ENVERGEX LLC
&
INSTITUTE FOR ENERGY STUDIES, UNIVERSITY OF NORTH DAKOTA

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

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

August 14, 2018

PROJECT PARTICIPANTS

- US Department of Energy - NETL
  - Steve Richardson, John Rockey and Gregory O'Neil – Program Manager
- Envergex, LLC
- University of North Dakota- Institute for Energy Studies

INTRODUCTION

- **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_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

BACKGROUND

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

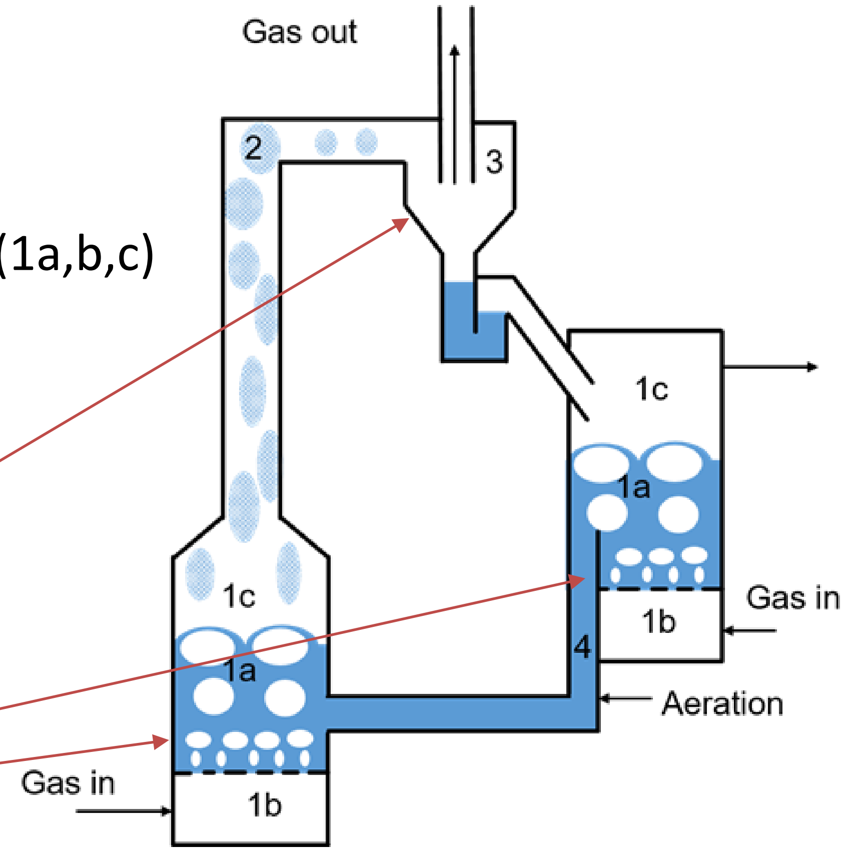


Image taken from Galinsky *et al*. (2017)[3]

- **Main regions of concern[1, 2, 3]**
  - Cyclone
  - Jet

1. Scala, F. ed., 2013. *Fluidized bed technologies for near-zero emission combustion and gasification*. Elsevier.

2. Rydén, M., Moldenhauer, P., Lindqvist, S., Mattisson, T. and Lyngfelt, A., 2014. Measuring attrition resistance of oxygen carrier particles for chemical looping combustion with a customized jet cup. *Powder Technology*, *256*, pp.75-86.

3. Galinsky, N., Samuel, B. and Breault, R, 2017. Attrition Prediction Model for Chemical Looping and Other CFB Systems. *National Energy Technology Laboratory.*

PROJECT GOALS

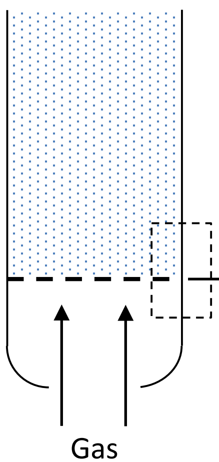
- **Phase II**

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*

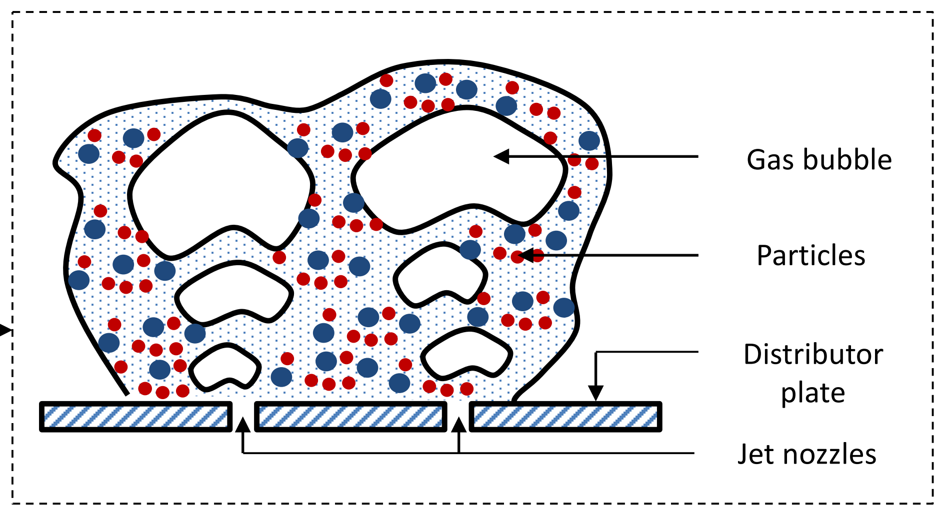
JET ATTRITION DETAILS

➢ Jet attrition

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



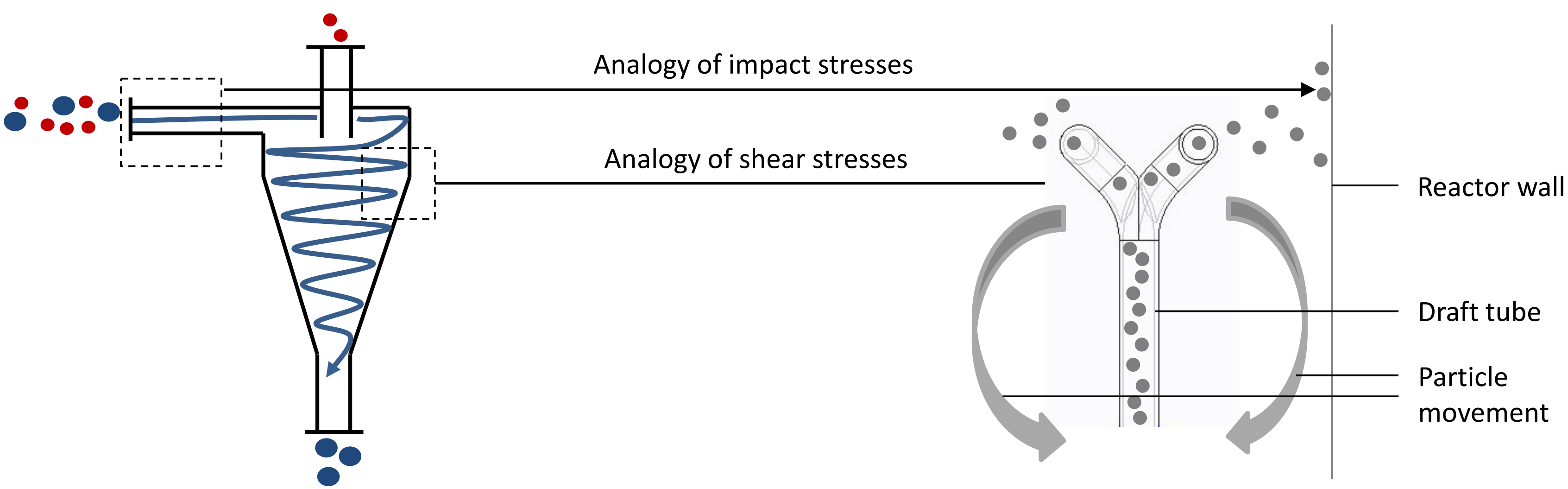
Oxidizer/Reducer Reactor



Jetting Region

CYCLONIC ATTRITION DETAILS

- **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*



Cyclone **Cyclone/Impaction Method**

OXYGEN CARRIER EVALUATION UNIT

Hot Flow Test Unit

Mass Flow Controllers

Electrical Controls

Filters

Settling Chamber

Reactor

Reactor Heater

Laser Gas Analyzer

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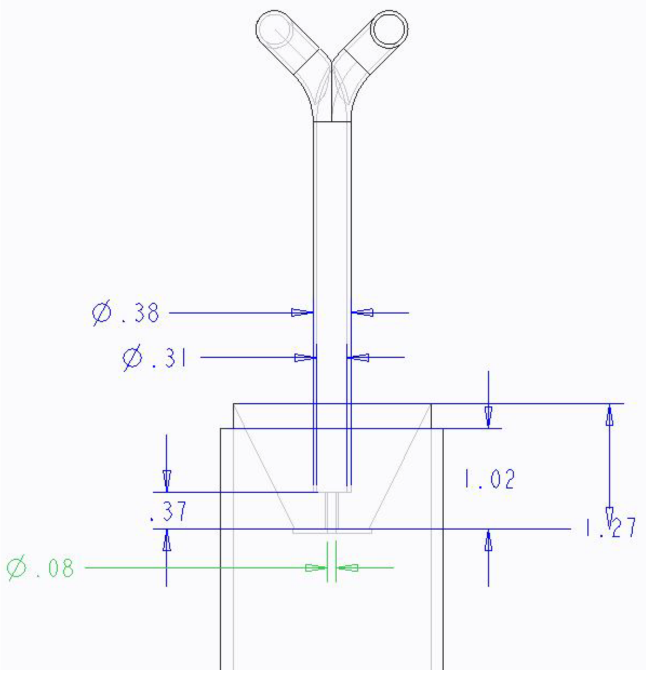
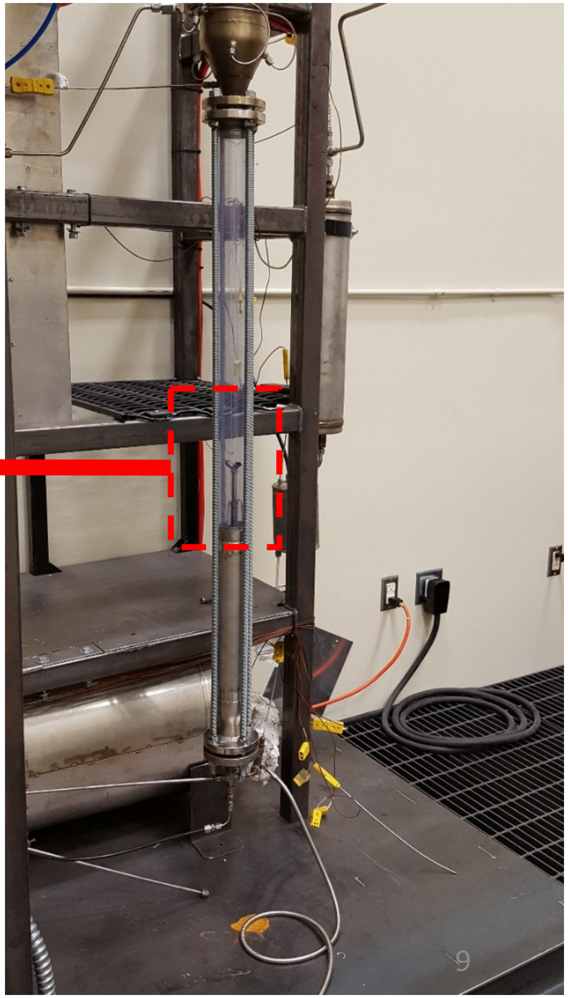
UNIQUE REACTOR ATTRIBUTES

Envergex Sparking Innovations

- **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)

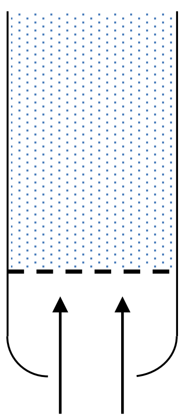




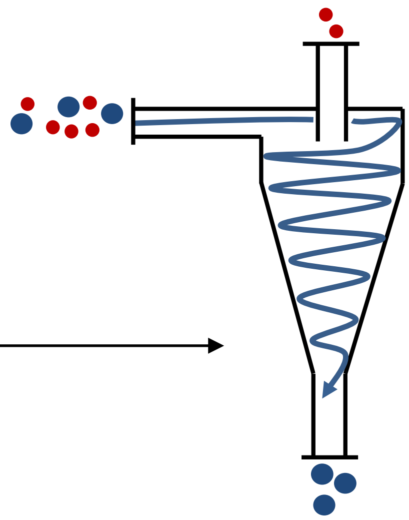
METHODOLOGY

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 H_2)*, H_2O and N_2
- Oxidizing gases: *O_2* diluted by N_2
- Sample size ≥ *30 g jet attrition*; ≥ *70 g cyclonic attrition*
- *Jet velocity 280 ~ 500 m/s* at temperature
- *Cyclone inlet velocity 5-20 m/s* at temperature



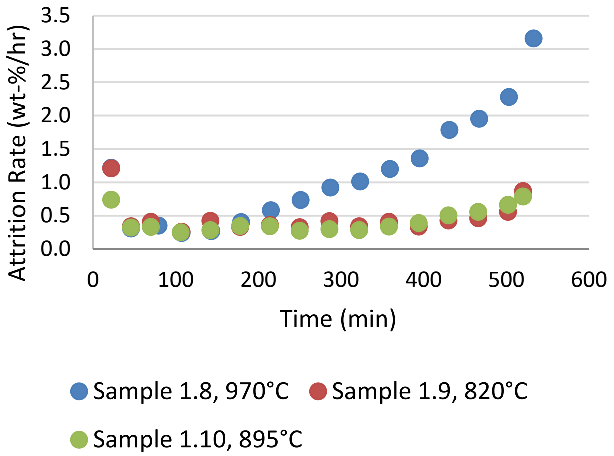
Attrition in CLC systems

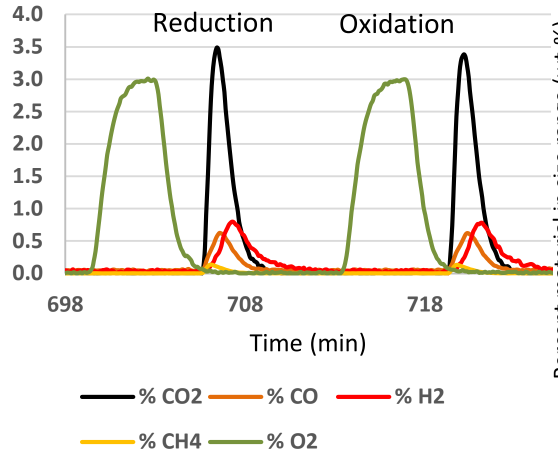


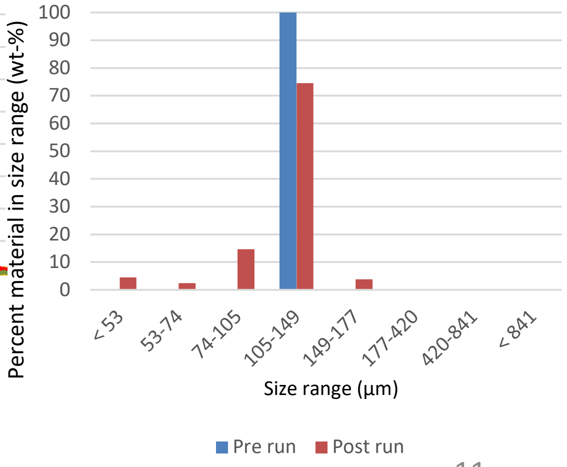
METHODOLOGY

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/H_2)
- Reactivity – expressed as *% conversion for each given cycle*
- *Particle size distribution* pre and post test

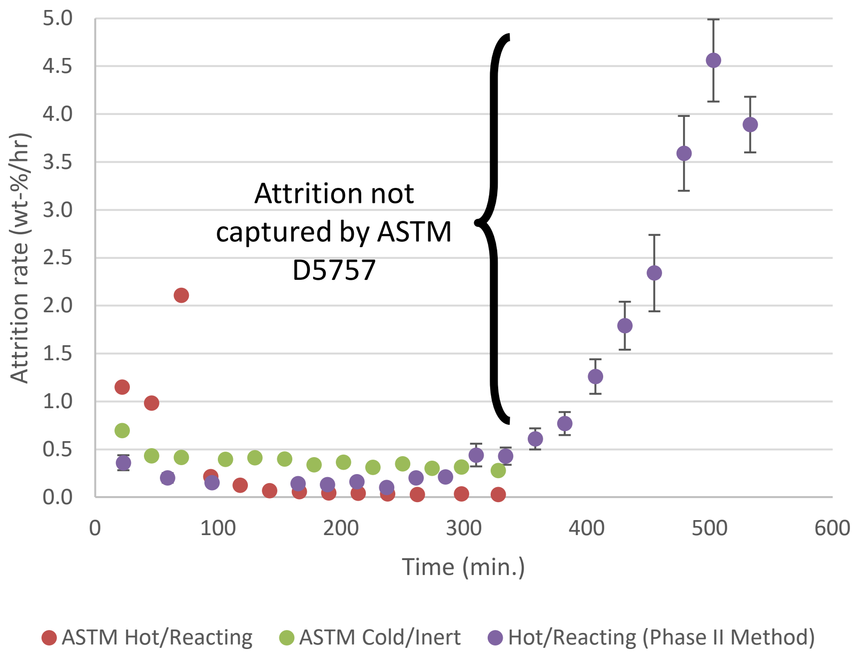


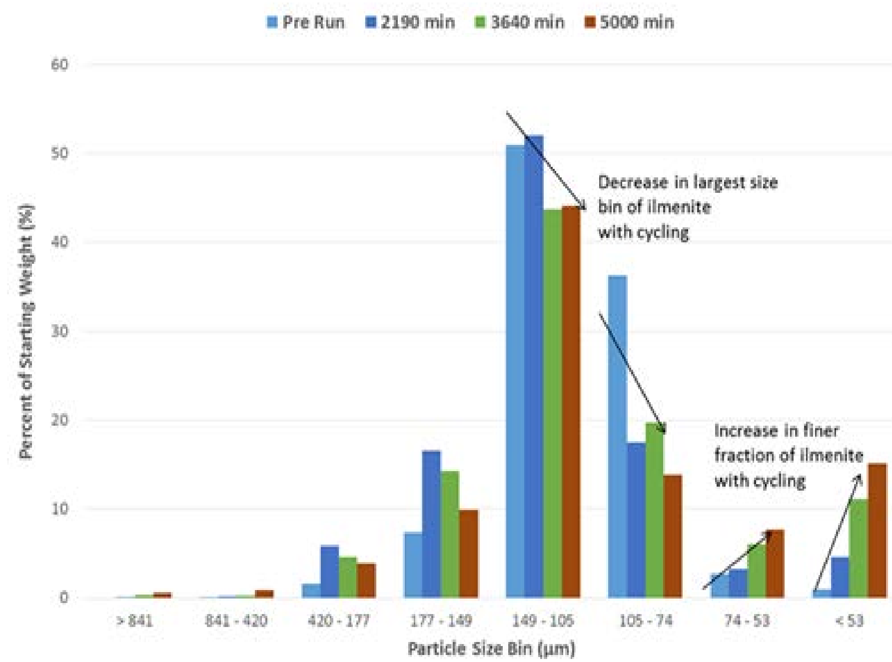




RESULTS - JET ATTRITION

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

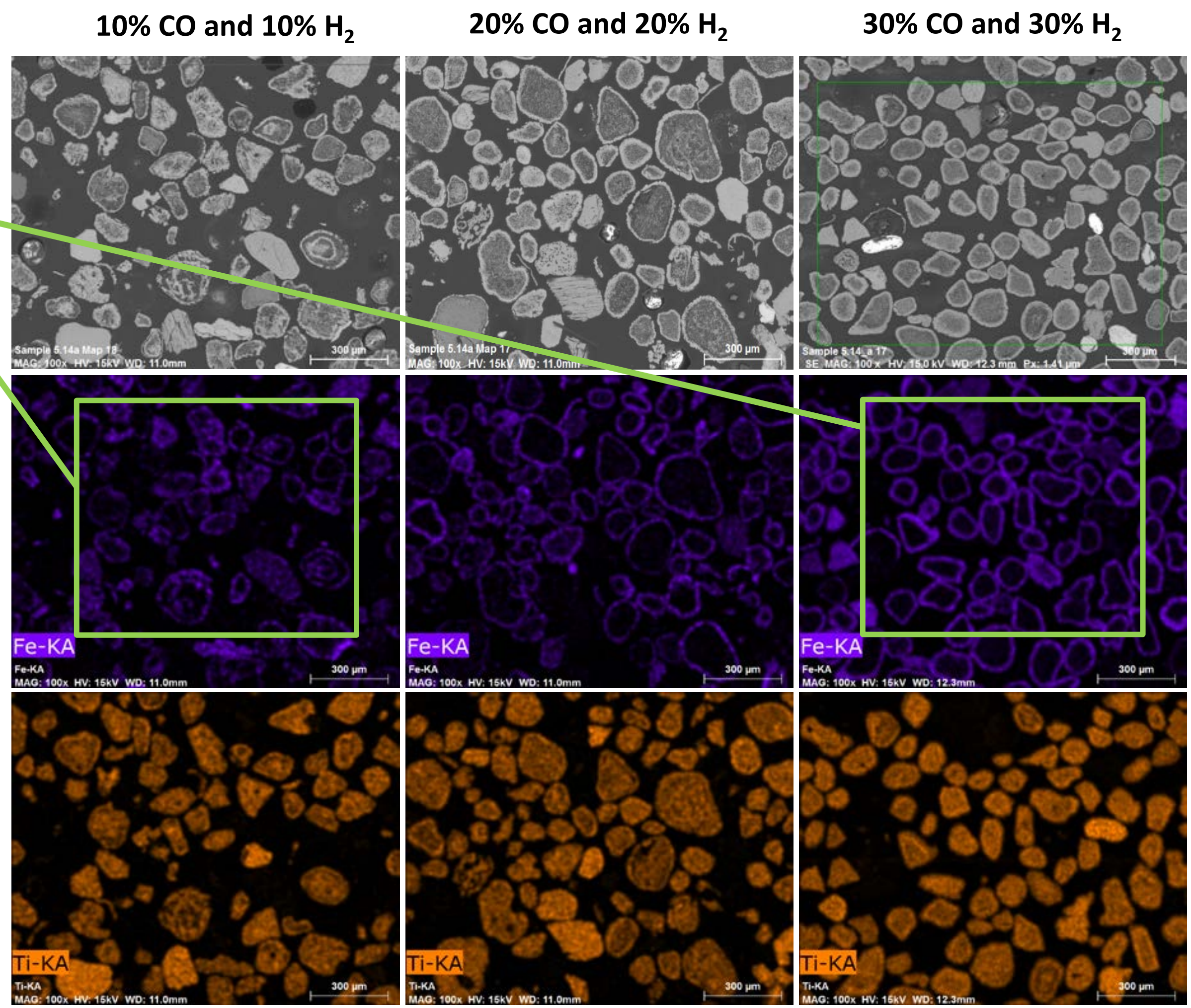




RESULTS - JET ATTRITION

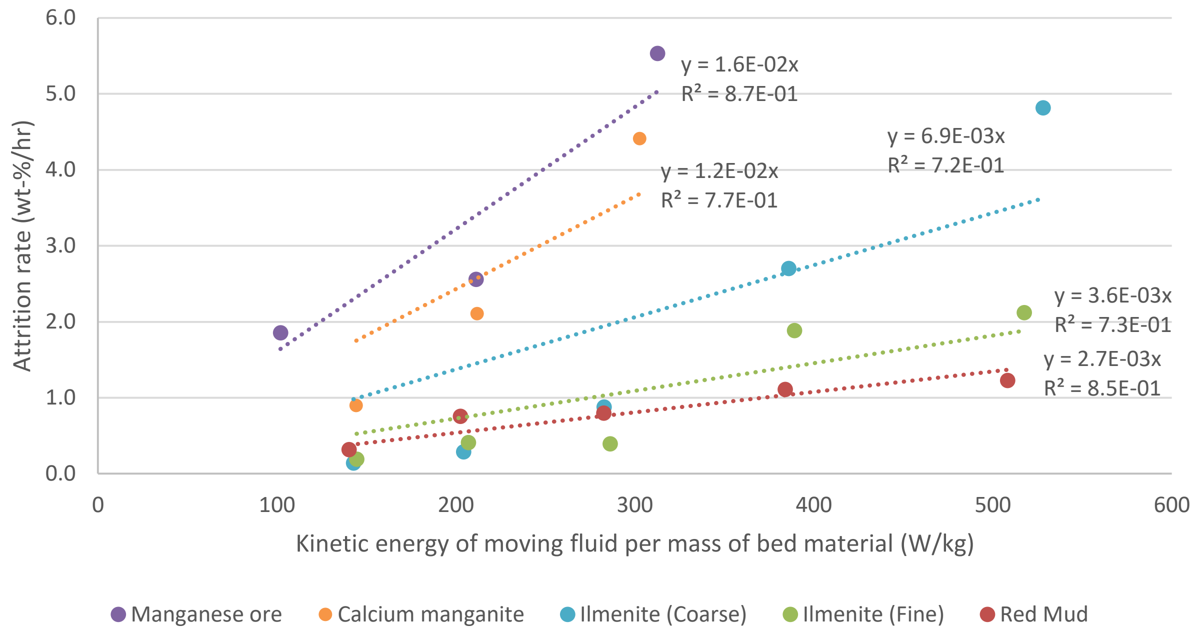
➢ Reactivity (SEM cross-sectional analyses: Post-run ilmenite samples)

- Material structure less defined at 10% vs 30% fuels cases
- *Outer Fe_xO_y-layer* more pronounced at 30% fuel conc.
- *Enhanced availability of Fe_xO_y* in outside layer → higher fuel conversion
- *Reduced attrition* at *higher fuel concentrations* (agglomeration)
- *O_2 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



RESULTS - JET ATTRITION

- **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



RESULTS - JET ATTRITION

➢ Rate of attrition expression

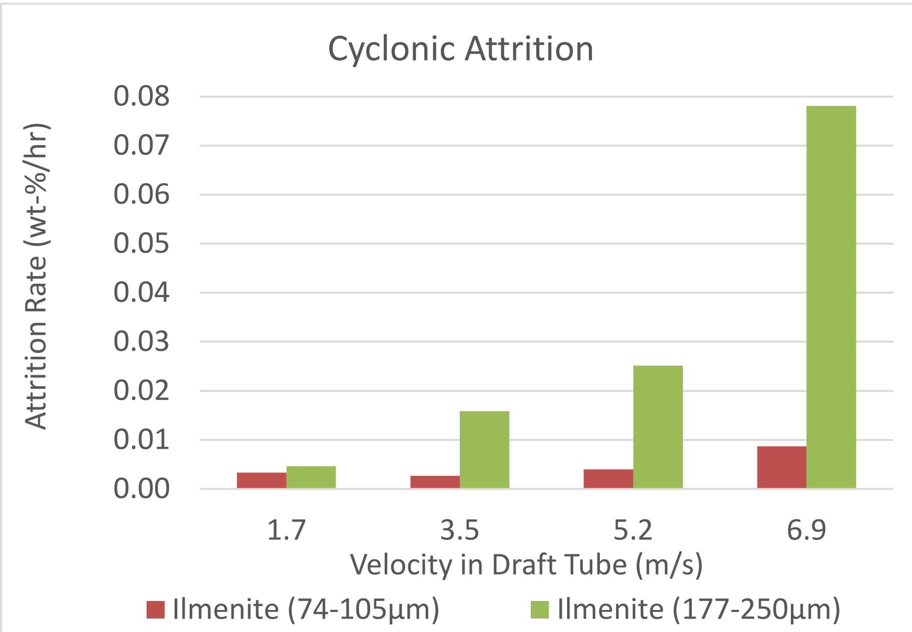
- Model results compared to 10 kW_{th} unit (Berguerand & Lyngfelt (2008b)
- Attrition rate (model): 2.0E-02 - 3.4E-02 wt-%/hr
- Attrition rate (experimental): 2.02E-02 wt-%/hr
- Differences - Attributable to wide operating ranges used in experiments

10 kW_{th} unit	Source			
	Linderholm et al. (2009)	Källén et al. (2013)	Berguerand and Lyngfelt (2008a)	Berguerand and Lyngfelt (2008b)
Oxygen carrier	$NiO/NiAl_2O_4$	$CaMn_{0.9}Mg_{0.1}O_{3-\delta}$	$FeTiO_3$ (Ilmenite)	$FeTiO_3$ (Ilmenite)
OC density (kg/m^3)	3250-3800 (material)	1932 (bulk)	2100 (bulk)	- (presumed to be 2100)
Particle size distribution (µm)	90-212	90-180	90-250	90-250
Air reactor flow rate (NLPM)	-	100-200	-	110-145
Material inventory (kg)	15-16 (5.9 in air reactor)	13-17	13 (6.3 in air reactor)	13
Solids circulation rate (kg/min)	2-4	-	1-6	-
Temperature (°C)	1000	1000	1000	920-990
Loss of fines, particles < 45 µm(wt-%/hr)	0.003	0.0085	-	0.01-0.03
Inlet nozzle velocity (m/s)	100	100	100	100

Berguerand, N. and Lyngfelt, A., 2008b. Design and operation of a 10 kWth chemical-looping combustor for solid fuels–Testing with South African coal. *Fuel*, *87*(12), pp.2713-2726.

RESULTS – CYCLONIC ATTRITION

➢ Cyclonic attrition: Cold flow



Ilmenite (74-105µm)

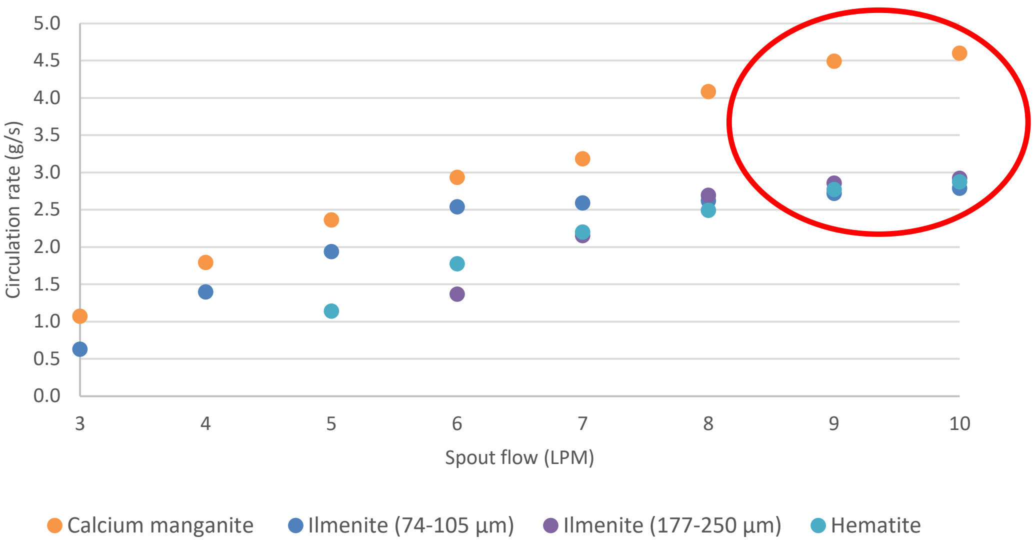
Ilmenite (177-250µm)

- 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



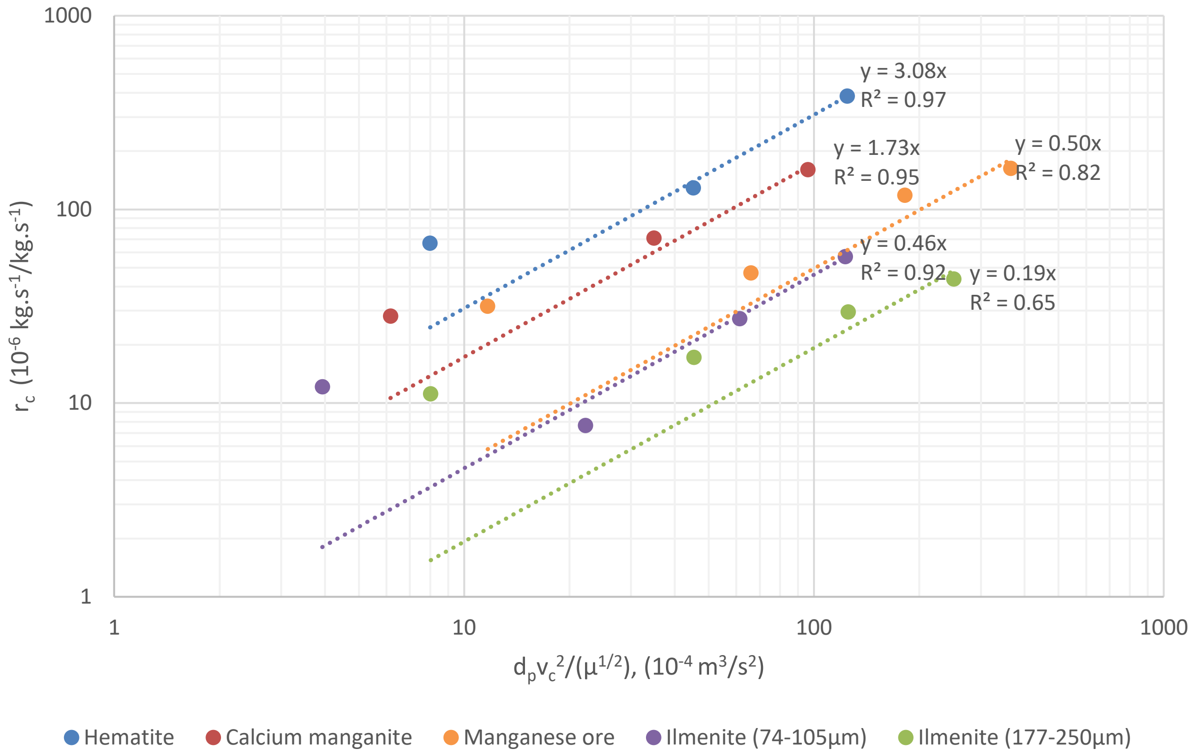
RESULTS – CYCLONIC ATTRITION

➢ **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

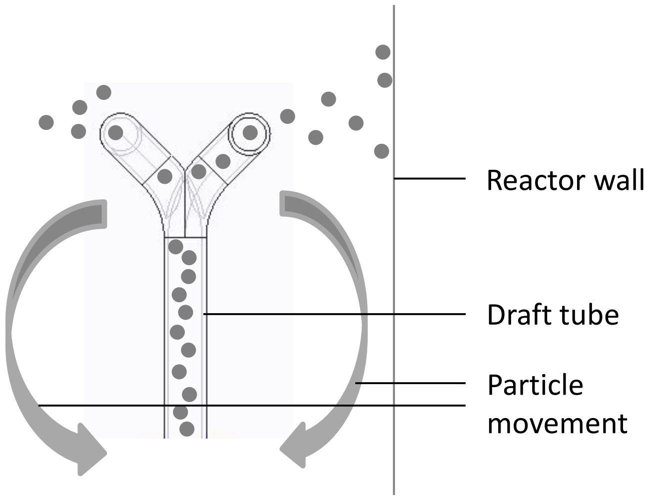


* Reppenhagen, J. and Werther, J., 2000. Catalyst attrition in cyclones. *Powder technology*, *113*(1-2), pp.55-69.

RESULTS – 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



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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 $\geq$ 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*

ACKNOWLEDGEMENT

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- *Steve Richardson, John Rockey and Gregory O’Neil*

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