Research Efforts at NETL to Improve Gasifier Performance

James Bennett
National Energy Technology Laboratory – USDOE
E-Mail: james.bennett@netl.doe.gov
Phone: 541-967-5983
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)

Contact: James Bennett, NETL, james.bennett@netl.doe.gov 541-967-5983
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](https://mfix.netl.doe.gov)

Contact: Bill Rogers, NETL, william.rogers@netl.doe.gov, 304-285-4272
### 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

Contact: Evan Granite, NETL, evan.granite@netl.doe.gov 412-386-4607
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*)

Failed Refractory Material

Failed Thermocouple
Current Wear Mechanisms
*(Corrosion and Spalling – refractory service life = 3-36 months)*

**Spalled Material**

**Impact of Spalling**

- Corrosion and Spalling
- Refractory service life = 3-36 months

**Stage** | **Sample** | **Description**
--- | --- | ---
1 |  | New
- Refractory may contain internal cracks from pressing, firing.
2 |  | Preheat
- Pinch spalling due to hoop stresses
3 |  | Infiltration, Corrosion
- Molten slag infiltration on hot face, cracks and pores.
- Surface corrosion due to slag begins
4 |  | Horizontal Crack Formation due to:
- Thermal cycling
- Stress accumulation
- Creep
5 |  | Void Formation
- Cracks join
- Internal void formation
- Spalling (peeling) begins
- Creep occurs on slag penetrated hot face
- Hot face corrosion continues
6 |  | Renewed Cycle
- Material breakoff on hot face
- Steps 3-5 repeat

---

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

NETL-developed phosphate containing high Cr$_2$O$_3$ refractory marketed by Harbison and Walker Refractory Co. under the product name Aurex 95P.
Commercial Performance of Phosphate Containing High Cr$_2$O$_3$ Refractory

Conventional 90 wt pct Cr$_2$O$_3$ Refractory

Phosphate containing 95 wt pct Cr$_2$O$_3$ Refractory

Gasifier Refractory Lining (3 Years Service)
Chrome Oxide Refractory Research (Cr\(^{+6}\))

**Atmospheric \(O_2\) Partial Pressure**

- **Amount of Cr\(^{+6}\) based alkaline compounds (gram)**
  - \(K_2CrO_4(s)\)
  - \(Na_2CrO_4(s)\)
  - Temperature (°C)

- **Amount of Cr\(^{+6}\) based gaseous species (gram)**
  - \(CrO_3(g)\)
  - \(CrO_2(OH)_2(g)\)
  - \(CrO(OH)_4(g)\)
  - Temperature (°C)

- **90 Wt % \(Cr_2O_3 – 10 \text{ wt} \text{ pct } Al_2O_3 // Slag, Temperature, and Oxygen Partial Pressure Interactions**

- **Cr\(^{+6}\) formation not an issue with current carbon feedstock**

- **10\(^{-8}\) \(O_2\) Partial Pressure (Gasifier Condition)**
Sensor Research – Refractory Filler

- 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

Different lining movement causes shear

Thermocouple shear, slag/refractory corrosion

Syngas, Slag, Char, and Fe interact with Pt

Thermocouple assembly

FeS

Fe
Current Program Emphasis – Slag Management
(mixed carbon feedstock- coal, lower grade western coal, petcoke)

**GOALS**
- **Primary** – control refractory wear and slag flow
- **Secondary** - minimize syngas cooler fouling
Phase Diagram/Thermodynamic Research
(vanadium oxide phase study)

1500°C, $P_{O_2} = 10^{-8}$ atm
CaO = 7.0 wt%, FeO = 13.5 wt%

---

American Ceramic Society Spriggs Award

- 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; 541-967-5983
Visit NETL Gasification Website
www.netl.doe.gov/gasification-portal.html

Google the term “Gasifipedia”
DISCLAIMER:

"This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."