The Overview of the Refractory Technology from the Mini-Mill Application Perspective

Tomas Richter
General Manager Europe
HarbisonWalker International
Content

1. Type of Refractories
2. Raw Materials
3. Bonding Systems
4. Manufacturing Process
5. Wear Mechanisms
6. Standard Brick Shapes and Anchors
7. EAF Refractory Lining Considerations
8. Ladle Refractory Lining Considerations
9. Tundish Refractory Lining Considerations
Type of Refractories

Shaped Products
- Hydraulic Press
- Fused Cast
- Isostatic Press
- Assem. w/cast.

Unshaped Products
- Gunning Mixes
- Vibratables
- Cast-ables
- Mortars
Type of Refractories

Shaped Products

- Hydraulic Press
- Fused Cast
- Isostatic Press
- Prefab Shapes
Type of Refractories

Unshaped Products

Monolithics

- Gunning Mixes
- Dry Vibratables
- Castables
- Mortars
# Manufacturing Process - Refractories

<table>
<thead>
<tr>
<th>RAW MATERIALS</th>
<th>MIXING</th>
<th>SEMI-FINISHED PRODUCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHAPING</td>
<td>TEMP. TREATMENT</td>
<td></td>
</tr>
</tbody>
</table>

**Final Product**  
**BRICKS**

**At Customer Site**

<table>
<thead>
<tr>
<th>MIXING</th>
<th>SHAPING</th>
<th>TEMP. TREATMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNOW-HOW</td>
<td>Equipment</td>
<td>Machinery Service etc.</td>
</tr>
</tbody>
</table>

**MIXES**

<table>
<thead>
<tr>
<th>RAW MATERIALS</th>
<th>MIXING</th>
</tr>
</thead>
</table>

**What is a BRICK?**

- **MUCH KNOW-HOW**
- Equipment
- Machinery
- Kilns
- etc.

**Installation**

- **MUCH KNOW-HOW**
- Equipment
- Machinery
- Service
- etc.
Refractory Classifications

- Acid
  - Silica
  - Alumino-Silicate

- Neutral
  - Alumina
  - Chromic Oxide
  - Magnesia

- Basic
  - Magnesia
  - Lime
  - Magnesia-Chrome
Refractory Classification for Steelmaking

<table>
<thead>
<tr>
<th>Refractory Type</th>
<th>Silica</th>
<th>Fireclay</th>
<th>Mullite</th>
<th>High Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main Raw Material</td>
<td>Quartz</td>
<td>Flint Clay</td>
<td>Kaolinitic Clay</td>
<td>Bauxite and Corundum</td>
</tr>
<tr>
<td>Dominant Application</td>
<td>Coke Ovens</td>
<td>Coke Ovens</td>
<td>Blast Furnace</td>
<td>Ladles EAF</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Refractory Type</th>
<th>Magnesia</th>
<th>Zirconia</th>
<th>Doloma</th>
<th>Magnesia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main Raw Material</td>
<td>Magnesite</td>
<td>Zircon and Zirconium Oxide</td>
<td>Dolomite</td>
<td>Magnesite</td>
</tr>
<tr>
<td>Dominant Application</td>
<td>Secondary Steelmaking Ladles, EAF</td>
<td>Flow Control</td>
<td>Ladles AOD</td>
<td>Ladles BOF EAF</td>
</tr>
</tbody>
</table>

Mini-mill applications in red
Melting points of pure refractory oxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Melting Point [°C]</th>
<th>Melting Point [°F]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>1530</td>
<td>2786</td>
</tr>
<tr>
<td>Al2O3</td>
<td>1702</td>
<td>3128</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>2050</td>
<td>3722</td>
</tr>
<tr>
<td>CaO</td>
<td>2275</td>
<td>4127</td>
</tr>
<tr>
<td>ZrO2</td>
<td>2500</td>
<td>4712</td>
</tr>
<tr>
<td>MgO</td>
<td>2700</td>
<td>5072</td>
</tr>
</tbody>
</table>

Steel:
- Silica: 1530 °C (2786 °F)
- Alumina: 1702 °C (3128 °F)
- Chromia: 2050 °C (3722 °F)
- Calcia: 2275 °C (4127 °F)
- Zirconia: 2500 °C (4712 °F)
- Magnesia: 2700 °C (5072 °F)
Melting points of mixed oxides
Ternary Diagram

Figure 1
Magnesia

Sintered and Fused Magnesia

MgO between 90 to 99%

Purity (impurities)
- $\text{B}_2\text{O}_3$
- $\text{SiO}_2$
- $\text{Al}_2\text{O}_3$
- $\text{Fe}_2\text{O}_3$
- ($\text{CaO}$)

Crystal Size between 10 to 1000 microns
Density (porosity of grain) 3.10 to 3.45 g/cc
Microstructure

Sintered Magnesia

Magnesia

Fused Magnesia
## Bonding System Classification

<table>
<thead>
<tr>
<th>Class</th>
<th>Characteristics</th>
<th>Result Of:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic</td>
<td>Strong to high temps, brittle, low porosity</td>
<td>High Temp Firing</td>
</tr>
<tr>
<td>Chemical</td>
<td>Strong to intermediate temps, flexible continuous matrix</td>
<td>Acid/Alkali Reaction</td>
</tr>
<tr>
<td>Hydraulic</td>
<td>Strong to intermediate temps, low permeability, high porosity</td>
<td>Cement/water Reaction</td>
</tr>
<tr>
<td>Carbon</td>
<td>Strong to very high temps, oxidation continuous matrix, low porosity</td>
<td>Resin decomposition Carbide development</td>
</tr>
</tbody>
</table>
Ceramic bond

Theory: unsintered  sintered
Reality: unsintered  sintered

Sintering will develop at presence of:
- additions (binder/sinter aid)
- high temperature
- impurities
- pressure (e.g.: ferrostatic pressure of steel bath)
- small crystals and grains
# Carbon Bonding

<table>
<thead>
<tr>
<th>Property</th>
<th>Pitch 55 – 70%</th>
<th>Resin 45%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon yield</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Oxydation resistance</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Structure</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Matrix strength</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Environment</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Behaviour at process</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

[Diagram of carbon bonding structure]
Cement is a **HYDRAULIC BONDING** agent for castables, gunning mixes and some mortars which develops hydrates in contact with water.

The type and quantity of hydrates determine the properties of the final refractory concrete.

Source: DL Hipps and JJ Brown, Jr.
## Classification of Castables

*(ASTM C401-91)*

<table>
<thead>
<tr>
<th>Category</th>
<th>CaO Level</th>
<th>Cement Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Castables</td>
<td>&gt;2.5%</td>
<td>15-30%</td>
</tr>
<tr>
<td>Low Cement Castables</td>
<td>1.0-2.5%</td>
<td>4-8%</td>
</tr>
<tr>
<td>Ultra-Low Cement Castables</td>
<td>&lt;1.0%</td>
<td>&lt;4%</td>
</tr>
<tr>
<td>Cement-Free Castables</td>
<td>&lt;0.2%</td>
<td>No Cement</td>
</tr>
</tbody>
</table>
2. Moisture Loss of Castables with Different Cement Contents

![Graph showing moisture loss vs. temperature for different castables with varying cement contents.](image-url)
3. Curing Temperature vs. Strength
Castable with 15% Cement Dried 24 hrs. @ 220°F

[Graph showing the relationship between curing temperature (°F) and strength (psi).]
4. Curing Temperature vs. Permeability

Castable with 15% Cement Dried 24 hrs. @ 220°F

![Bar graph showing the relationship between curing temperature and permeability constant.]
Manufacturing Process - Refractories

**BRICKS**

**PRODUCTION**

MUCH KNOW-HOW
Equipment
Machinery
Kilns
etc.

RAW MATERIALS
MIXING
SHAPING
TEMP. TREATMENT

**FINAL PRODUCT**

BRICK

**MIXES**

**PRODUCTION**

RAW MATERIALS
MIXING

Semi-finished Product
MIX

**At Customer Site**

MIXING
SHAPING
TEMP. TREAT.

MUCH KNOW-HOW
Equipment
Machinery
Service
etc.
Refractory Manufacture - Brick
Standard Refractory Shapes

- Typical Straight, Arch, Wedge, and Key Brick
Standard Refractory Shapes

- 9 Inch Straight: 9 X 4 1/2 X 3
- 9 - 2 Inch Split: 9 X 4 1/2 X 2
- 9 Inch No. 1 Wedge: 9 X 4 1/2 X (3 - 2 3/4)
- Small 9 Inch Straight: 9 X 3 1/2 X 3
- 9 Inch Split: 9 X 4 1/2 X 1 1/2
- 9 Inch No. 2 Wedge: 9 X 4 1/2 X (3 - 2 1/2)
Standard Refractory Shapes

9 Inch No. 1 Key
9 X (4½ - 4) X 3

9 Inch Edge Skew
9 X (4½ - 1½) X 3

9 Inch Neck
9 X 4½ X (3 - 5/8)

9 Inch No. 2 Key
9 X (4½ - 3½) X 3

9 Inch - 60° End Skew
(9 - 7¼) X 4½ X 3

9 Inch Jamb
9 X 4½ X 3
Standard Refractory Anchors

### Wire and Rod Anchor Spacing

<table>
<thead>
<tr>
<th>Locations</th>
<th>Lining Thickness (in.)</th>
<th>Anchor Centers (in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Walls, Cylinders, Slopes</td>
<td>2–4</td>
<td>6</td>
</tr>
<tr>
<td>Walls, Cylinders, Slopes</td>
<td>4–6</td>
<td>9</td>
</tr>
<tr>
<td>Walls, Cylinders, Slopes</td>
<td>6–13 ½</td>
<td>12</td>
</tr>
<tr>
<td>Overhead, Roofs, Bullnoses</td>
<td>2–4</td>
<td>6</td>
</tr>
<tr>
<td>Overhead, Roofs, Bullnoses</td>
<td>4–7</td>
<td>9</td>
</tr>
<tr>
<td>Overhead, Roofs, Bullnoses</td>
<td>7–9</td>
<td>12</td>
</tr>
<tr>
<td>Floors</td>
<td>2–5</td>
<td>9</td>
</tr>
<tr>
<td>Floors</td>
<td>5–9</td>
<td>15</td>
</tr>
<tr>
<td>Floors</td>
<td>9+</td>
<td>24</td>
</tr>
</tbody>
</table>
Standard Refractory Anchors

1A

2A & 3A

4A

5A & 6A

7A

3R

KL

1L & 2L Clips for 2A & 3A Anchors

876 Series

TC Series

WC Series

TI Anchor
Wear Mechanisms

- Thermal Temperature
- Erosion by Mechanical, Scrap

Corrosion by Slag

Chemical
Temperature Wear
Wear Mechanisms

- Corrosion by Slag
- Chemical

Thermal Temperature

Erosion by Mechanical Scarp

Corrosion by Slag

Chemical
Mechanical Wear

Thermal Expansion of Refractories

- Magnesia
- Dolomite
- Chromite
- 90% Corundum
- 80% Bauxite
- Mullite
- SiC
- Graphite

Temperature [°C] vs. Thermal Expansion [%]

0 500 1000 1500

Temperature [°C]

Thermal Expansion [%]
Thermal Conductivity of Refractory Bricks

Mechanical Wear

Thermal Conductivity of Refractory Bricks

Temperature, [° F]

Thermal Conductivity, BTU.in/(hr. ft².F)

Mag Carbon 20% C
Mag Carbon 15% C
Mag Carbon 10% C
Mag Carbon 5% C
Dolomite or MgO - Fired
Dolomite C - Bonded
Alumina Magnesia Carbon
Mag-Chrome Fired
80% Alumina - Fired
80% Alumina - Fired
Reasons for thermal stresses

One-sided heating
One-sided expansion
tensile + compression stresses
cracks

One-sided cooling down
One-sided shrinking
compression + tensile stresses
cracks

Fig. 4. Distribution of thermal stress in heating one side of brick\(^3\)
Wear Mechanisms

- Corrosion by Slag
- Chemical

Thermal Temperature

Erosion by Mechanical Scrap
Solutions consisting primarily of molten metal oxides

- Float on top of the steel because of specific gravity lower than that of molten steel
- Primarily liquid at steel making temperatures
- Play an essential role in the steel making process

\[
\begin{align*}
2C + O_2 & \rightarrow 2CO \\
2Fe + O_2 & \rightarrow 2FeO \\
4Al + 3O_2 & \rightarrow 2Al_2O_3 \\
Si + O_2 & \rightarrow SiO_2 \\
4P + 5O_2 & \rightarrow 2P_2O_5 \\
2Mn + O_2 & \rightarrow 2MnO
\end{align*}
\]
Slag Formers – Lime and Dolo-lime

Alumina absorption: \[ \text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{CaO}.\text{Al}_2\text{O}_3 \]

Silica absorption: \[ 2\text{CaO} + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4 \]

Phos. oxidation: \[ 2\text{P} + 5\text{FeO} \rightarrow \text{P}_2\text{O}_5 + 5\text{Fe} \]

Phos. absorption: \[ 4\text{CaO} + \text{P}_2\text{O}_5 \rightarrow \text{Ca}_4\text{P}_2\text{O}_9 \]

Sulfur absorption: \[ \text{CaO} + \text{S} \rightarrow \text{CaS} + \text{O} \]
PRIMARY SOURCES OF SLAGS

- Oxidation of Si, Al & Mn in scrap
- Ash in charge & injection C
- Gangue & FeO in DRI/HBI
- Dirt in scrap (gangue)
- Oxidation of Si & Mn in Pig Iron
- Refractory wear
- Flux: lime & dolomite
- Residual slag in EAF
- FeO/rust on scrap
- Oxidation of Fe => FeO
Solubility of Magnesia in a Steelmaking Slag

Percent of MgO Dissolved in the Liquid

Lime-Silica Ratio of the Liquid Slag (CaO/SiO2)

- 3100°F*
- 3000°F**
- 2900°F
- 2750°F
Four Variables:
- MgO content
- FeO content
- Temperature
- Basicity

ISD’s show phase relations of MgO and FeO content at fixed basicity and temperature

Figure 6. Isothermal Solubility Diagram (ISD) for a basicity (B₃) of 1.5. (Where C₂S = Ca₂SiO₄, MW = Magnesio-wustite, and L = Liquid)
Solubility of Magnesia in Steelmaking Slag
EAF Refractories

- Magnesia Carbon: fused / sintered
  - Carbon content 10-15%
  - Metal additions for oxidation and strength
- Burned Magnesite: impregnated with pitch
- Hearth / Anode: 70 - 80% Magnesia
- Gunning; 60 to 98% Magnesia
- Delta: 80-85% alumina
**Stadium**—The stadium design, the original bottom design used for EAFs, consists of brick laid in the design of a stadium. This bottom design takes significant time and brick laying skill to install properly, but provides a certain safety factor to the operation when installed properly. To repair damage to this type of bottom, brick in the damaged area must be removed and then new brick must be installed.
**Monolithic**—The monolithic bottom design consists entirely of dry vibratable material. It is the easiest to install, can be installed relatively quickly, and requires little bricklaying skill. The dry vibratable material is installed via supersacks and then compacted using vibrating spikes and seds. Repair of this type of bottom requires only removal of the steel skull and reinstallation of the hearth material.

**Safety Liner and Monolithic (Shiner)**—This design combines the best features of both the stadium and monolithic designs. The brick on the bottom is usually one or two courses of burned brick laid in a horizontal direction directly on the bottom steel shell. The dry vibratable material is then installed directly over this course of brick and vibrated in. This design combines the safety of the stadium brick bottom with the ease of installation and maintenance of the monolithic hearth bottom design.
Hearth Installation

- De-air using pitchforks, vibrators or walking on until proper compaction is attained
- Repeat these steps several times until desired depth is achieved
- Final compaction should be very firm
- Final grade may be finished off by using vibrating sled if desired
Examples or Refractory Applications – Electric Arc Furnace at Installation
Magnesia-Carbon Bricks

Carbon Levels (usually 5-20%)

- Higher levels: more slag resistant
- Higher levels: resist EAF and LMF arc flare
- Higher levels: more thermal shock resistant
- Higher levels: less oxidation resistant
Magnesia- Carbon Bricks

Metal Additions

• Higher levels yield stronger bricks.
• Higher levels yield more oxidation resistant bricks.
• Higher levels cost much more.
• Higher levels – Bricks more brittle
Welded Door Jambs
EAF Taphole Designs

Steel flow through tapholes
EAF Straight Bore Taphole

Tap Times thru 6” Straight Bore Taphole

Minutes

Heats
EAF Conical Bore

Tap Times thru 6” ISOTAP® Taphole

Minutes

Heats
EAF Delta and Roof

• Primary function of Delta is to protect the roof from the electrode arc generated during the melting operation.

• It is exposed to arc flare, thermal shock, oxidation, chemical corrosion, post combustion and high temperatures.
Furnace Mono Installation Equipment
Furnace Gunning
Steel Ladles Safety Lining

Both brick and monolithic safety linings are used today in the refractory industry. While historically brick safety linings have been used predominantly, monolithic ladle linings have become more common over the last 10 years.

Brick Safety Lining

The three most common brick safety lining designs are listed below:

- *Arch-wedge construction* provides one of the tightest safety linings.
- *Book-tile construction* gives added protection against steel penetration.
- *Semi-universal construction* is easy and quick to install, important factors when a ladle fleet is small and turn-around time is important.

Monolithic Safety Lining

Monolithic safety linings are installed either by casting or by shotcreting. The casting method delivers a very compact and geometrically precise safety lining, but requires a mandrel for casting. The mandrel is shop-specific and depends on the specific ladle geometry. The shotcreting method is a very attractive form-free method; however, the final geometry of the safety lining is not exact and could create some difficulties for the brick construction of the working lining. In this case, a half-inch layer of dry vibratable is recommended to separate the shotcrete safety lining from the working lining.
Steel Ladles

**Universal Circle Brick**
- Easy to install
- Starter sets available
- Curved design conforms well to the curved shells of round ladles
- Good for round and oval ladles

**Beveled Edge Arch Brick**
- Tight safety lining construction
- Good bricklaying skills required
- Good for round, obround, and oval ladles

**Tongue and Groove Brick**
- Tight safety lining construction
- Courses and brick locked together
- Good bricklaying skills required
- Good for round, obround, and oval ladles

2.5-, 3-, and 4-in. thickness available; 6-in. height available

2.5- and 3-in. thickness available; 9-in. height available
INSULATION

• Insulation – Brings Freeze Plane into Brick
• Best Scenario - No Insulation
• 2nd Best - Minimize Insulation
Insulation versus no Insulation

Thermal Profile

Temperature (°F)

Lining Depth (in)

Hot

Cold Face

The Freeze Plane of 2650°F occurs at 2.05 in. into COMANCHE

Thermal Profile

Temperature (°F)

Lining Depth (in)

The Freeze Plane of 2650°F occurs at 2.26 in. into COMANCHE
Steel Ladles – Working Linings

Ladle working linings are refractories directly in contact with molten steel and slag in the bottom, barrel, and slagline. They must be able to withstand any secondary refining, heating, rinsing, and alloying. These operations affect the slagline, as well as the barrel and bottom of the ladle. Working linings can be either brick or monolithic and are selected on the basis of operating conditions and slag compatibility.
Steel Ladles

Semi-Universal Brick
- Easy to install
- Starter sets available
- Small brick height conforms well to tapered steel ladle shells
- Good for round, obround, and oval ladles

3-, 4-, 5-, 6-, 7-, 8-, and 9-in. thickness available;
3-in. 100 mm heights available

Mini-Keys
- Keyed lining hot face to cold face
- Keyed lining can be worn thinner, therefore longer service life
- Keyed lining can be laid tighter than semi-universal without mortar
- Keyed linings remain tighter to safety linings at trunnions during service, especially in oval and obround ladles

4-, 5-, 6-, 7-, 8-, and 9-in. thickness available;
3-in. 100 mm heights available

Soldiered Arch-Wedge Brick
- Tight safety lining construction
- Good bricklaying skills required
- Good for round, obround, and oval ladles
Steel Ladles - Bottom

Full bottom design.

Plug bottom design.
Precast and Composite Bottoms
Gas Purging Systems

- **Stir Plugs** - Multiple Designs and Compositions in Both Porous and Directional

- **Pocket Blocks** – Multiple Compositions
  - Conventional Cast
  - Compression Cast
  - ISO Pressed

- **Plug Assemblies** – Could have some safety and life benefits

- **Plug Exchange Systems**
  - Multiple Systems usually supplied by the plug manufacturer
Well Blocks
Steel Ladles

Working and Safety Linings Preheat
- Heat ladle at 200°F/hour to 1800°F-2000°F
- Hold at temperature for 1 hour per inch of working and safety lining thickness

Slagline Replacement Preheat
- Heat ladle at 200°F/hour to 1800°F-2000°F
- Hold at temperature for 1 hour per inch of slagline thickness
Successful Monolithic Installations

- Castables & Shotkast & Gunning Mixes
  - Material & Water Above 70 F
  - Cure at 70 to 90 F for High Strength
  - Use Recommended Amount of Clean, Drinkable Water
  - Follow Recommended Heat-Ups
Tundish Technologies
Tundish Baffles
Tundish Impact Pads
Cast Tundish lining
Dry Vibe vs. Spray Technology

Profile with dry vibe

Profile with spray
Tundish Spray Machines

What is important?
- Reliable Control Equipment.
- Easy operation.
- Simple maintenance.
- Recycle options.
- Rapid, reliable spray application.
- Auxiliary material handling systems.

- Manual Spray systems.
- Full Robotic systems for high volume shops.
Spraying Tundish
Sprayed Tundish w/Baffle
Tundish Dryer
Dry-Vibe Mandrel/Curing Unit
Dry-Vibe Working Lining
Thank You