Overview of Refractories

for

Slagging Gasifier Applications

Facts, Research Review, and Needs

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Outline of Talk

- Refractory Facts and Trends
- Review of Previous Refractories Research for Slagging Gasifiers
- Refractories Research Issues
- Points to Consider for Slagging Gasifiers

Refractories are the

"BACKBONE OF INDUSTRY"

because they are essential for all thermal and chemical processing worldwide

Refractories are Variable materials because their manufacture involves:

- A multiple step process
- Heterogeneous, multi-component raw materials
- Size-graded raw materials
- Processing equipment
- People

- NOTE – Metals are standardized, so generic data are usable, but refractories are not the same.

Elements of Refractory Structure

1. Aggregate
2. Bonding Matrix
3. Aggregate/Matrix Interface
4. Porosity/ Microcracks
5. Bulk (Composite) Structure

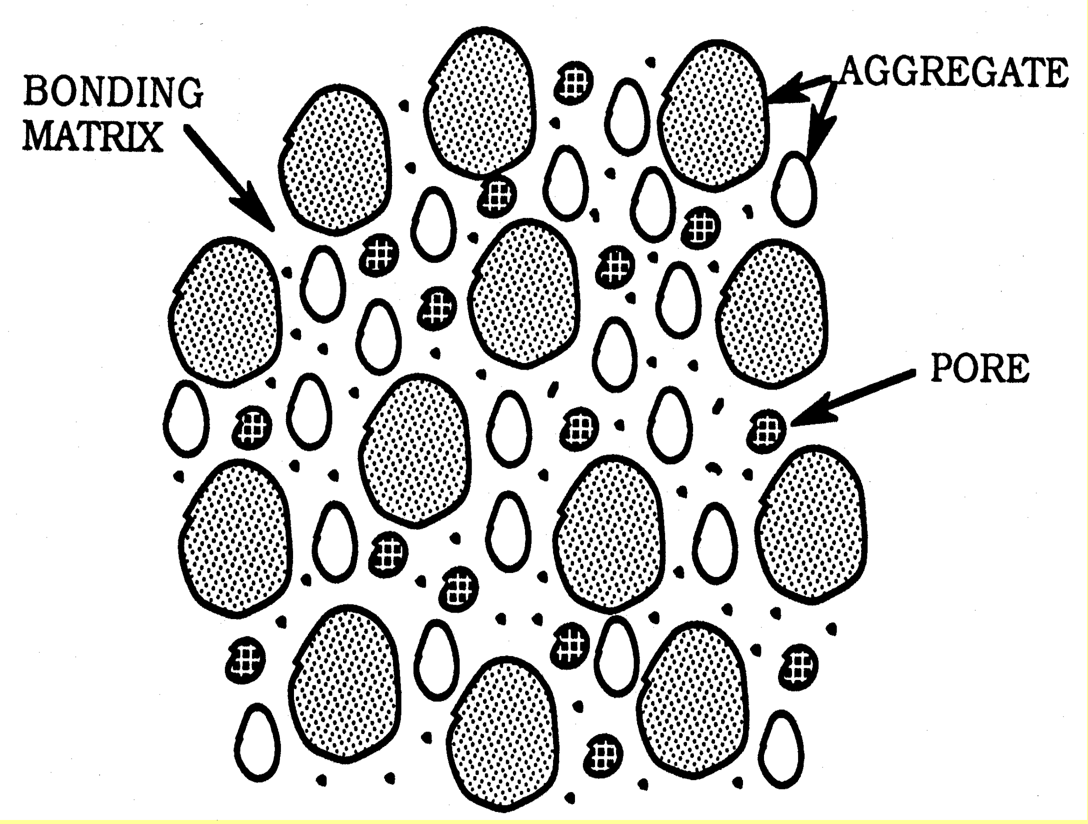
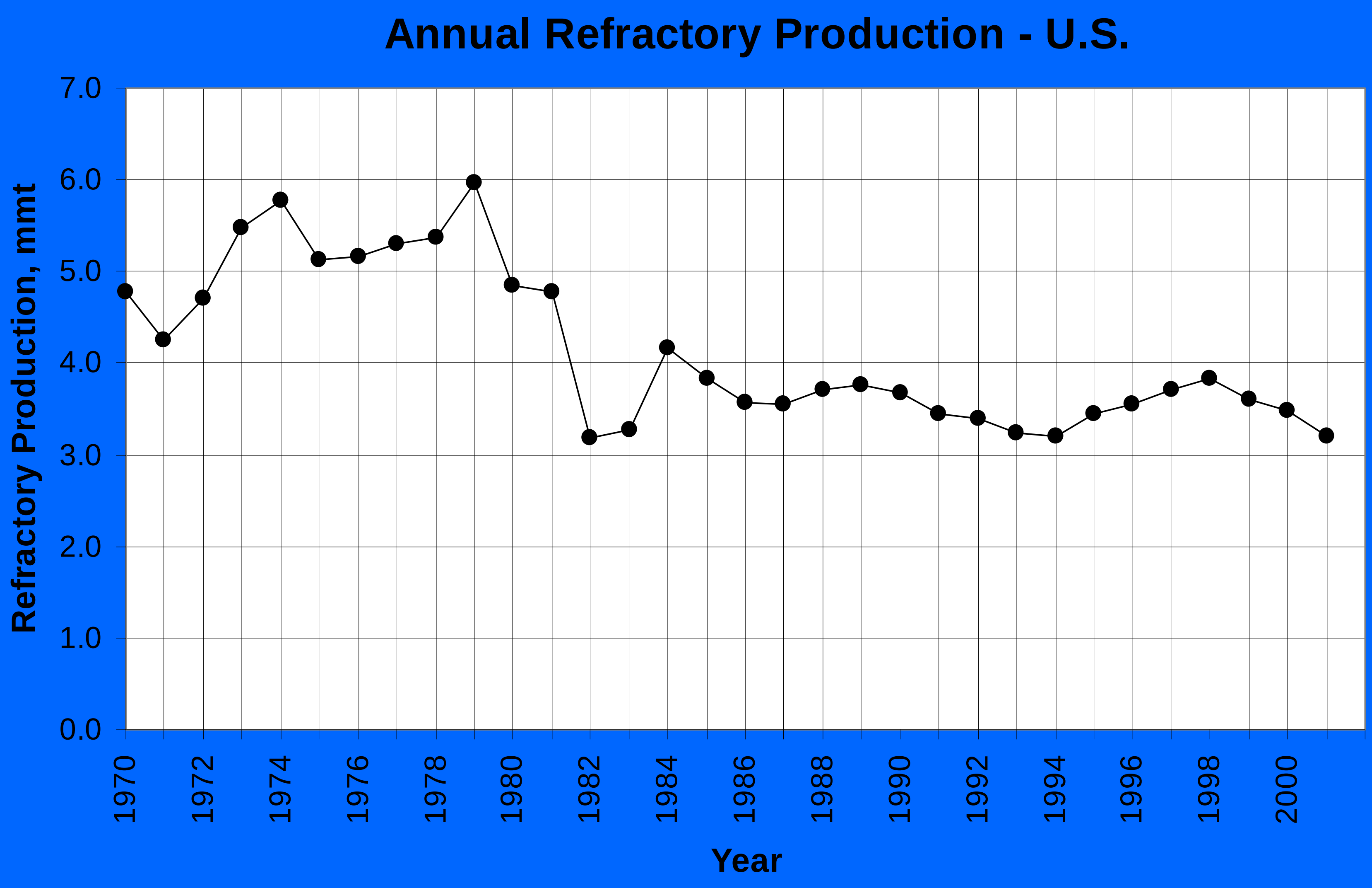


Figure 1. Schematic Representation of Refractory Microstructure

Refractory consumption rate has continually decreased in all industries

- Continuous improvement of refractories
- Improved refractories have longer service life
- Common that consumption rate has been reduced by 50% or more
- Global overcapacity of refractory production
- Consolidation and downsizing
- Emphasis has shifted from quantity to value
- Less research and service

General Decline in Refractory Production



Refractory Raw Materials

- More use of high purity, synthetic materials
- Greater attention to particle sizing
- More use of ultrafine materials
- Control of aggregate shape
- Microstructure engineering is important
- Spinel (e.g. $MgAl_2O_4$) - Primary & In-Situ

Advances in Monolithic Refractories

1. Castables – Traditional, LCC, ULC, NCC
2. Properties can be better than pressed bricks
3. Production and use now exceeds bricks!!
4. Installation methods have been improved
5. Ability to install in “Hot Standby” mode
6. New applications are frequent

Selected Refractory Facts

- Reaction/wear increases exponentially with increasing temperature
- Temperature cycling will cause cracks, loss of strength, and spalling of material
- Tradeoffs are common in refractories
- Stronger is not always better
- Lining life is controlled by the “weakest link”
- Shorter service life can be more cost effective

Refractories Research for Slagging Gasifiers

- M. Crowley, Standard Oil, BACS 54 (12) 1975

  "Future reactors are apt to experience slag attack, erosion by fluidized particles, thermal shock, and other destructive forces. Designers will have to be very critical in their selection of materials to insure a successful lining."

- 1st International Conference on Materials for Coal Conversion and Utilization. NBS-1977

Refractories Research for Slagging Gasifiers

C. Kennedy, Argonne – 1975-1977

- Evaluated commercial refractories (15) under conditions expected in slagging coal-conversion systems. Fusion-cast 80% chromia magnesia spinel was most slag resistant, but thermal shock resistance was suspect. SiC probably not stable in coal gasification atmospheres.

- Test method did not provide sufficient distinction between refractories.

Refractories Research for Slagging Gasifiers

- W. Bakker, EPRI, BACS 62 (12) 1983

  Slagging gasifiers operate at high temp. and the coal ash is removed as liquid slag. The viscosity of the liquid slag must be sufficiently low to permit slag tapping.

- W. Bakker, EPRI, BACS 63 (7) 1984

  Major factors affecting refractory performance are temp., coal ash composition, gas composition, slag velocity and turbulence, and thermomechanical stresses. Operating temperature is probably the most important factor.

Refractories Research for Slagging Gasifiers

E. Chen and O. Buyukozturk, MIT, BACS 64 (7) 1985

- Slag attack of refractories involves – dissolution or diffusion, penetration, and erosion
- A predictive model was developed for long-term corrosion behavior of refractories in slagging gasifiers
- Model was applied to 90% alumina and 80% chromia
- Can extrapolate results of short-term corrosion tests to predict long-term corrosion behavior, including spalling
- Can be used with other analyses (economics, operations, efficiency, etc.) for gasifier optimization.

S. Greenberg & R. Poeppel, Argonne, 1986

- Knew that >55% chromia refractories had superior corrosion resistance in coal-ash slag.
- Used rotating cylinder slag test: 1480°C – 1600°C
- Slag viscosity was not a significant factor in refractory corrosion. Slag temp. and composition more important.
- 60-80% chromia were little affected at 1500°C, but more distinction observed at 1600°C.
- Fusion-cast 80% chromia-MgO showed best corrosion resistance. Sintered 80% chromia-MgO and 75% chromia-alumina had low corrosion and less costly.

Refractories Research for Slagging Gasifiers

C. Dogan, et.al, DOE-Albany, Ind. Heating, 9/02

- “Widespread adoption of coal gasification by the power generation industry depends on whether reliability and gasifier operations/economics issues can be resolved.”
- Slagging gasifier linings are typically replaced after 10-18 mos., at a cost up to $2 mil. The gasifier is off-line for 3-4 weeks for the lining exchange.
- Structural spalling is a prime failure mechanism in slagging gasifiers, due to cracking, penetration, reaction, and slabbing.

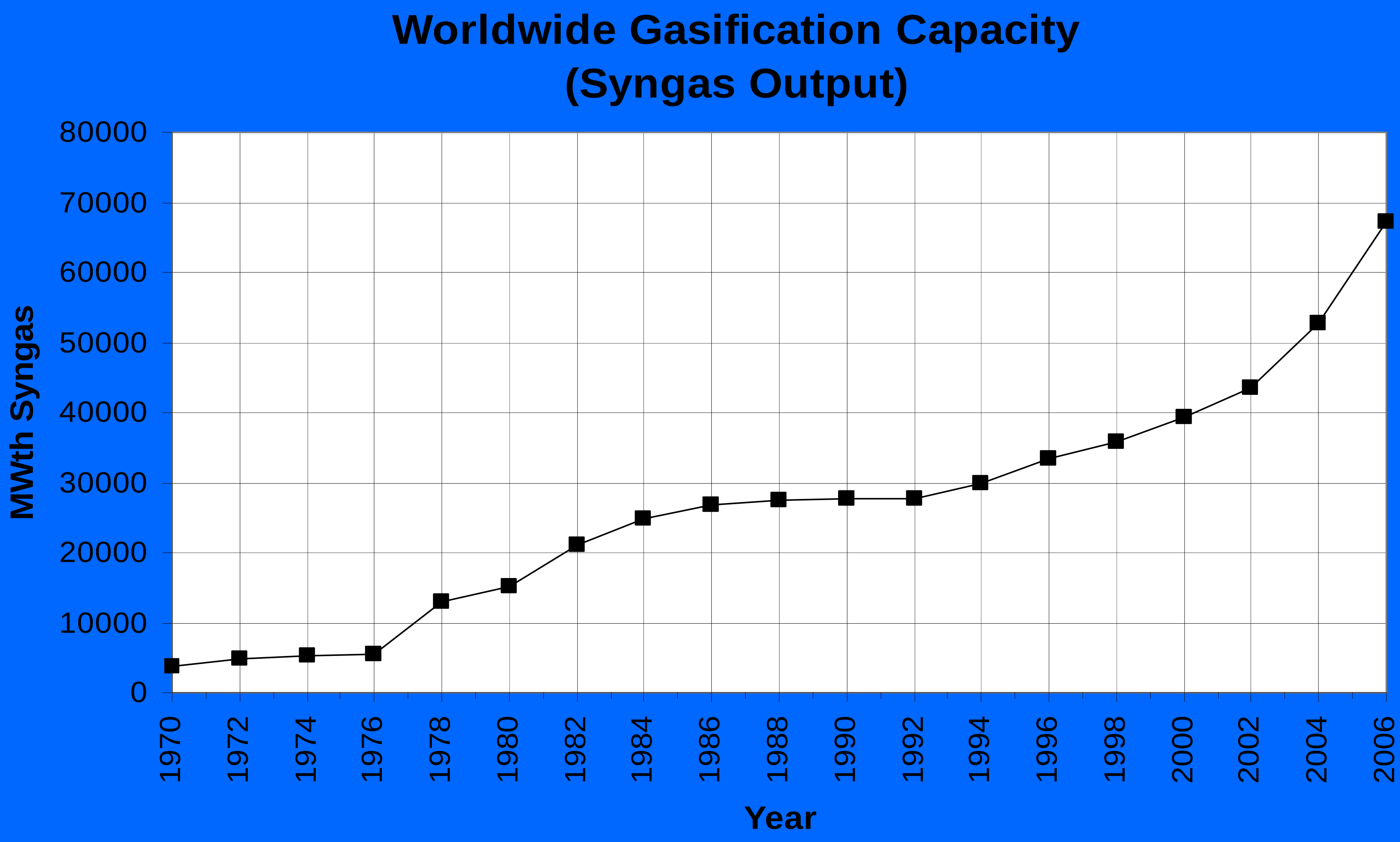
Refractories Research for Slagging Gasifiers

C. Dogan, et.al, DOE-Albany, Ind. Heating, 9/02

- Ways to reduce slag penetration –
  - Change wetting characteristics of slag
  - Reduce wettability of refractory
  - Reduce interconnected porosity in refractory
  - Change the pore-size distribution
  - Induce in-situ microstructure changes to seal the refractory

80% chromia brick with phosphate additive had much less slag penetration than 90% chromia brick, after 24 hrs. at 1600°C. Could double the service life.

Trend in Slagging Gasifiers



Top 10 Commercial Gasification Projects

	Location	Gasifier	MWth Syngas
1.	S. Africa	Lurgi	5,090
2.	S. Africa	Lurgi	5,090
3.	USA	Texaco	2,761
4.	USA	E-Gas	2,029
5.	USA	Lurgi	1,900
6.	Spain	Texaco	1,654
7.	USA	Texaco	1,407
8.	USA	Texaco	1,400
9.	USA	Texaco	1,367
10.	Italy	Texaco	1,217
		Total	23,915

D. Simbeck, "World Gasification Survey", Pittsburgh Coal Conference, Newcastle, NSW, 4/01

Important Refractories Research Topics

- Raw materials and additives
- Particle sizing and shape
- Phase equilibrium (experimental and computer)
- Microstructure (including optical microscopy)
- Testing – more hot data and simulated exposure
- Modeling/Finite element analysis
- Manufacturing and installation

Points for Consideration - Gasifiers

1. Develop Cr-free bricks (Health/Environmental liability)
   - Steel ladle sidewall refractory research
   - Consider prescription spinel compositions
   - Optimum brick/shape size (life, manfacturing, etc.)
   - Role of mortar in brick lining degradation
2. High-Tech castables (Possibly better than bricks)
   - Quick, automated, computerized installation possible
   - Everlasting lining concept (less refractory waste)
   - Shorter lining life may be more cost effective
   - Pre-cast and cured (microwave) blocks

Points for Consideration - Gasifiers

3. Slag control and coating options

4. Document specific variations in gasifier operations to clearly establish refractory material/lining requirements

5. Given the anti-oxidation advances, could C-containing refractories (not wet by slag) be considered?

6. Initiate the evaluation of novel refractory products

7. Increase the data base of hot refractory properties

Points for Consideration - Gasifiers

8. Re-evaluate the effect of lining design on the lining life and gasifier operation and efficiency

9. Develop new, or apply existing, methods for external monitoring of lining thickness and temperature

10. Organize a forum to review the current facts and other research/experience, to establish the best path or paths forward

<u>“Innovations in Materials Design”</u>

AFRL Technology Horizons, March 2000, p. 20

“For millenia, materials have been developed by empirical correlation of processing and properties. With increased cost of experiments and decreased cost of computation, there is more reason to base materials design/discovery on science-based models, and a minimum of experiments..”