



# NATIONAL ENERGY TECHNOLOGY LABORATORY



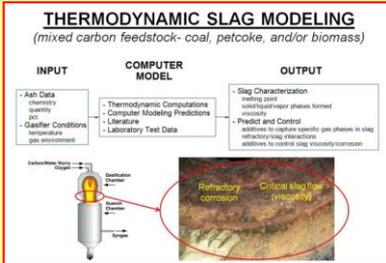
CSC Fouling



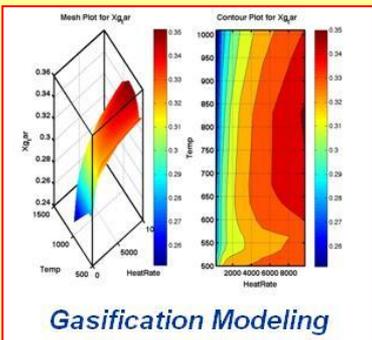
Refractory/TC Wear



RSC Fouling



## Research Efforts at NETL to Improve Gasifier Performance



James Bennett

National Energy Technology Laboratory – USDOE

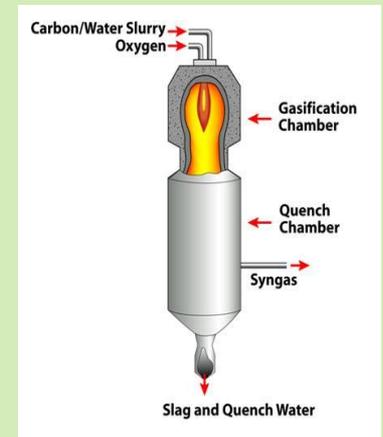
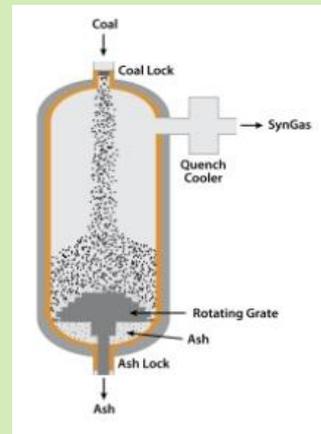
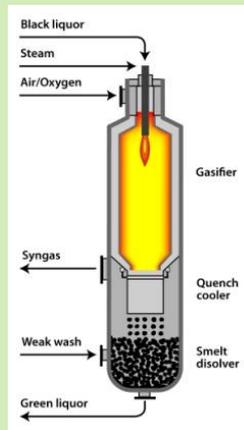
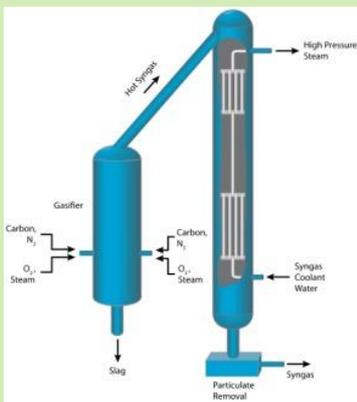
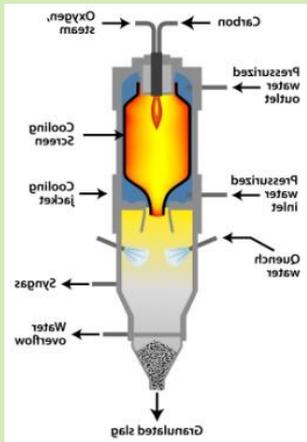
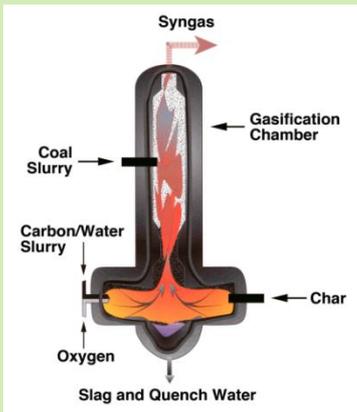
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# OUTLINE

- Research Objectives
- Program Overview
- Materials Research Focus (Refractories)
  - *Scope of work*
  - *Impact to date*
  - *Long range goals*
- Industrial Involvement
- Summary/Disclaimer

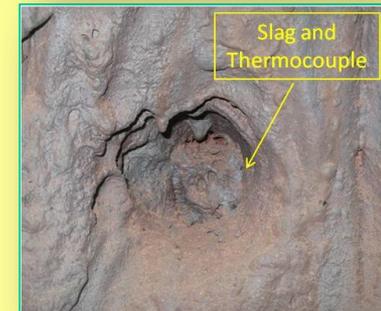
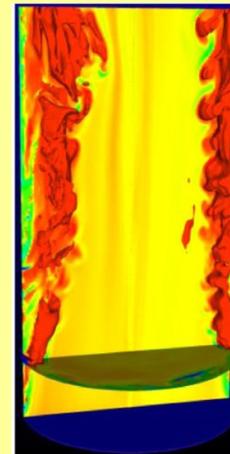
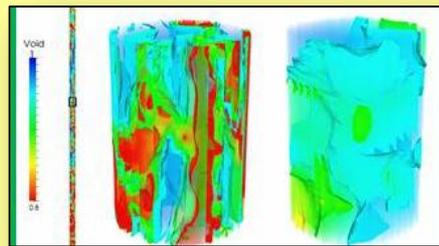
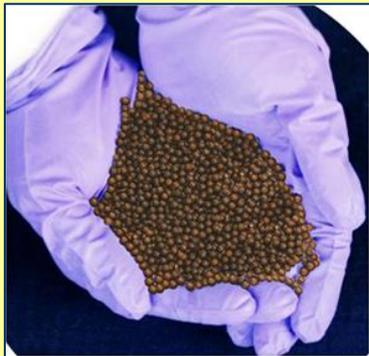


# Advanced Gasification

**Goals:** increase gasifier efficiency, reduce capital and operational costs, reduce cost of electricity, develop predictive gasifier models, meet/exceed EPA emission targets, and increase carbon feedstock flexibility (including U.S. low rank coals)

**Target:** work with industry to increase gasifier availability by 10 pct

**Program Approach:** 1) materials, 2) modeling, and 3) emissions

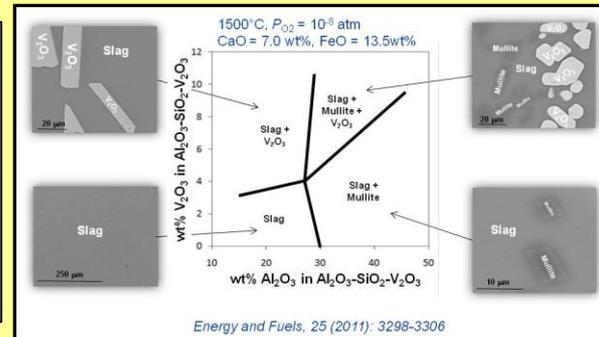
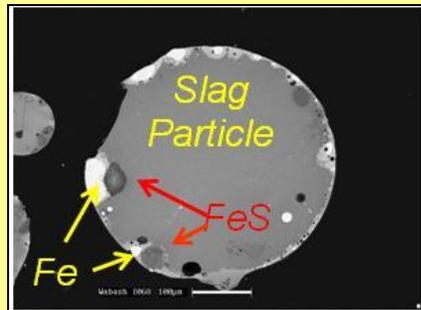


# 1) Materials

**Research Objective:** Improve the performance of existing materials/develop improved performance materials used in gasification systems - with the goal of increasing gasifier reliability, availability, and maintainability (decrease system downtime).

## Ongoing Research:

- high temperature molten ash phase study/thermodynamic determination
- slag management for control of slag viscosity and refractory/slag interactions
- study material wear/failure, develop improved performance materials/processes (gasifier liners, thermocouple sensors, syngas coolers)

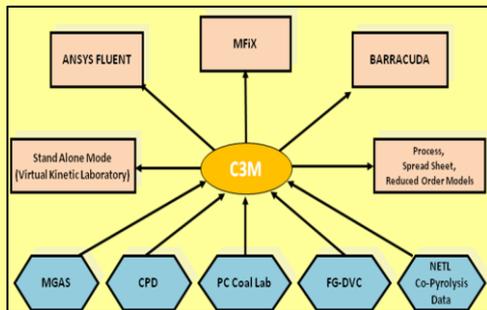


## 2) Modeling/Simulations

**Research Objective:** develop physics-based simulation models for conducting applied research on gasification systems. Models are based on kinetic software and real world data of carbon feedstock gasification.

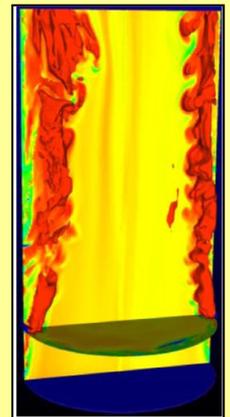
### Ongoing Research:

- provide a user friendly, comprehensive interface between reliable sources of kinetic data and reacting, multi-phase CFD models
- TARGETS: modeling a gasifier to a high degree of confidence and accuracy, modeling mixed carbon feedstock properties and behavior to assist in feedstock selection, and developing computer software in C3M and MFiX to provide significant insight in feedstock properties.



**MFiX – NETL developed open source software for gasification system prediction ≈ 3100 registered users**

**MFiX/C3M – available at:**  
<https://mfix.netl.doe.gov>

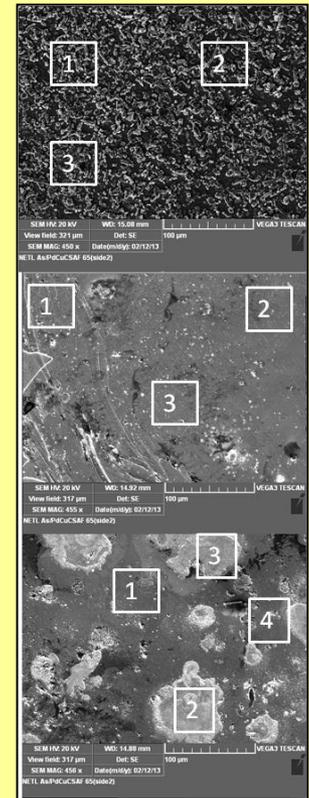
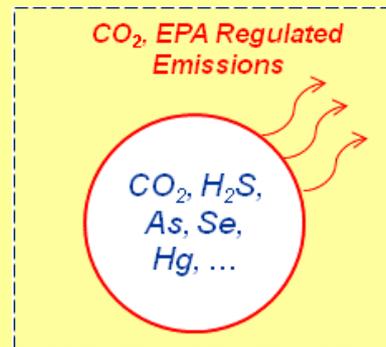
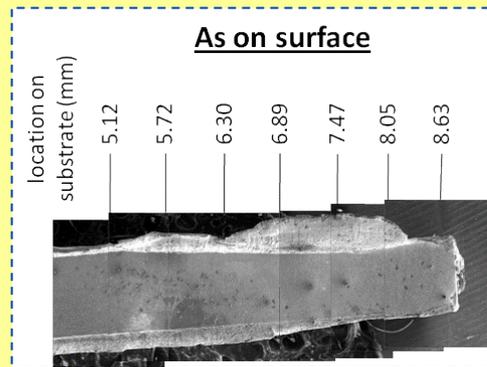


# 3) Emissions

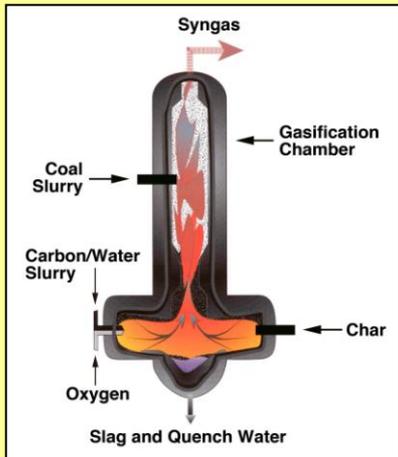
**Research Objective:** synthesis gas requires cleaning before use, must meet or exceed EPA regulations associated with toxic emissions from gasification processes by a cost effective process.

## Ongoing Research:

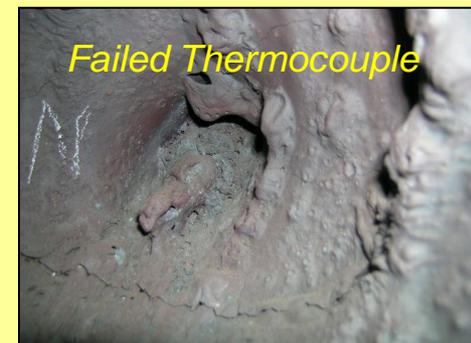
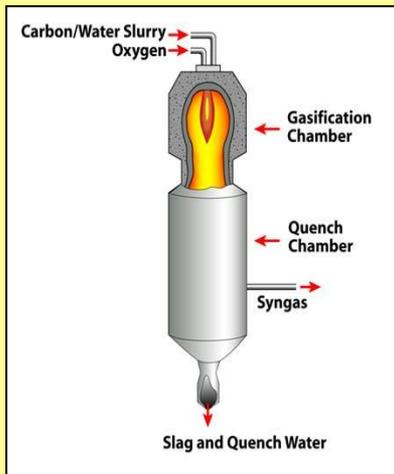
- field trials evaluated the use of Pd to remove Hg, As, Se, S from warm gases. Evaluating the rate of impurity removal, quantity of material removed, process cost
- researching lower cost alternative materials for selective ion removal



# Objectives - Refractory Material Development

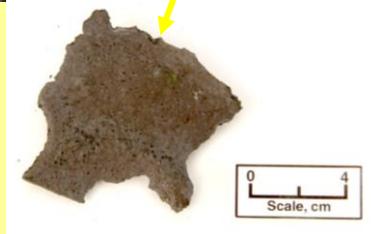
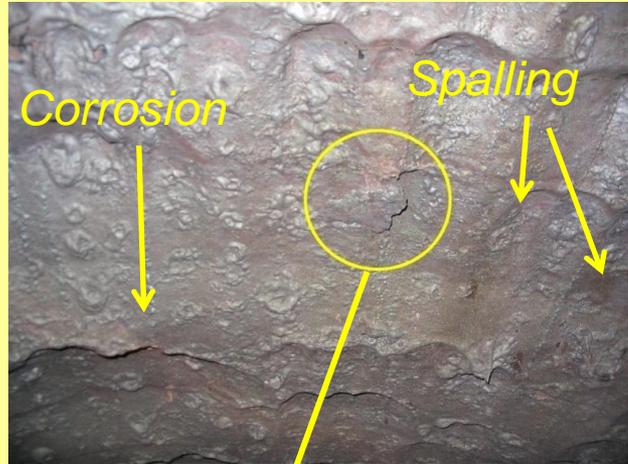


- **Develop refractories with improved performance** (*longer and predictable service life*)
- **Develop refractories that are environmentally friendly and cost effective** (*Cr+6*)
- **Develop refractories with carbon feedstock flexibility**
  - *characterize gasifier slag (chemistry, viscosity, slag phases)*
  - *control slag/refractory interactions and slag viscosity*
- **Develop reliable sensors** *that accurately monitor gasification temperature*
- **Model gasifier slag and refractory wear** (*maximize refractory service life, correct slag fluidity, determine additives to control slag properties and refractory wear*)

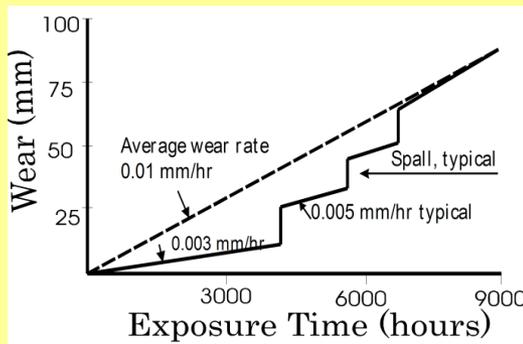


# Current Wear Mechanisms

(Corrosion and Spalling – refractory service life = 3-36 months)



**Spalled Material**



**Impact of Spalling**

Stage	Sample	Description
1		<b>New</b> <ul style="list-style-type: none"> <li>Refractory may contain internal cracks from pressing, firing.</li> </ul>
2		<b>Preheat</b> <ul style="list-style-type: none"> <li>Pinch spalling due to hoop stresses</li> </ul>
3		<b>Infiltration, Corrosion</b> <ul style="list-style-type: none"> <li>Molten slag infiltration on hot face, cracks and pores.</li> <li>Surface corrosion due to slag begins</li> </ul>
4		<b>Horizontal Crack Formation due to:</b> <ul style="list-style-type: none"> <li>Thermal cycling</li> <li>Stress accumulation</li> <li>Creep</li> </ul>
5		<b>Void Formation</b> <ul style="list-style-type: none"> <li>Cracks join</li> <li>Internal void formation</li> <li>Spalling (peeling) begins</li> <li>Creep occurs on slag penetrated hot face</li> <li>Hot face corrosion continues</li> </ul>
6		<b>Renewed Cycle</b> <ul style="list-style-type: none"> <li>Material breakoff on hot face</li> <li>Steps 3-5 repeat</li> </ul>

**Repeative Cycle of Spalling**

# NETL-Refractory Research for Improving the Reliability and Performance of Gasification

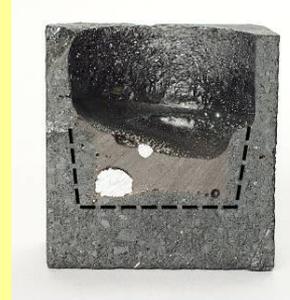
## Failure mechanisms Identified



Spent refractory from commercial gasifier



## Chromium-Oxide based Composition Developed at NETL



NETL-develops and patents chromium-oxide refractory in laboratory tests resists failure mechanism



## NETL Refractory Scales up for Field Trials in Comm. Gasifiers

**Product Data**

AUREX® 95 P

Classification: Chrome - Alumina Brick

Apparent Porosity, %: 12.3

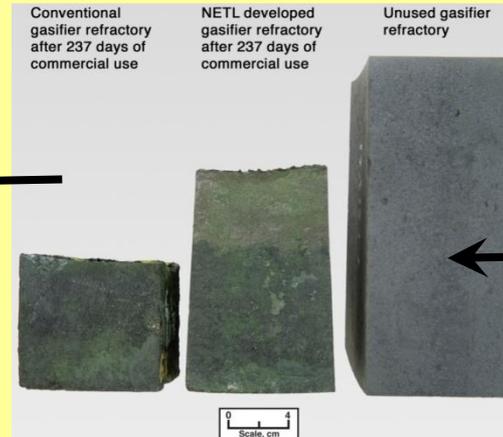
Chromium Oxide (Cr<sub>2</sub>O<sub>3</sub>): 92.0

Phosphorous Pentoxide (P<sub>2</sub>O<sub>5</sub>): 3.3

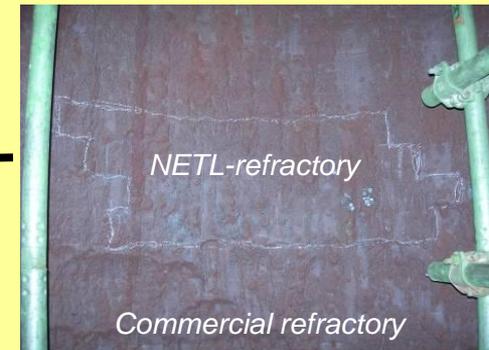
Licensing agreement signed

production. The test data cannot be taken as minimum or maximum values for specification purposes. ASTM test procedures used when applicable.

**Technology Transfer**  
**NETL-ENGINEERED**  
**ADVANCED REFRACTORY**  
**FOR SLAGGING GASIFIERS**



Bricks after 237 of operation

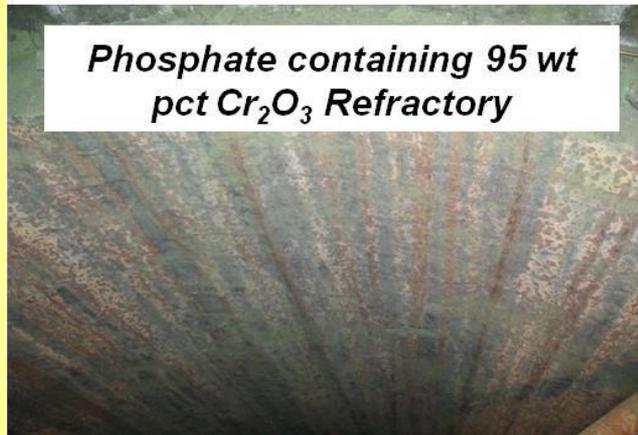


**NETL developed phosphate containing high Cr<sub>2</sub>O<sub>3</sub> refractory marketed by Harbison and Walker Refractory Co. under the product name Aurex 95P.**

# Commercial Performance of Phosphate Containing High Cr<sub>2</sub>O<sub>3</sub> Refractory



*Conventional 90 wt pct Cr<sub>2</sub>O<sub>3</sub> Refractory*



*Phosphate containing 95 wt pct Cr<sub>2</sub>O<sub>3</sub> Refractory*



Conventional gasifier refractory after 237 days of commercial use

NETL developed gasifier refractory after 237 days of commercial use

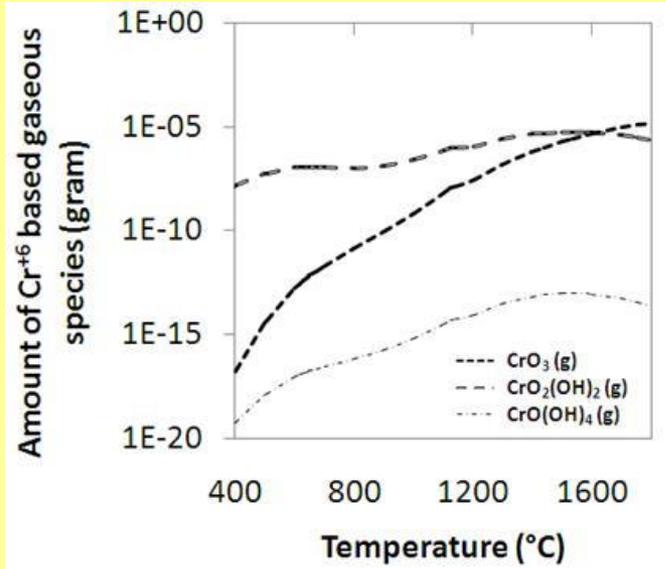
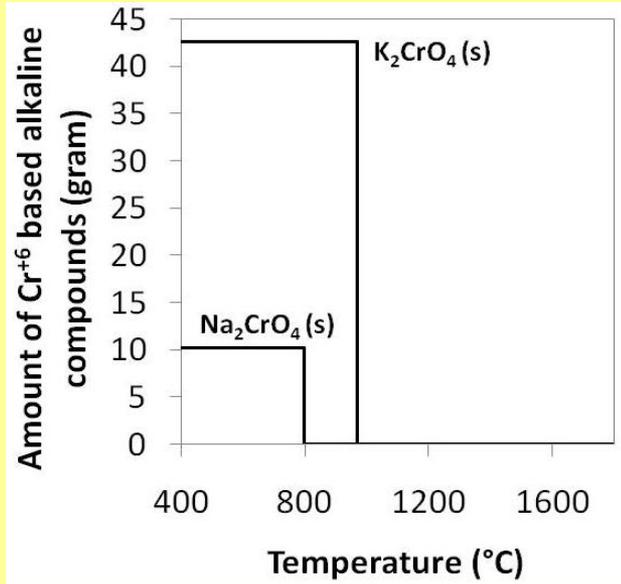
Unused gasifier refractory

0 4  
Scale, cm

**Gasifier Refractory Lining**  
*(3 Years Service)*

# Chrome Oxide Refractory Research ( $\text{Cr}^{+6}$ )

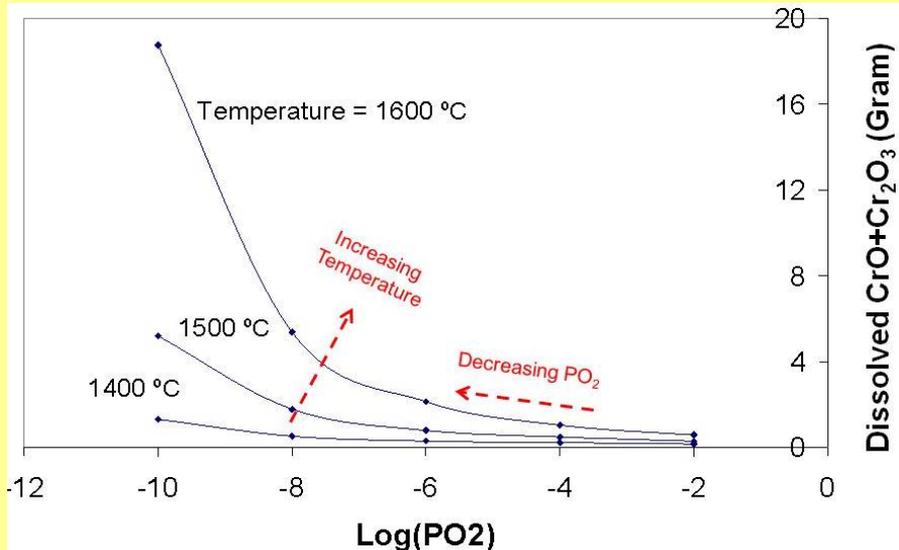
**Atmospheric  
 $\text{O}_2$  Partial  
Pressure**



**$10^{-8}$   $\text{O}_2$   
Partial  
Pressure  
(Gasifier  
Condition)**

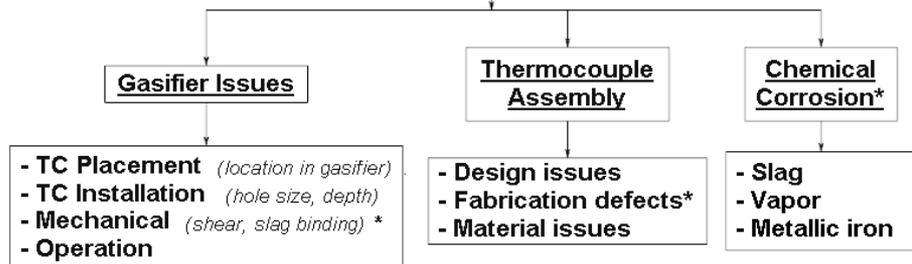
**$\text{Cr}^{+6}$  formation  
not an issue with  
current carbon  
feedstock**

**90 Wt %  
 $\text{Cr}_2\text{O}_3$  – 10 wt  
pct  $\text{Al}_2\text{O}_3$  //  
Slag,  
Temperature,  
and Oxygen  
Partial  
Pressure  
Interactions**



# Sensor Research – Refractory Filler

## Thermocouple Failure



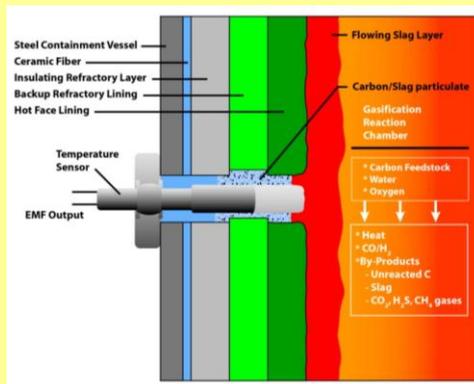
\* = Possible refractory related issue

- Determine causes of failure – evaluate TC assemblies from several gasifier sites.
- Evaluating interaction of gasifier environment with thermocouple assembly and components

## Causes of thermocouple failure

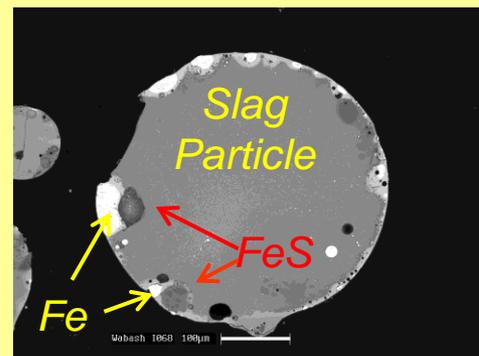


Thermocouple shear, slag/refractory corrosion



Thermocouple assembly

## Syngas, Slag, Char, and Fe interact with Pt



# Current Program Emphasis – Slag Management

*(mixed carbon feedstock- coal, lower grade western coal, petcoke)*

## INPUT

- Ash Data  
chemistry  
quantity  
pct.
- Gasifier Conditions  
temperature  
gas environment

## COMPUTER MODEL

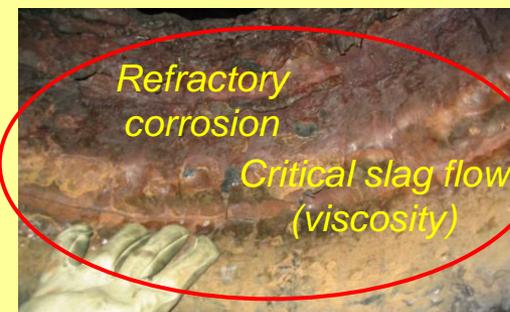
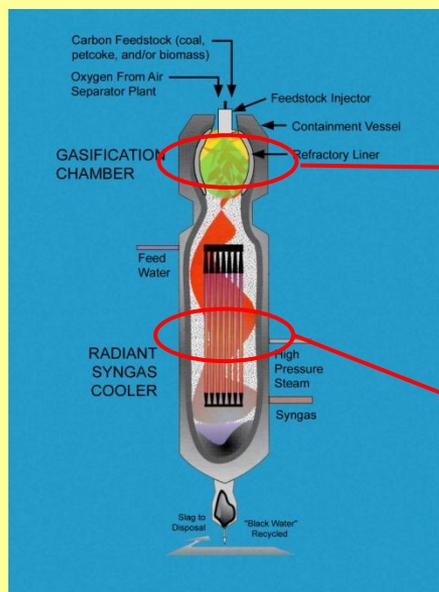
- Thermodynamic Computations
- Computer Modeling Predictions
- Literature
- Laboratory Test Data

## OUTPUT

- Slag Characterization  
melting point  
solid/liquid/vapor phases formed  
viscosity
- Predict and Control  
additives to capture specific gas phases in slag  
refractory/slag interactions  
additives to control slag viscosity/corrosion

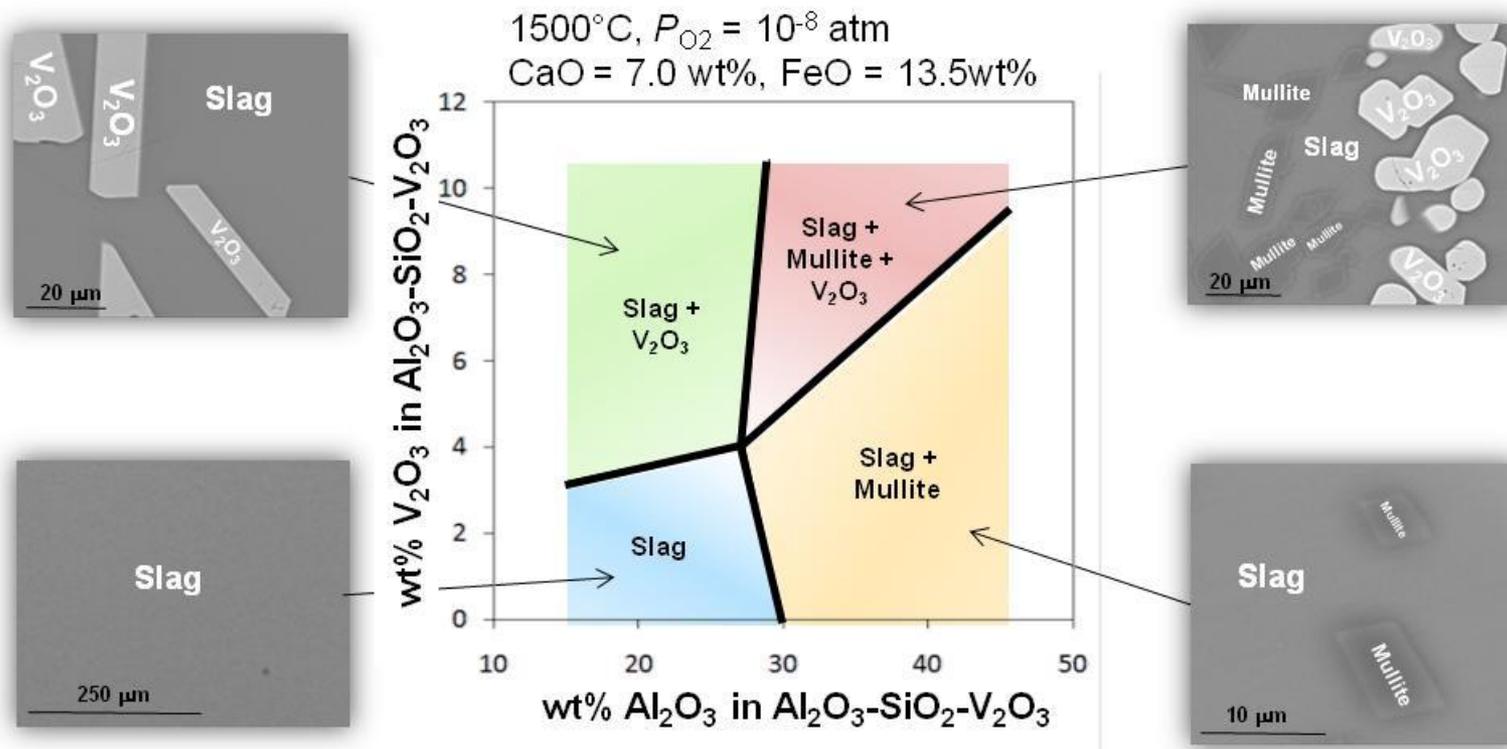
## GOALS

- **Primary** – control refractory wear and slag flow
- **Secondary** - minimize syngas cooler fouling



# Phase Diagram/Thermodynamic Research

(vanadium oxide phase study)



*Energy and Fuels*, 25 (2011): 3298-3306

American Ceramic Society Spriggs Award

## Slag

- Impacts gasification temperature
- Refractory wear
- Lack of vanadium thermo data for predictive modeling

# **PARTNERSHIPS/AGREEMENTS**

*(Refractory Program)*

- **NDA's – 2 gasifier sites**
- **Confidentiality – one gasifier site**
- **Academia – CMU, WVU, McGill Univ. Penn State, University of Tokyo, Chiba Institute of Technology**
- **Commercial – FactSage™, ExxonMobile, BP**
- **Government Agencies – CanmetENERGY, Canadian Light Source**

**Industrial cooperation in all aspects of the Advanced Gasification Program is encouraged and welcomed. Confidentiality agreements, cooperative research and development agreements, non-disclosure agreements, or other forms of joint research can be arranged.**

## Summary

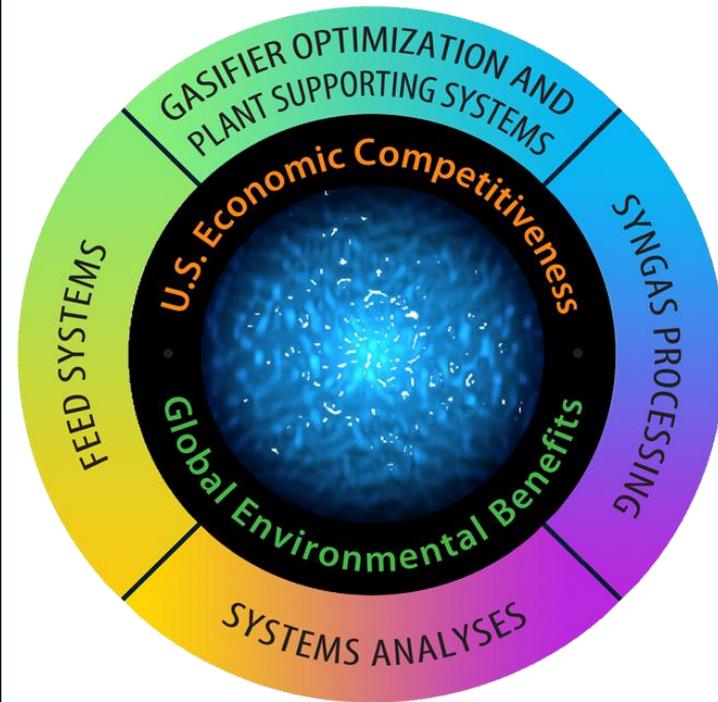
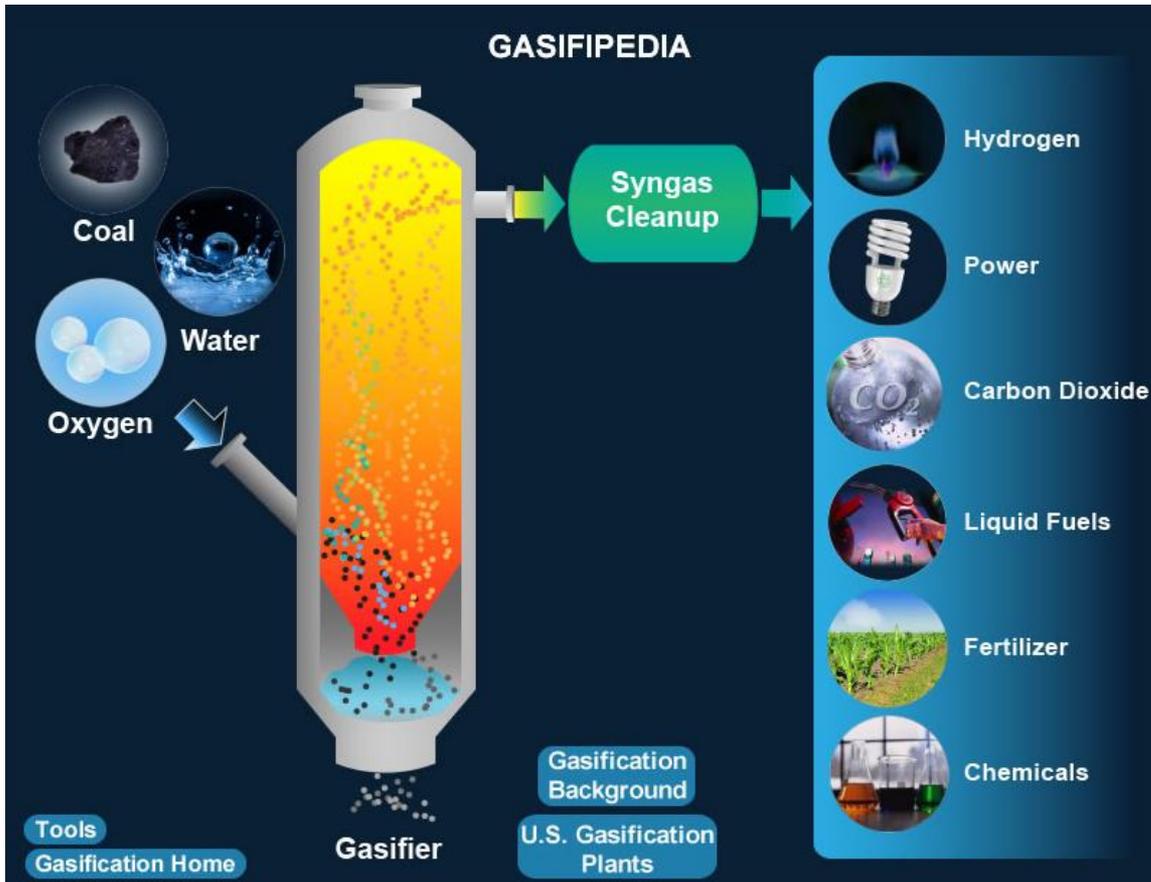
- Overview given of the Advanced Gasification Research Program within NETL related to
  - materials
  - modeling
  - emissions
- Refractory research success and future direction described (liner material development, sensor protection, and slag modeling for wear and corrosion, Cr+6)
- Industrial involvement welcomed – need for more producers/users in program research
- Contact information: James Bennett; National Energy Technology Laboratory; [james.bennett@netl.doe.gov](mailto:james.bennett@netl.doe.gov); 541-967-5983

# Visit NETL Gasification Website

[www.netl.doe.gov/gasification-portal.html](http://www.netl.doe.gov/gasification-portal.html)



Google the term “Gasifipedia” 



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