Chemical Looping Combustion – NETL Operating Experiences

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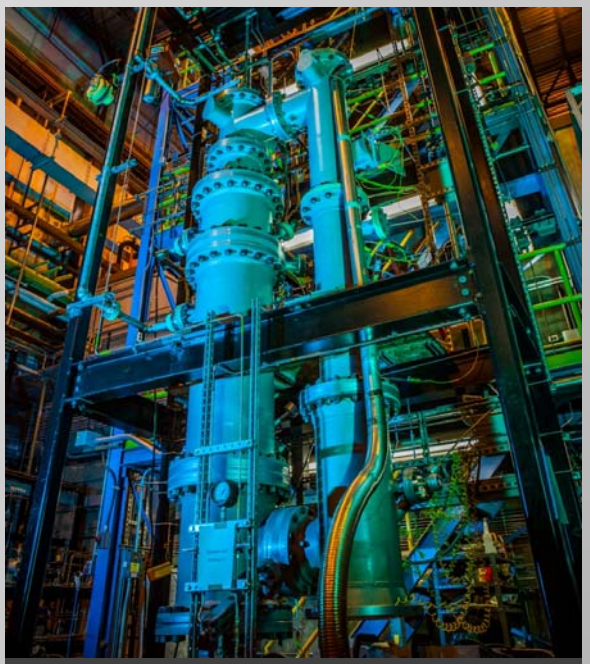
Energy Process Innovation Division



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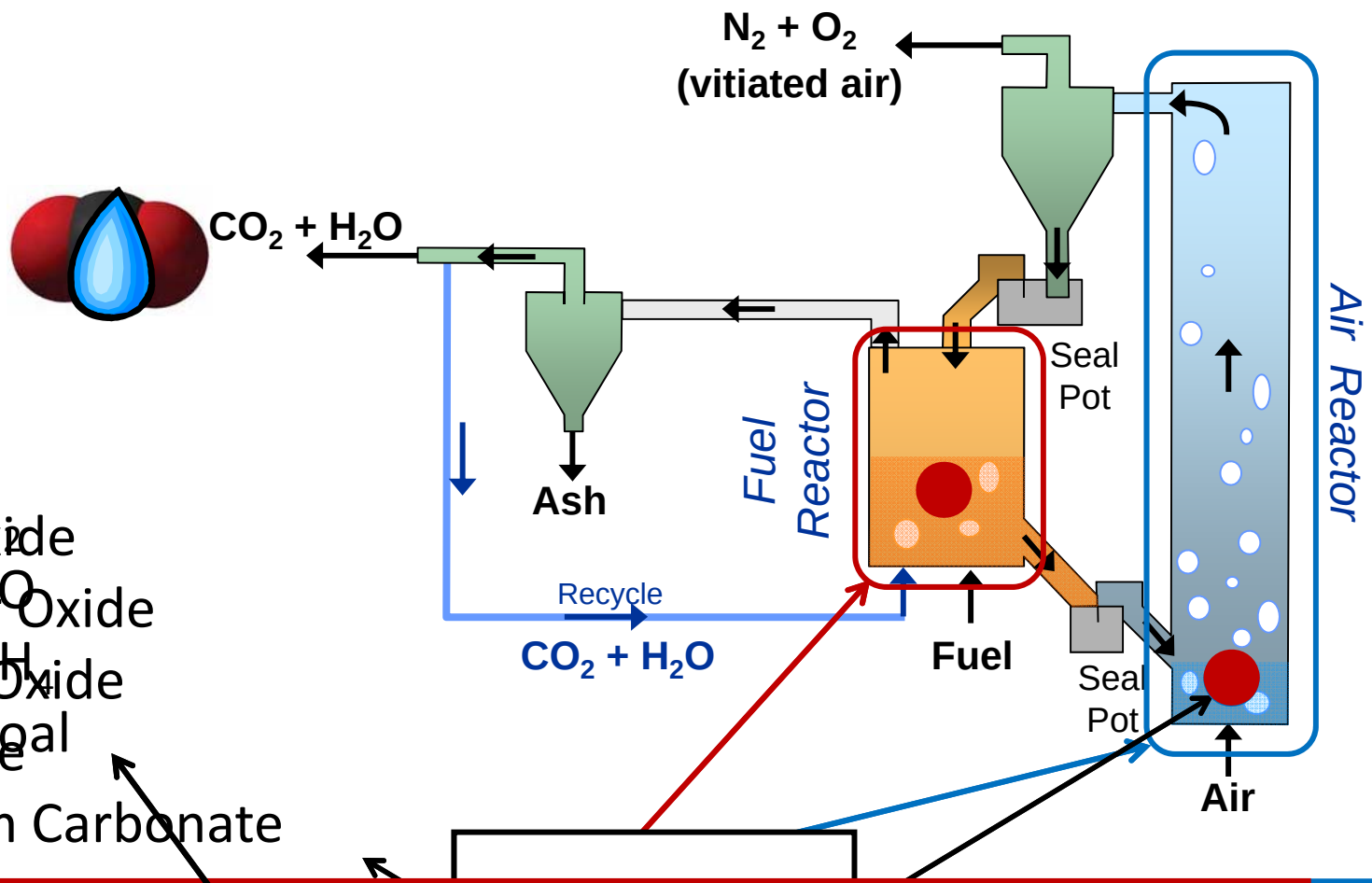
Outline

- **Review operating experience with chemical looping combustion test facility**
  - What is Chemical Looping Combustion?
  - Design basis
  - Nomenclature
  - Operating modes
  - Shakedown test experience
- **Summarize some lessons learned**

What is Chemical Looping Combustion (CLC)?

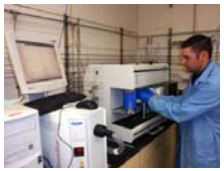


Iron Oxide
Copper Oxide
Nickel Oxide
Ilmenite
Calcium Carbonate

H_2
CO
CH_4
Coal

$$MeO_z + C_xH_y \Leftrightarrow xCO_2 + \frac{y}{2}H_2O + MeO_{z-(2x+\frac{y}{2})}$$

NETL's Integrated Experimental & Modeling Effort

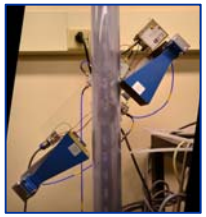


TGA and Mass-Spec

Lab-scale Fixed Bed Reactor

Integrated Cold Flow Unit

Single Fluidized Bed Reactor



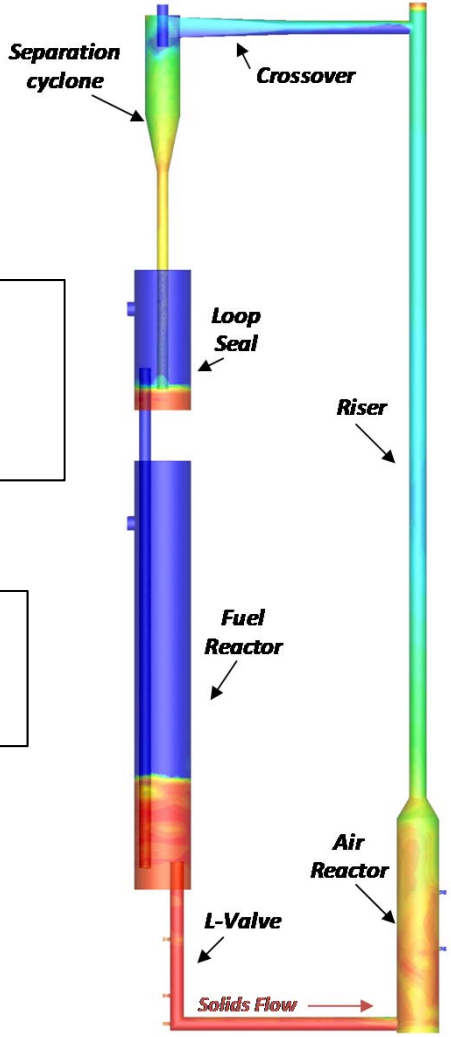
Microwave Sensor

Carrier Development/Evaluation
reaction model development via. parameter estimation

Bed Reaction Rate
Reaction model validation
Small scale validation of hydro, reaction and interactions

Circulating Hydrodynamics V&V
Solids Handling and Process Development

Solids Circulation Rate Measurement

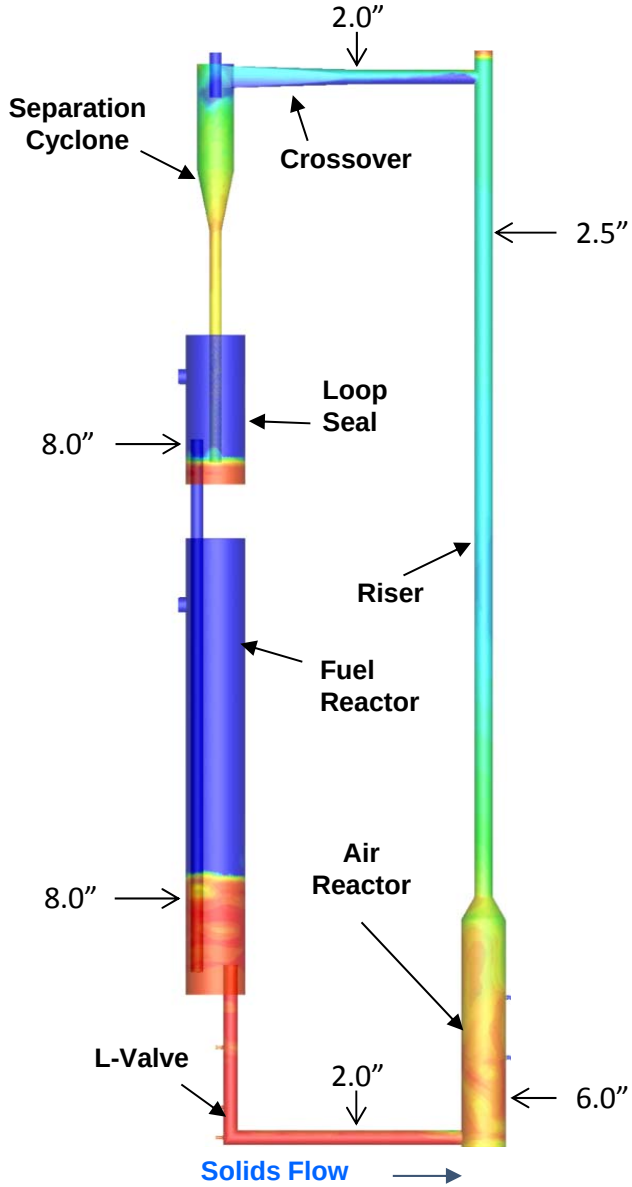


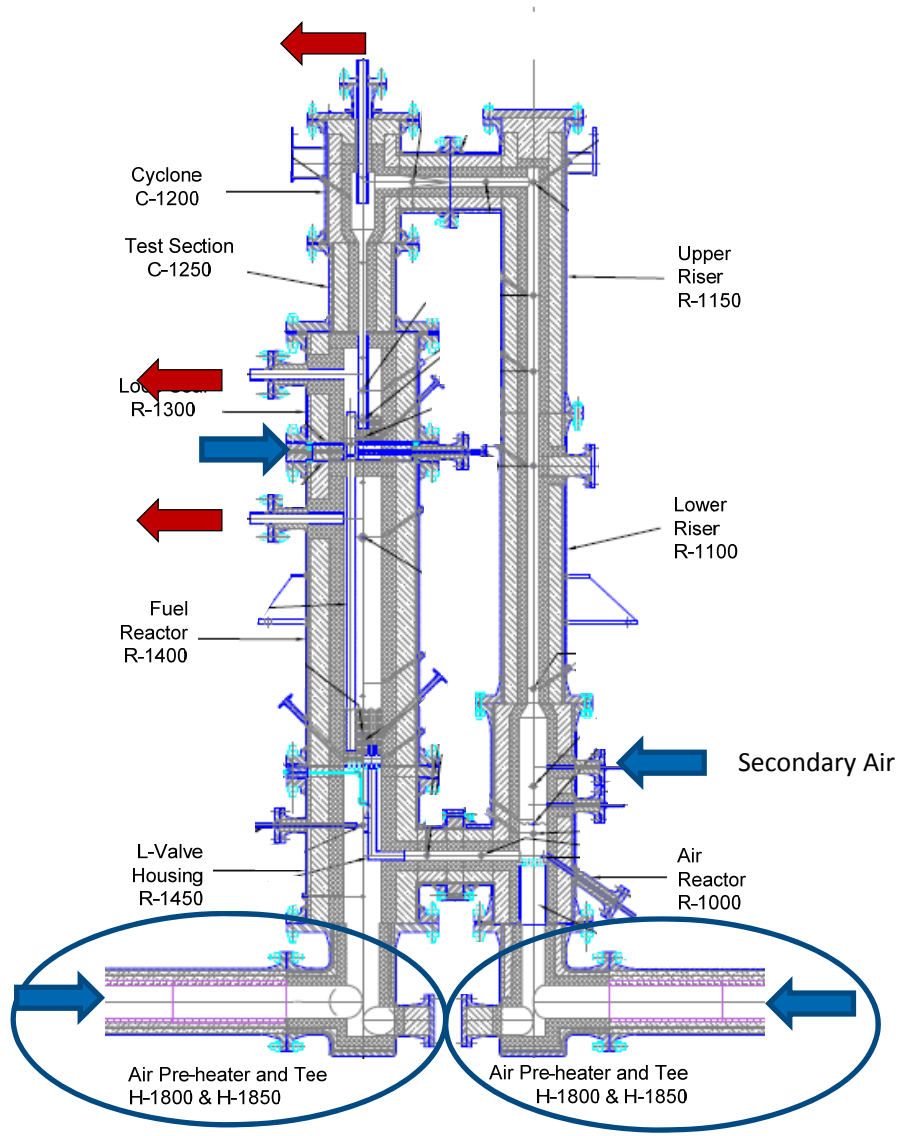
3D multi-phase CFD modeling

Design Basis For NETL's 50kW Chemical Looping Reactor Unit

- **Improve/verify modeling predictions**
  - Wall effect considerations
- **Integrated single loop /two reactor configuration**
  - Solids handling and control issues
  - Heat integration issues
- **Fuel-flexible (gas or solid fuels)**
  - Not an optimal reactor design
- **Carrier flexible**
  - Wide operating temperature range
  - Wide range of possible sizes
- **Small-scale**
  - No external heat addition to solids flow path

Nomenclature and Key Dimensions

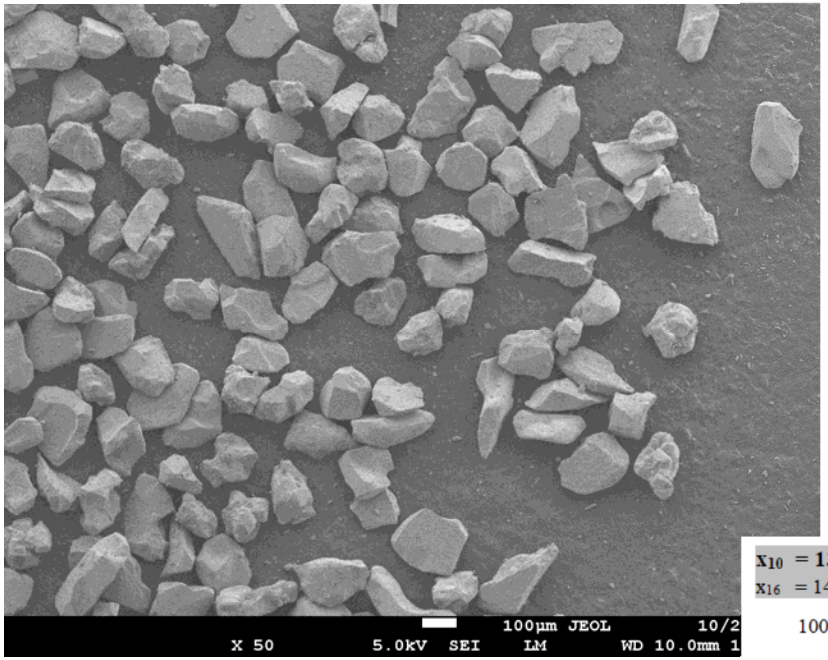


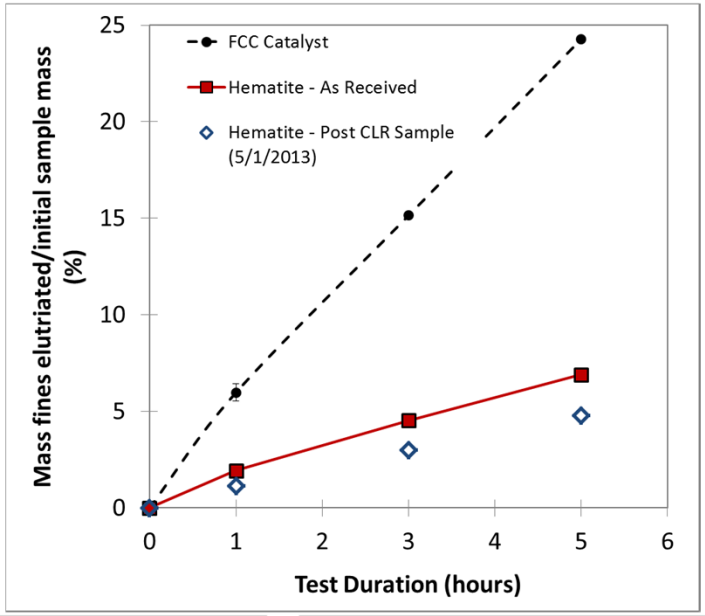


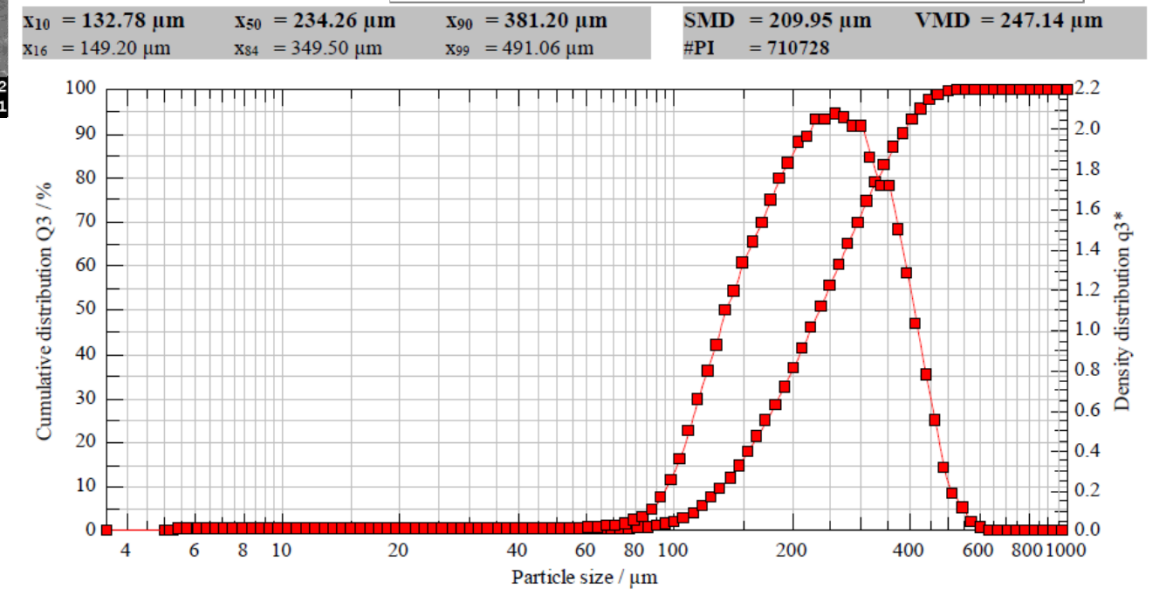
CLR – Key Operating Modes

- **Electric preheat**
  - Room temperature → Auto-ignition temperature
- **Natural gas augmented preheat**
  - 1200F to 2000F
  - Gas phase combustion in both reactors
- **Carrier addition**
  - Reduce gas flows
  - Add carrier in batches via lockhopper
- **Chemical looping combustion**
  - Transition from air to N2 as fluidizing gas in FR
  - Adjust natural gas flow for CLC

Baseline Oxygen Carrier – Hematite Concentrate



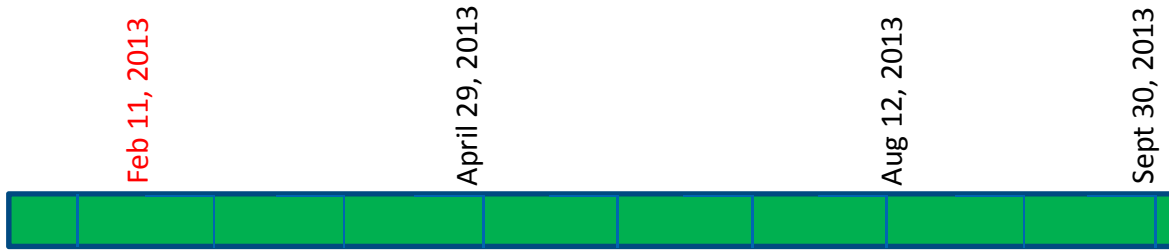




XRF Analysis

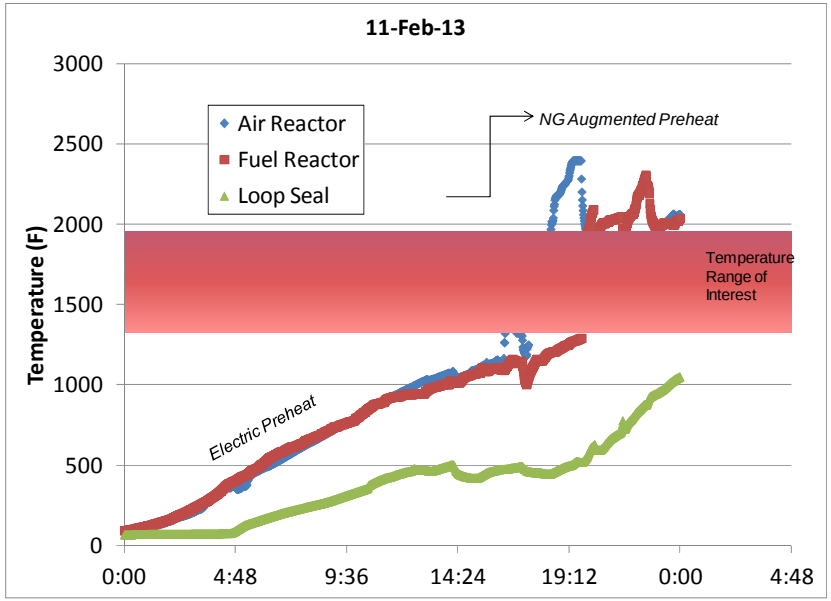
Fe2O3	81.89
SiO2	12.10
MnO	5.63
Al2O3	0.24
K2O	0.08
CaO	0.06

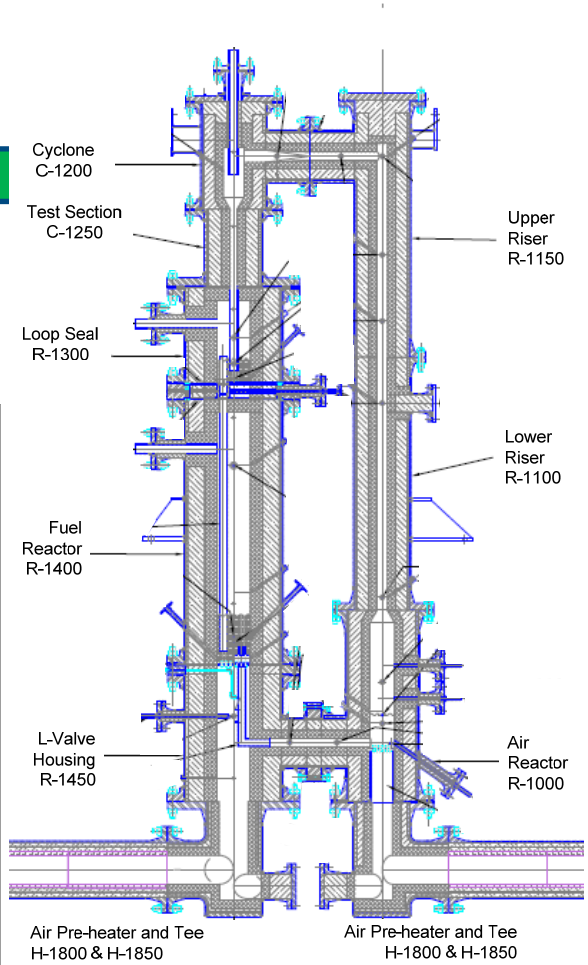
CLR Shakedown Testing Timeline



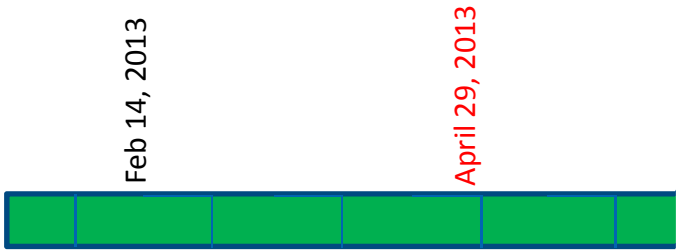
- Temps > 1000C in AR and FR
  - Single NG fuel loop
- Solids addition needs work
- Internal leakage issues
  - FR to AR

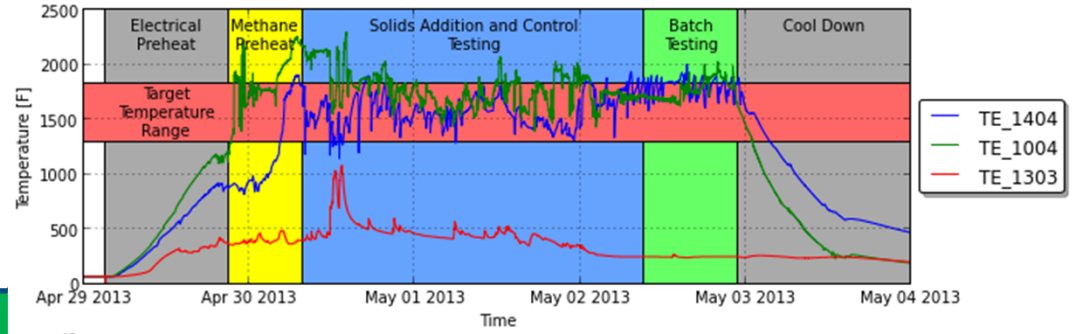
Air Reactor Distributor Plate

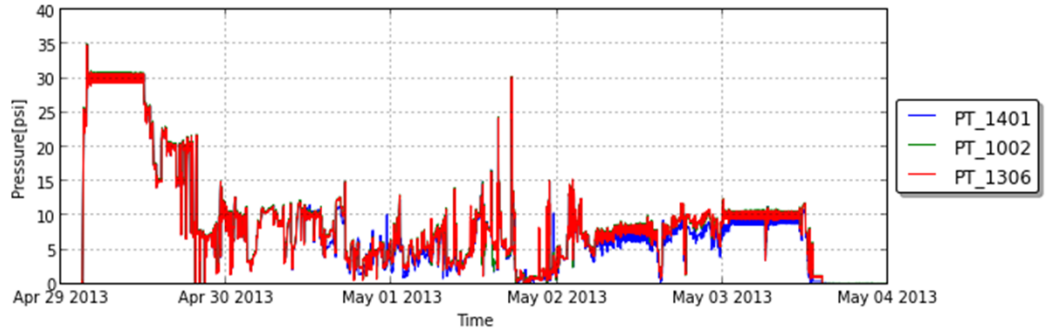




CLR Shakedown Testing Timeline

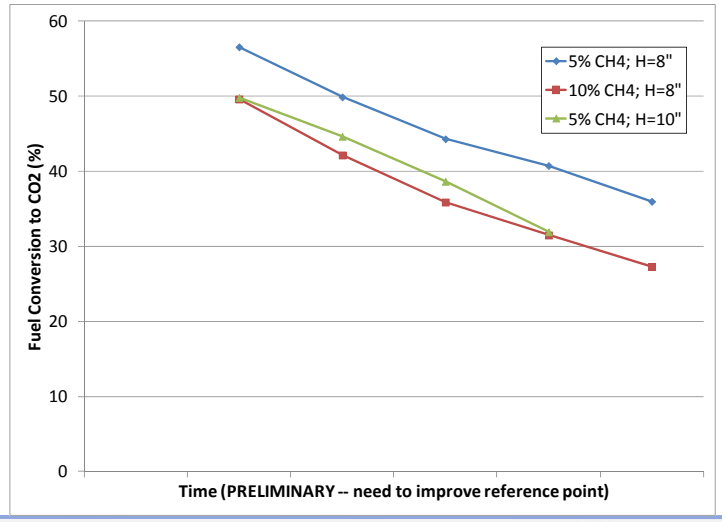






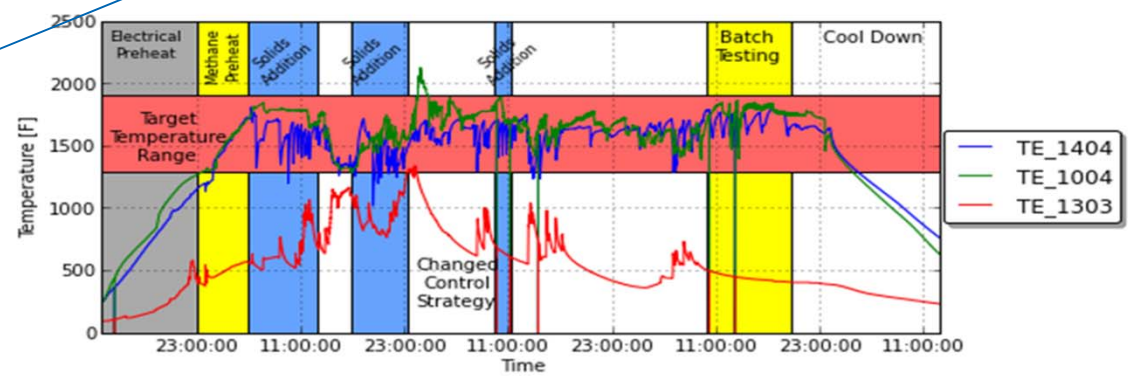
- Second NG flow loop
  - Independent control of FR/AR temps
- Solids addition procedure improved
- Elutriation/condensate issues
- Internal leakage issues
  - High temps in FR during NG preheat
  - Hot spot on vessel wall

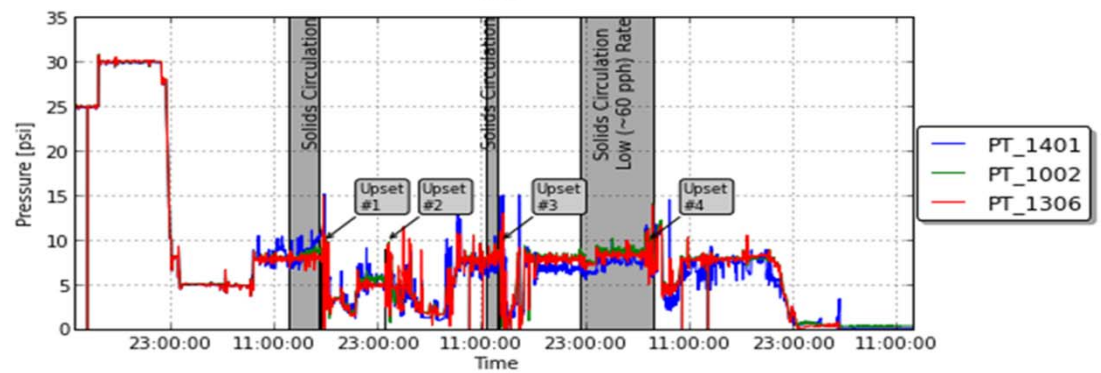
Fuel Reactor Agglomeration



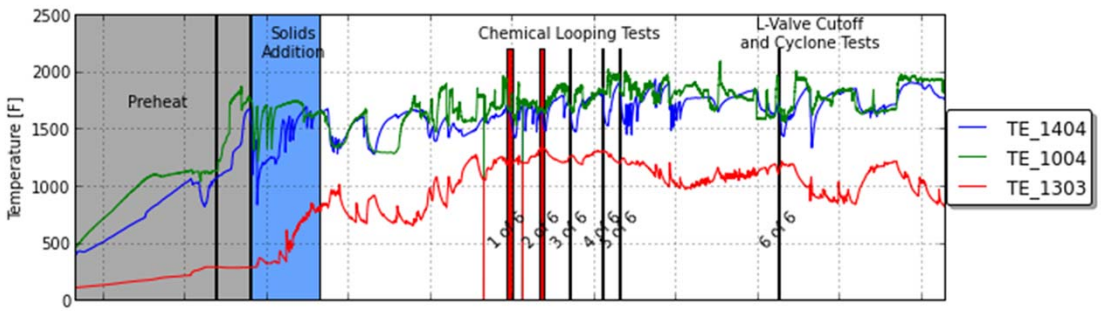
CLR Shakedown Testing Timeline

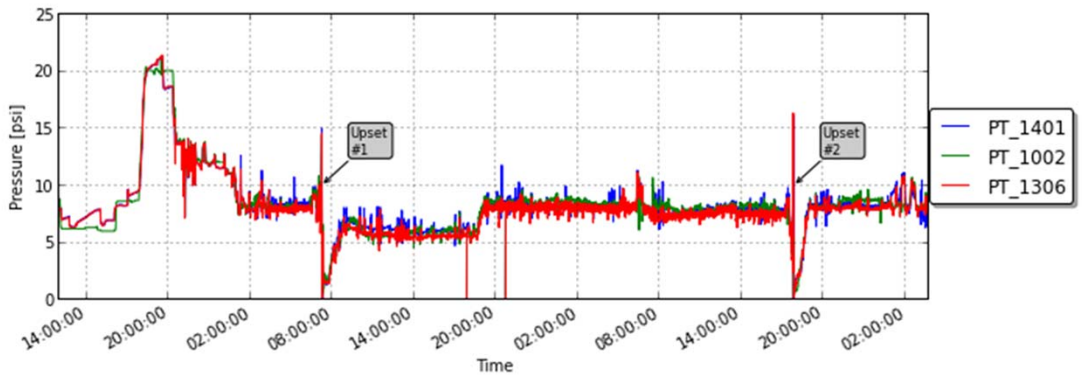
- Internal leakage issue addressed
- Solids addition issues addressed
- Operating margin is too narrow
  - Process upsets in cyclone
  - Solids loss due to gas flow up cyclone dip-leg
- Some batch testing results on hematite
  - Approx. 50% fuel conversion





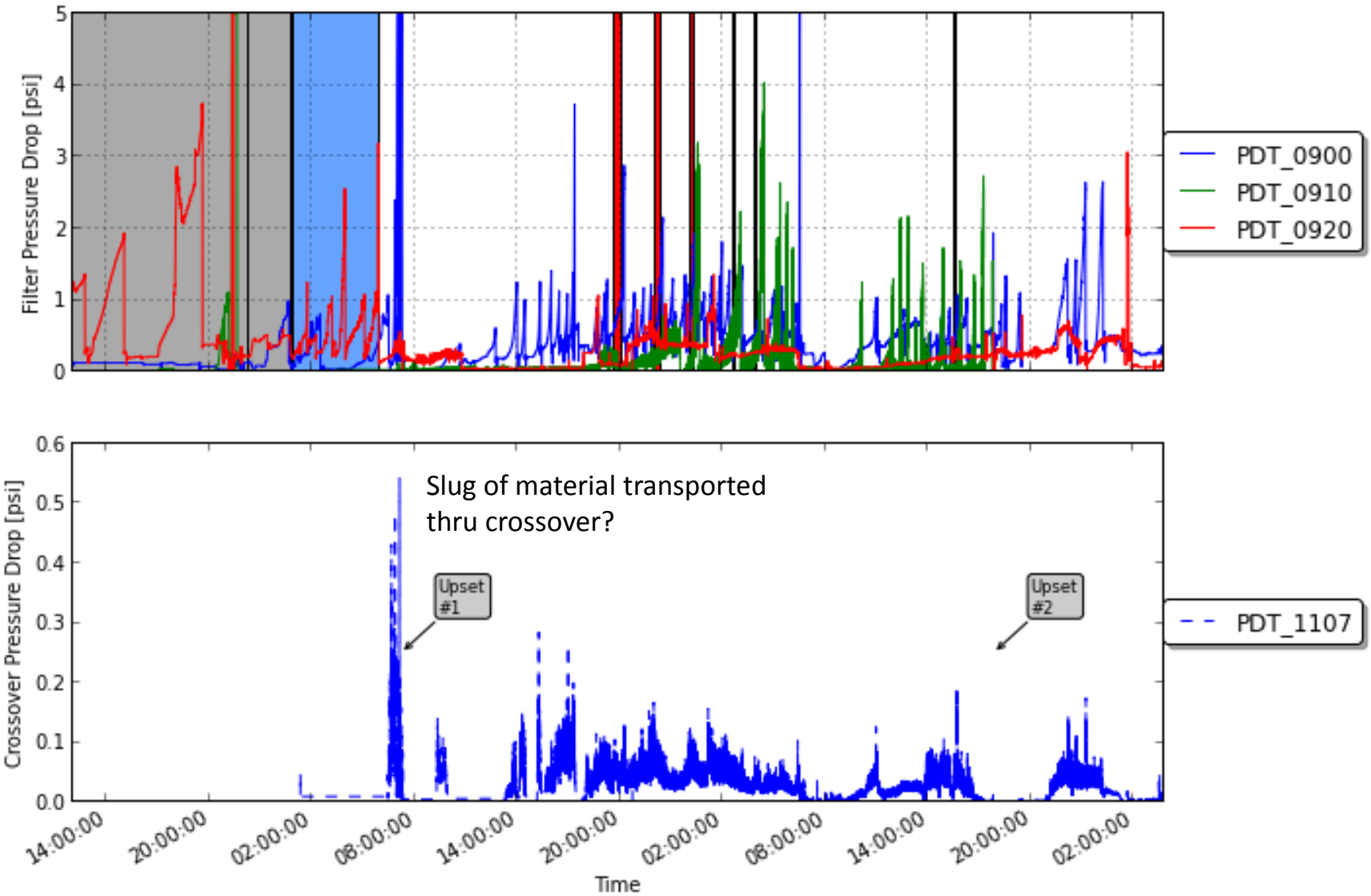
CLR Shakedown Testing Timeline



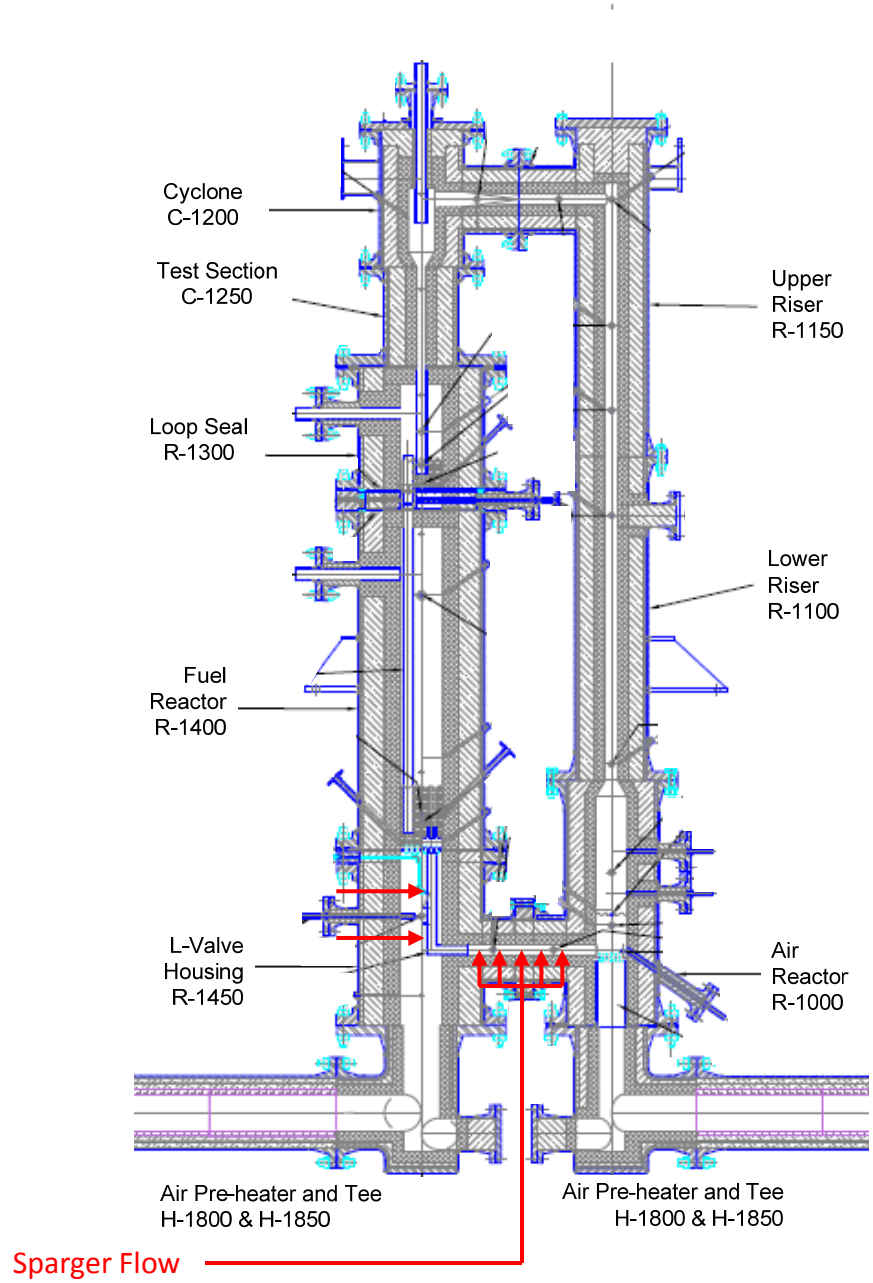


- Cyclone outlet pipe modified
- Operating margin improved
- Circulation rates quantified
- Cyclone efficiency assessed
- Some circulating tests on hematite

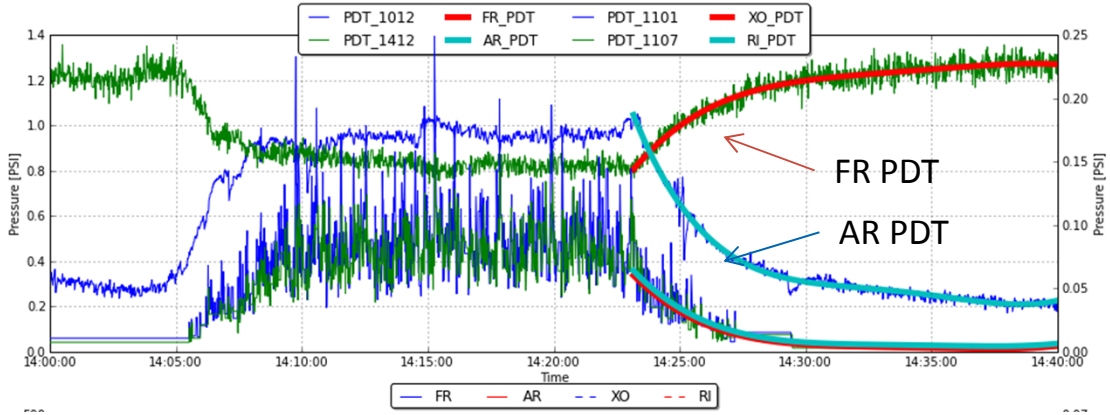
Filter Pressure Drops/Crossover DP – Oct Test

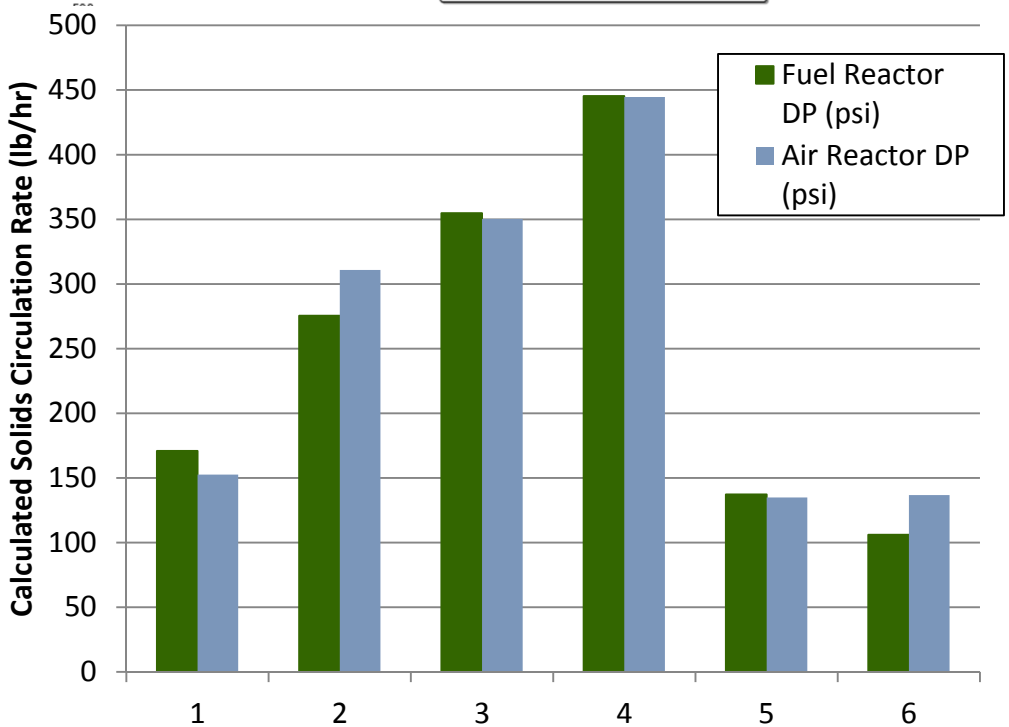


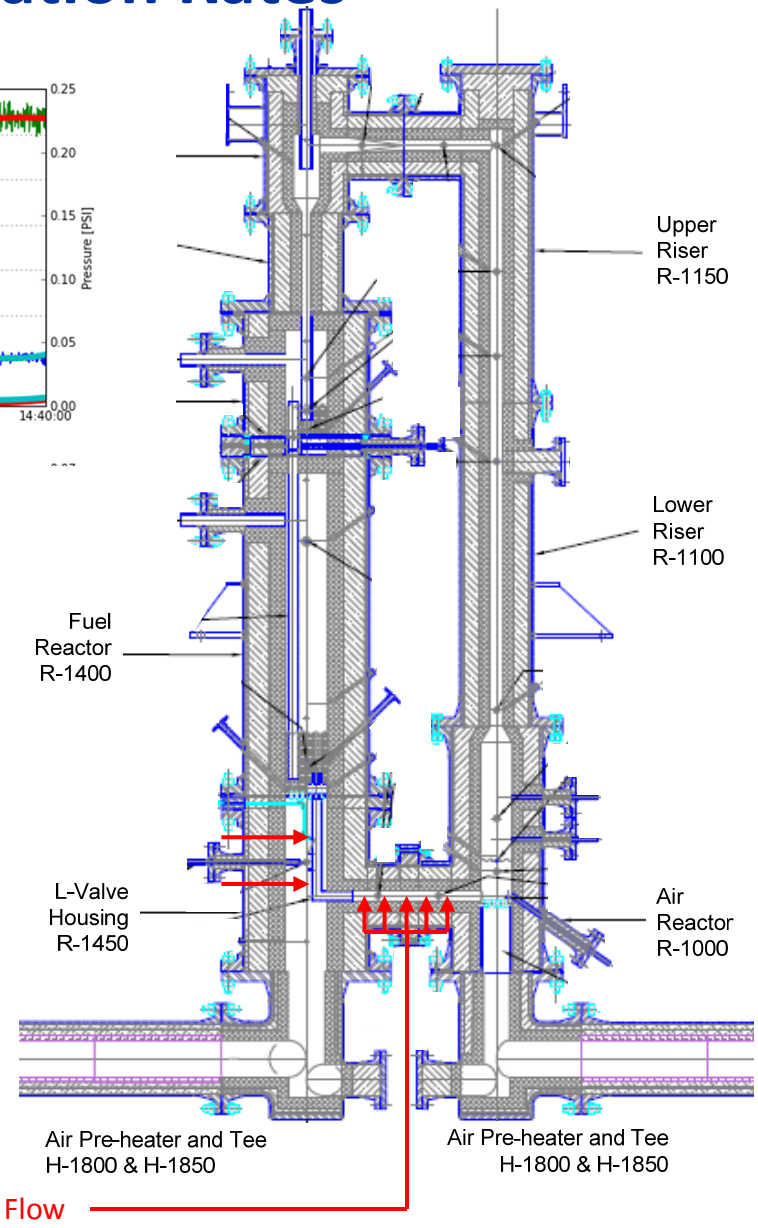
- **Solids Circulation Rate**
  - Transient L-valve cut-off tests
  - Bed pressure drops
    - $\Delta p = \frac{mg}{A}$
    - $\frac{d(\Delta p)}{dt} = \frac{g}{A} \cdot \frac{dm}{dt}$
- **Cyclone efficiency**
  - $\eta_{cyclone} = \frac{\frac{m_{filter}}{\Delta t}}{\frac{dm}{dt}}$



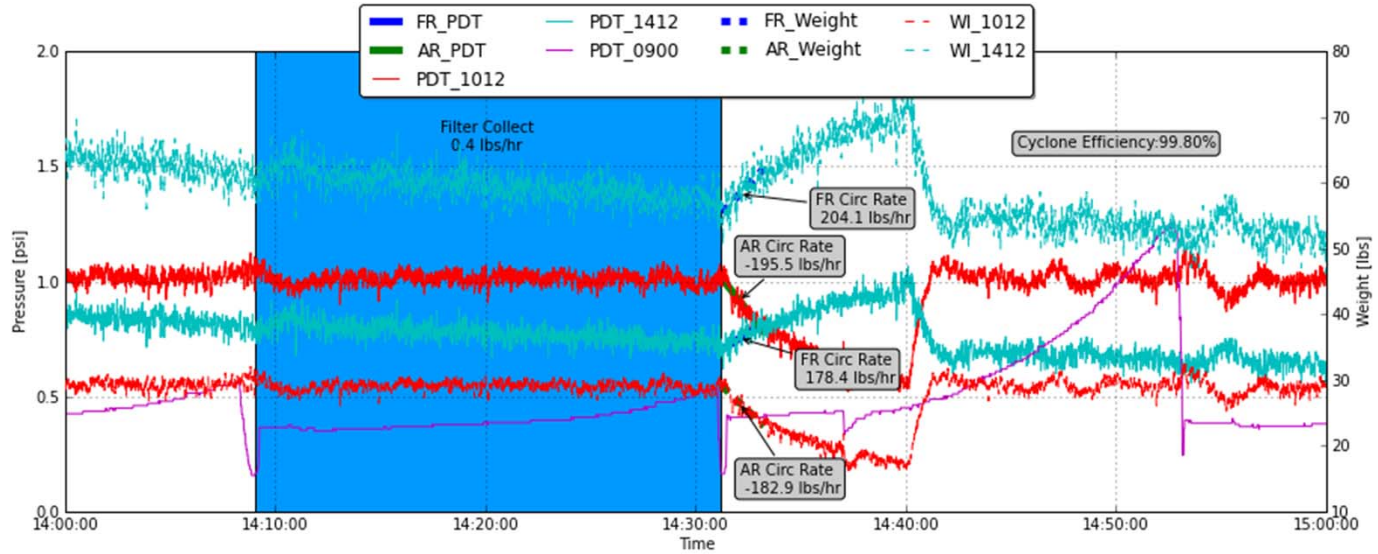
Calculated Solids Circulation Rates

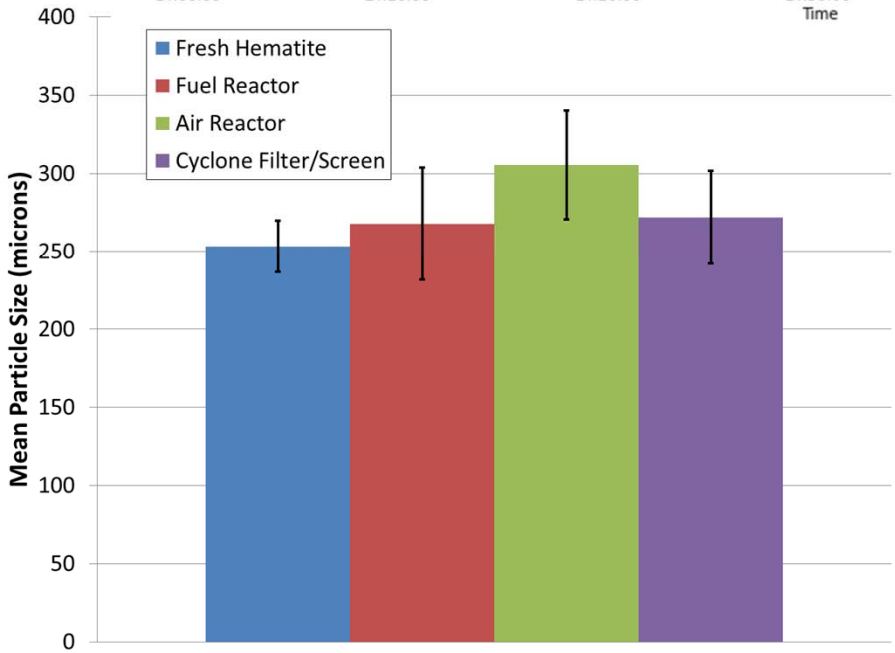






Cyclone Efficiency and Particle Sizes





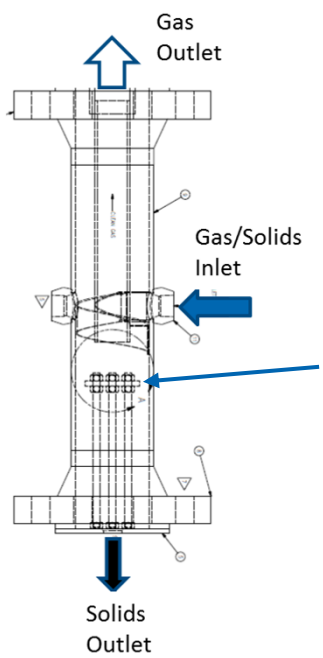
Test	Efficiency
1*	91.07
2	99.8
3	98.32
4	99.5
5	99.1

*Solids in filter were wet

Secondary Cyclone
(Unconventional Compact Approach)

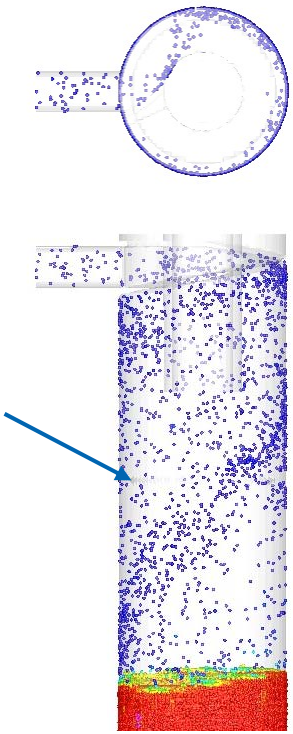
- **At high circulation rates (800 lb/hr) – 99% efficient cyclone is not good enough**
- **Simplified option for secondary cyclone**

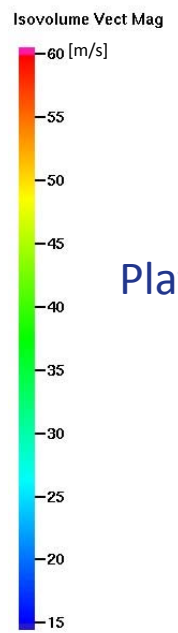
Existing
Pipe Spool Piece



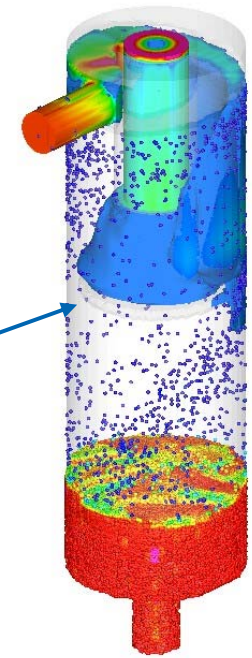
Plate

CFD Model

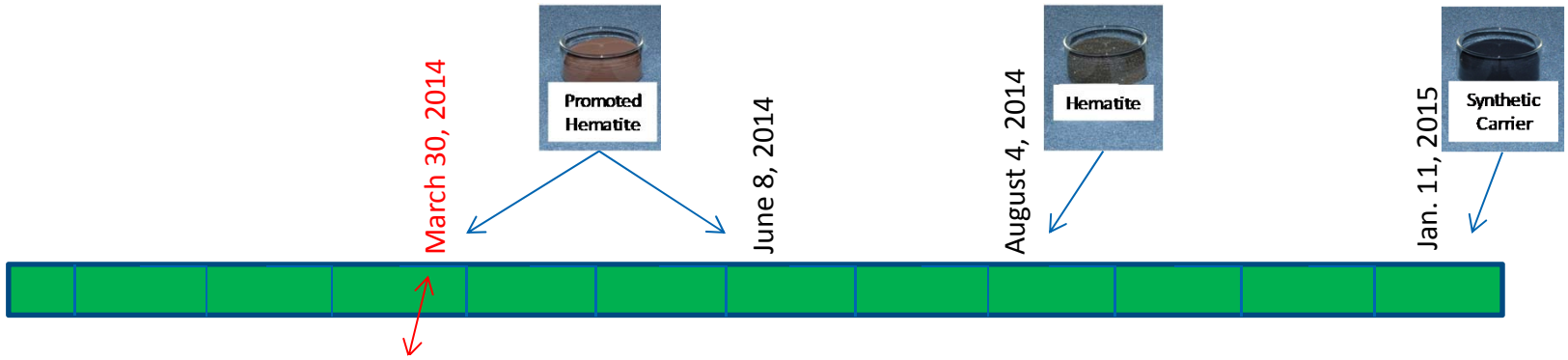


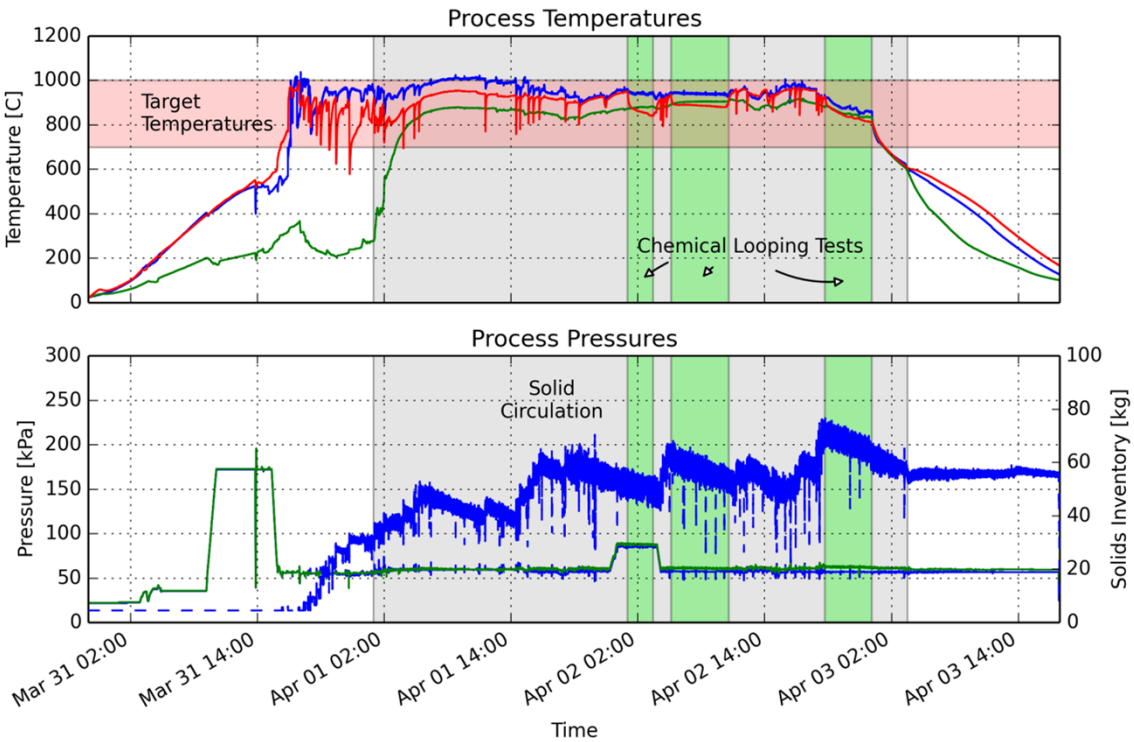


Plate



Recent NETL 50kW Chemical Looping Tests





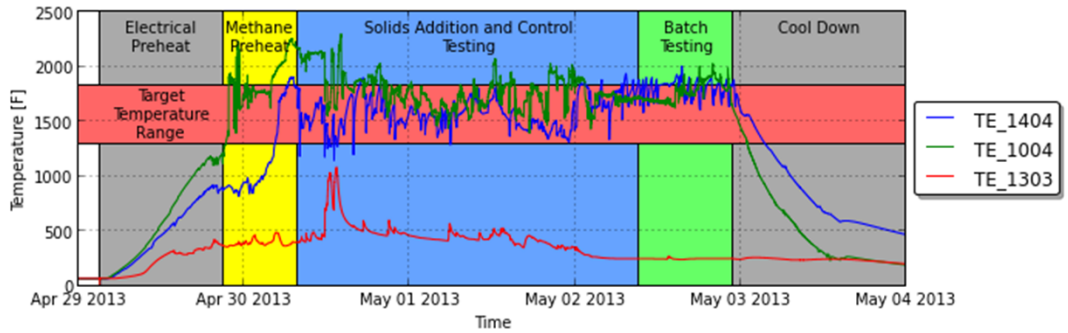
Continuous Chemical Looping periods of 2.3, 5.5, and 4.3 hours (12.3 hrs total)

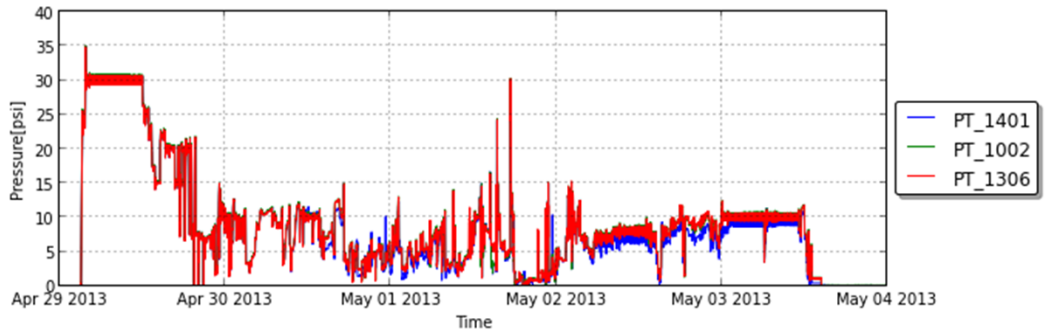
CH4 conversion to CO2 was less than 50% for most conditions

Carrier circulation rates were not well characterized

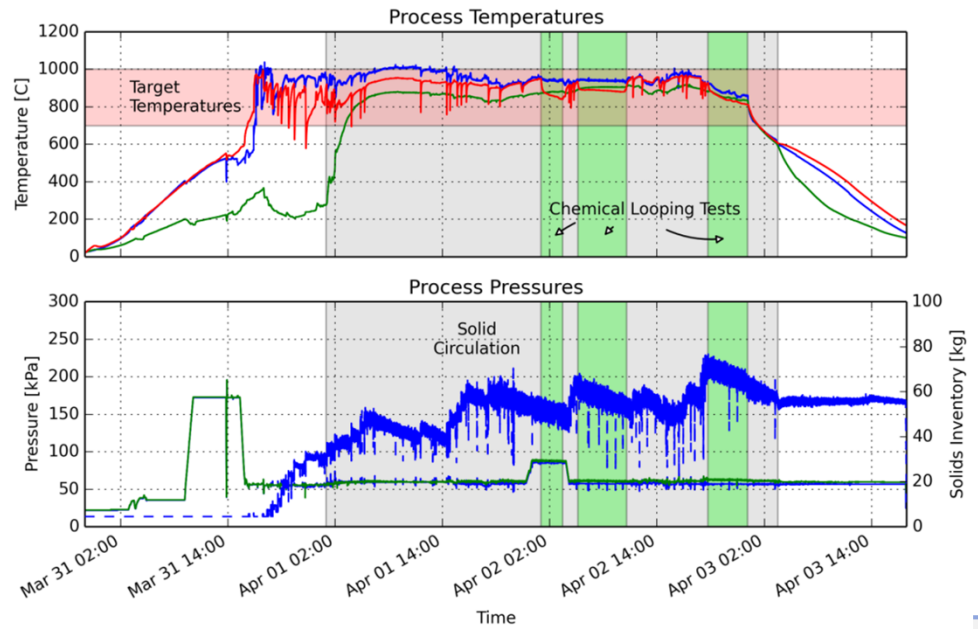
L-valve internal leak path

Shakedown Testing





1 year later . . .



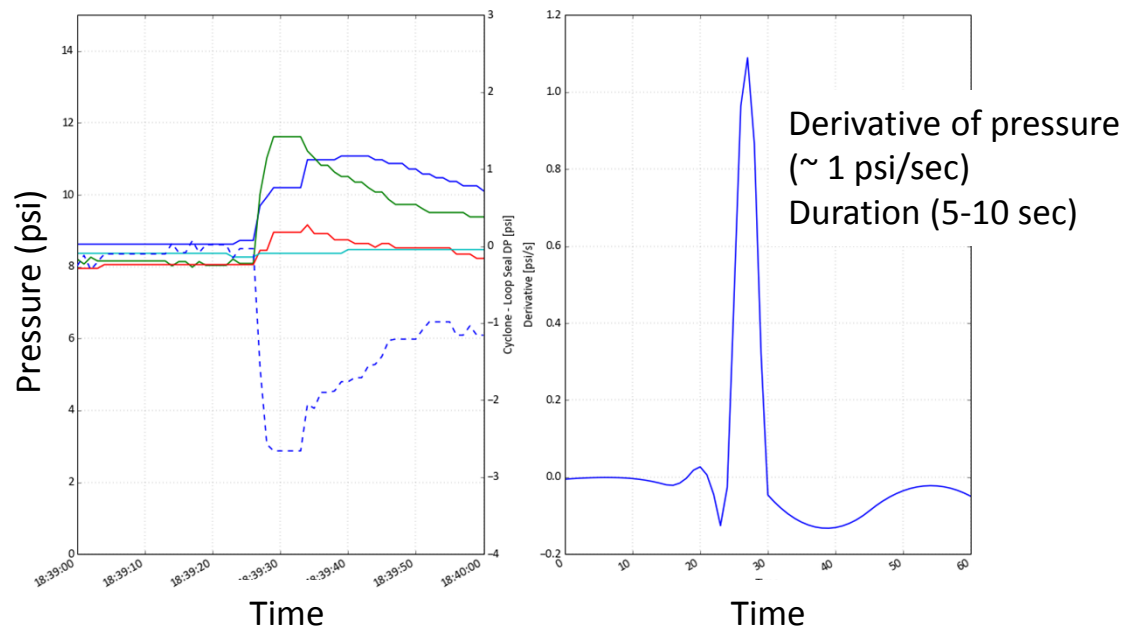
Summary – The Good, The Bad, and The Ugly

- **Temperature control is much easier than solids control**
- **When adding solids to the process**
  - Addition to the bottom of a fluidized bed was problematic
  - Pressure and flow control to/from lock-hopper was important
- **Refractory issues**
  - Internal leak paths have been observed (also discovered voids in refractory)
  - Fiberboard layer between refractory and inner wall of vessel
  - Non-mechanical valve design/operation required custom seal design
- **Solids plugging in straight vertical pipes and diplegs**
  - Not a permanent agglomeration effect
  - Dry particle interlocking (cannot be cleared with 20 psi pressure difference)
  - Changes to fluidization pattern have occured

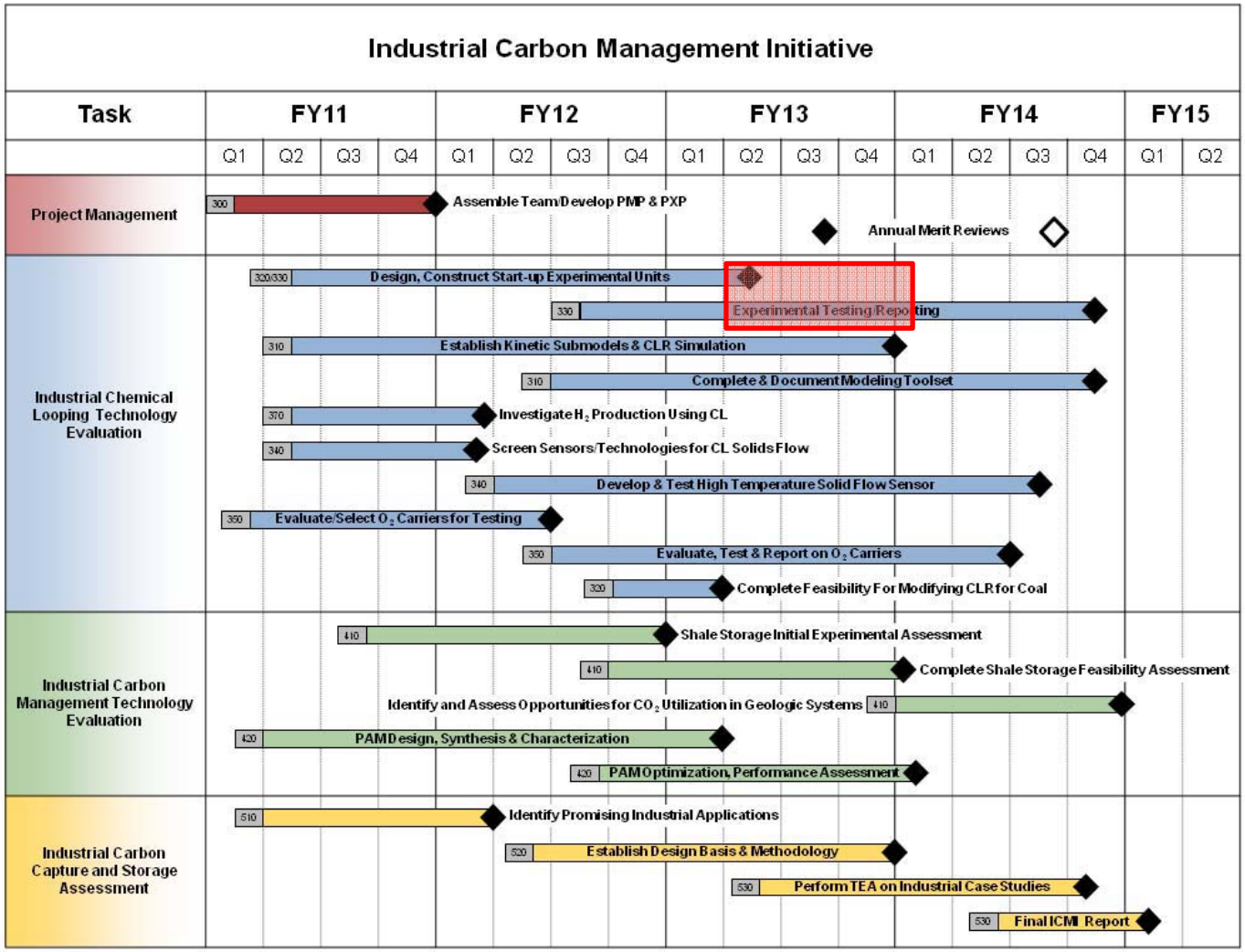
Summary – The Good, The Bad, and The Ugly

- **In a circulating system, pressure control is critical**
  - Eliminate valve hysteresis with position feedback controllers
  - Downstream filter changes can result in ugly process upsets,
- **Condensate issues complicate downstream components**
  - Condensate in the filter/screens
  - Condensate in the piping

Pressure Upset Condition



Extra Slides

ICMI Project Schedule

(Focus on a small part of overall effort)