



# Biomass Program

## Refractory for Black Liquor Gasifiers

Black liquor can be highly corrosive and process equipment such as the reactor vessel, heat exchanger tubes, and hot-gas filters must be resistant to the severe thermal and chemical process conditions. The primary objective of this project was to develop cost-effective materials to address the material challenges presented by black liquor gasification.

Researchers investigated and analyzed various refractory materials to determine how well they perform in the severe gasifier operating environment. Emphasis was placed on functional properties, longevity and stability of materials, and economics.

### R&D Pathway

Refractory materials were selected based on their capability to meet at least one of these criteria: (1) ability to react with the gasifier environment to form protective surfaces in-situ; (2) functionally-graded to give the best combination of thermal, mechanical, and physical properties and chemical stability; or (3) relatively inexpensive, reliable materials.

Material property analyses were conducted on the selected materials. These included

microstructural and phase analysis, measurement of bulk physical properties for comparison of corrosion resistance, and measurements of both the contact angle between the refractory and the smelt and the depth of smelt penetration at elevated temperatures.

Materials considered included:

- Aluminum oxide ( $\text{Al}_2\text{O}_3$ )
- Cerium oxide ( $\text{CeO}_2$ )
- Magnesium oxide ( $\text{MgO}$ )
- Calcium oxide ( $\text{CaO}$ )
- Zirconium oxide ( $\text{ZrO}_2$ )
- Lithium oxide ( $\text{Li}_2\text{O}$ )
- Yttrium oxide ( $\text{Y}_2\text{O}_3$ )
- Lanthanum oxide ( $\text{La}_2\text{O}_3$ )
- Lithium aluminum oxide ( $\text{LiAlO}_2$ )
- Barium aluminate ( $\text{BaAl}_2\text{O}_4$ )
- Magnesium aluminate ( $\text{MgAl}_2\text{O}_4$ )
- Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ )

$\text{MgAl}_2\text{O}_4$  showed the highest contact angle with sodium carbonate while  $\text{MgO}$  showed the highest contact angle with potassium carbonate. Contact angle indicates the tendency of a liquid to form droplets on the solid surface (angle greater than  $90^\circ$ ) or spread out over the surface (angle less than  $90^\circ$ ). For refractory materials, a higher contact angle is desired.

Although  $\text{CeO}_2$  and  $\text{MgO}$  did not show high contact angles with sodium and potassium carbonate, they did demonstrate chemical stability with both smelts.

## Thermochemical R&D

### Benefits

- **Increased reliability of black liquor gasification systems**

### Applications

**Improved refractory materials for black liquor gasifiers will increase system reliability and contribute to greater economic viability of the process.**

### Project Partners

University of Missouri-Rolla

### Project Period

FY 2003 – FY 2006

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