to wide operating ranges used in experiments

<table>
<thead>
<tr>
<th>10 kW\textsubscript{th} unit</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen carrier</td>
<td>NiO/NiAl\textsubscript{2}O\textsubscript{4}</td>
</tr>
<tr>
<td>OC density (kg/m\textsuperscript{3})</td>
<td>3250-3800 (material)</td>
</tr>
<tr>
<td>Particle size distribution (µm)</td>
<td>90-212</td>
</tr>
<tr>
<td>Air reactor flow rate (NLPM)</td>
<td>-</td>
</tr>
<tr>
<td>Material inventory (kg)</td>
<td>15-16 (5.9 in air reactor)</td>
</tr>
<tr>
<td>Solids circulation rate (kg/min)</td>
<td>2-4</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1000</td>
</tr>
<tr>
<td>Loss of fines, particles &lt; 45 µm(wt-%)/hr</td>
<td>0.003</td>
</tr>
<tr>
<td>Inlet nozzle velocity (m/s)</td>
<td>100</td>
</tr>
</tbody>
</table>

Cyclonic attrition: Cold flow

- Tests conducted at ambient conditions
- Graph and filters show effects of increasing draft tube velocity
- Attrition at cold flow – Coarser ilmenite (177-250 µm) more sensitive to draft tube velocity than finer ilmenite (74-105 µm)
RESULTS – CYCLONIC ATTRITION

➢ Cyclonic attrition: Circulation rate through draft tube

- Several materials tested – Varied cyclone inlet velocity (5 – 20 m/s)
- Determined circulation rate for each material at ambient conditions
- Choked particle flow reached = Constant circulation rate
- Velocity effect on attrition measurable – Constant circulation rate
Hot flow cyclonic attrition results:

- Attrition rate: Rate of fines generated divided by circulation rate in cyclone
- Model*
  \[ r_c = \frac{C_c d_p v_{c, in}^2}{\sqrt{\mu_c}} \]
- Similar trend to jet attrition
- Supported Fe-based OC performance > than Mn-based OCs

RESULT S – CYCLONIC ATTRITION

Rate of attrition expression

- Model results compared to 10 kW_{th} unit (Berguerand & Lyngfelt (2008b))
- Cyclonic attrition rate (model): 2.5E-02 - 5.9E-02 wt-‰/hr
- Attrition rate (experimental): 2.02E-02 wt-‰/hr
- Apparent – cyclonic attrition more important compared to jet attrition

CONCLUSIONS – COMPARISON BETWEEN MODES OF ATTRITION

- **Attrition rate greatly affected by combination of factors**
  - Gas flows, solids inventory, circulation rate and velocity dependence
  - *Cyclonic attrition: Comparable to full-scale systems*
  - Sped up process since higher frequency of particle impacts
  - *Attrition mechanism better represented by cyclonic attrition unit*

- **Indication: Cyclonic attrition ≥ Jet attrition**
  - *Jet attrition exaggerated* (at jet velocities ≥ 100 m/s)
  - Jet attrition – good *short term, quick screening*
  - *Cyclonic attrition unit – good particle lifetime estimation*
  - Cyclonic and jet attrition units = *Valuable tools*
  - *Rapidly screen/test potential oxygen carriers* for larger scale testing
COMMERCIAL SUCCESS

- **Babcock & Wilcox**
  - Testing of materials from different vendors (*Compositional analyses*)

- **University of Kentucky**
  - Effect of different *heat pre-treatments* on carrier performance

- **Alstom/General Electric**
  - Testing of different *limestone samples for CLC*
  - Assessment of different sulfated and spent materials for CLC

- **Commercial Client**
  - *Limestone attrition* resistance testing and comparison
  - *Sulfur dioxide capture* efficiency comparison

- **DOE-NETL**
  - *Proposal awards* based on testing capabilities
  - *Manufacturing of OCs*
The United States Department of Energy

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