Magnesite as a Refractory Brick Material

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Main Topic

- Technical advantages and disadvantages of different MgO mineral compositions
- Is magnesite being replaced by dolomite?
- How does supplying and price make a difference?
- How is the industry faring during economic slowdown and will this continue?
MgO Application

- 56% Refractory Industry
- 44% Agriculture
  - Chemical
  - Construction
  - Environmental
  - Other industrial applications
Sources of MgO

- Magnesium carbonate
- Magnesium hidrooxide
  - Brucite
  - Derived from sea water and brine
- Crystalline structure of magnesite
  - Cryptocrystalline – lagoons, salt lakes or fresh water lakes
  - Crystalline – sedimentary rocks (replacement of lime stone and dolomite)
Types of MgO Considering Thermal Treatment

- Light burned or caustic calcined MgO (800 ~ 900°C)
- Dead burned MgO
  - Single fired ~ 1800°C
  - Doubled fired ~ 2200°C
- Fused MgO > 2800°C
Magnesite Ores

GENERAL VIEW OF POMBA MINE - HIGH PURITY MgO SOURCE
Magnesite Ores

MICROSTRUCTURE OF FRACTURES OF PEDRA PRETA (BLACK STONE) ORE
Single and Double Firing MgO Production Steps

MgO Sinter from Magnesite:
Processing: Production

AERIAL VIEW OF MAGNESITE ORE PROCESSING FACILITIES
Properties of MgO

Melting Point – 2800°C
High density – 3.10 ~ 3.45 g/cm³
Low porosity – 12 ~ 1 to 2%
Crystal size – 50 ~ 160 µm
MgO content – 90 ~ 99%
Impurities – B₂O₃ > Al₂O₃ > Fe₂O₃ > SiO₂ > CaO
Thermal Conductivity – high compared to other refractory oxides
Thermal Expansion – greatest compared to all pure refractory oxides
(approaching the thermal expansion of metals)
Quality Criteria to Select MgO

- MgO Content
- Impurity level
- Lime/silica ratio (desirable > 2)
- Crystal size
- Bulk density
- Apparent porosity
- Degree of direct bonding of MgO crystal
## Typical Characteristics of Some Dead Burned Magnesias

<table>
<thead>
<tr>
<th>Grades</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape</td>
<td>chunk</td>
<td>briquette</td>
<td>briquette</td>
<td>briquette</td>
<td>briquette</td>
</tr>
<tr>
<td>Chemical analysis; wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO$_3$</td>
<td>1.29</td>
<td>1.16</td>
<td>0.9</td>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.35</td>
<td>0.32</td>
<td>0.2</td>
<td>0.08</td>
<td>0.1</td>
</tr>
<tr>
<td>CaO</td>
<td>0.44</td>
<td>0.43</td>
<td>2.0</td>
<td>0.94</td>
<td>1.2</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.11</td>
<td>1.82</td>
<td>0.8</td>
<td>0.41</td>
<td>0.4</td>
</tr>
<tr>
<td>MnO</td>
<td>0.94</td>
<td>0.91</td>
<td>-</td>
<td>0.12</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>94.88</td>
<td>95.37</td>
<td>96.5</td>
<td>98.20</td>
<td>98.0</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
<td>0.01</td>
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<tr>
<td>CaO/SiO$_2$ (molar)</td>
<td>0.36</td>
<td>0.40</td>
<td>2.0</td>
<td>4.02</td>
<td>5.0</td>
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<tr>
<td>Bulk density; g/cm$^3$</td>
<td>3.07</td>
<td>3.30</td>
<td>3.25</td>
<td>3.33</td>
<td>3.42</td>
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<tr>
<td>Apparent porosity; %</td>
<td>11.7</td>
<td>3.20</td>
<td>3.0</td>
<td>2.4</td>
<td>2.0</td>
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<tr>
<td>Average MgO crystal diameter; µm</td>
<td>70.0</td>
<td>80.0</td>
<td>80.0</td>
<td>120.0</td>
<td>80.0</td>
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<td>Accessory minerals</td>
<td>M$_2$S</td>
<td>M$_2$S</td>
<td>C$_2$S</td>
<td>C$_4$S</td>
<td>C$_2$S</td>
</tr>
<tr>
<td></td>
<td>CMS</td>
<td>CMS</td>
<td>C$_3$MS$_2$</td>
<td>CMS</td>
<td>C$_3$S</td>
</tr>
<tr>
<td>MF</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
Typical Microstructure of Sinter A
Typical Microstructure of Sinter D
Typical Microstructure of Fracture of Sinter D
Microstructure of Sinter D; Electron-probe Microanalysis

35 µm

BE  Si  Ca
Mg  Fe  Mn
Fused MgO

- Raw Materials Feed
  - Calcined MgO
  - Dead burned MgO
  - Magnesite – Single step
- T-t - 2750°C x 12h (very energy intensive)
- High density – 3.50 ~ 3.58g/cm³
- Apparent porosity – 1 ~ 2%
- Large crystal size – 600 ~ 2300 µm
- Impurity level is reduced (silicate migrates to the surface of magnesia ingots)
Fused MgO

Fused Magnesia:

- Higher crystal size
- Lower porosity
- Higher density

- Mechanical Resistance
- Corrosion Resistance
- Abrasion Resistance
Fused MgO

Fused Magnesia:

Properties:

<table>
<thead>
<tr>
<th>Properties</th>
<th>MEF A</th>
<th>Typical</th>
<th>MEF B</th>
<th>Typical</th>
<th>MEF C</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD (g/cm³)</td>
<td>&gt;3.30</td>
<td>3.30</td>
<td>&gt;3.49</td>
<td>3.50</td>
<td>&gt;3.50</td>
<td>3.53</td>
</tr>
<tr>
<td>PA (%)</td>
<td>&lt;5.0</td>
<td>4.5</td>
<td>&lt;2.5</td>
<td>2.1</td>
<td>&lt;2.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Crystal Size (μm)</td>
<td>&gt;500</td>
<td>889</td>
<td>&gt;970</td>
<td>1220</td>
<td>&gt;1600</td>
<td>2279</td>
</tr>
</tbody>
</table>

Chemical Analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>MEF A</th>
<th>Typical</th>
<th>MEF B</th>
<th>Typical</th>
<th>MEF C</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>&lt;0.6</td>
<td>0.38</td>
<td>&lt;0.45</td>
<td>0.30</td>
<td>&lt;0.40</td>
<td>&lt;0.28</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>&lt;0.6</td>
<td>0.17</td>
<td>&lt;0.31</td>
<td>0.13</td>
<td>&lt;0.25</td>
<td>&lt;0.14</td>
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<tr>
<td>Fe₂O₃</td>
<td>&lt;0.6</td>
<td>0.45</td>
<td>&lt;0.60</td>
<td>0.45</td>
<td>&lt;0.55</td>
<td>&lt;0.48</td>
</tr>
<tr>
<td>MnO</td>
<td>&lt;0.15</td>
<td>0.09</td>
<td>&lt;0.15</td>
<td>0.09</td>
<td>&lt;0.15</td>
<td>&lt;0.08</td>
</tr>
<tr>
<td>CaO</td>
<td>&lt;1.4</td>
<td>1.01</td>
<td>&lt;1.15</td>
<td>0.93</td>
<td>&lt;1.10</td>
<td>&lt;0.94</td>
</tr>
<tr>
<td>MgO</td>
<td>&gt;96.5</td>
<td>97.9</td>
<td>&gt;97.5</td>
<td>98.1</td>
<td>&gt;97.50</td>
<td>&gt;98.07</td>
</tr>
</tbody>
</table>

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![Micrographs](image1.jpg)  ![Micrographs](image2.jpg)  ![Micrographs](image3.jpg)

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**magnesita**
Typical Microstructure of MgO-C bricks:

Bricks Whit No AOX:

Dead B. Magnesia

Flake Graphite

Fused Magnesia
Features of MgO Containing Refractories

The most used refractory for steel refining process (BOF, EAF and LF) – mainly MgO-C

The most important refractory for secondary refining process (RH degasser, VOD and AOD) – mainly MgO-Cr$_2$O$_3$

Excellent for ladle or ladle furnace operating with Al as deoxidizing agent

Capable to withstand severe operating conditions, mainly for high grade steels

Excellent for clean steel production

Intensively used in the cement and non ferrous industry (MgO-spinel and MgO-Cr$_2$O$_3$)
Stainless Steelmaking Processes - Preference of Dolomite over MgO Refractories

Most of the cases (90%) deoxidation agent is silicon, which is more compatible to dolomite bricks (C$_2$S formation).

Most of the world’s stainless steel production (80%) has a very low carbon specification (<0,05%) which demands a low carbon refractory. Fired dolomite is free carbon.
Mechanism of Coating Protection of Dolomite Bricks

Coating protection with doloma products:

\[2 \text{CaO} + \text{SiO}_2 \rightarrow \text{C}_2\text{S} \quad 2130 ^\circ\text{C}\]

(Desenhos: Guilherme Lenz – CPqD)
Mechanism of Coating Protection of Dolomite Bricks

Coating protection with doloma products:

The Ideal Coating does not show the brick joints!!!

$\alpha$-C2S $\rightarrow$ $\gamma$-C2S (725 °C)

(Desenhos: Guilherme Lenz – CPqD)
(Fotos: Cortesia Magnesita S.A.)
Magnesite as a Refractory Brick Material - Economic Considerations

- How does supply and price make a difference?
- How is the industry faring during the economic slowdown and will this continue?
Magnesite Mine Production and Reserves

<table>
<thead>
<tr>
<th>Magnesite</th>
<th>Mine production 2011</th>
<th>Mine production 2012e</th>
<th>Reserves</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>4.180</td>
<td>4.300</td>
<td>500.000</td>
</tr>
<tr>
<td>Russia</td>
<td>346</td>
<td>350</td>
<td>450.000</td>
</tr>
<tr>
<td>Korea,North</td>
<td>43</td>
<td>45</td>
<td>450.000</td>
</tr>
<tr>
<td>Australia</td>
<td>86</td>
<td>90</td>
<td>95.000</td>
</tr>
<tr>
<td>Brazil</td>
<td>140</td>
<td>140</td>
<td>86.000</td>
</tr>
<tr>
<td>Greece</td>
<td>86</td>
<td>90</td>
<td>80.000</td>
</tr>
<tr>
<td>Turkey</td>
<td>288</td>
<td>300</td>
<td>49.000</td>
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<tr>
<td>Slovakia</td>
<td>172</td>
<td>180</td>
<td>35.000</td>
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<tr>
<td>India</td>
<td>101</td>
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<tr>
<td>Austria</td>
<td>219</td>
<td>220</td>
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<tr>
<td>United States</td>
<td>W</td>
<td>W</td>
<td>10.000</td>
</tr>
<tr>
<td>Spain</td>
<td>133</td>
<td>130</td>
<td>10.000</td>
</tr>
<tr>
<td>Other countries</td>
<td>135</td>
<td>150</td>
<td>390.000</td>
</tr>
<tr>
<td><strong>World total (rounded)</strong></td>
<td><strong>5.930</strong></td>
<td><strong>6.100</strong></td>
<td><strong>2.190.000</strong></td>
</tr>
</tbody>
</table>

Source: USGS Magnesium Compunds Report; Magnesita review

Despite of high availability of different sources of MgO in China Market, it has been difficult to find high quality grades like 97,5% MgO.
Production Capacity of Magnesia (000 ton)

High grade sintered MgO is more available in Western Market, where manufactures have more rigid specification concerning MgO content and physical properties (Bulk Density, Apparent Porosity and Crystal Size).
In the last three years prices have been flat due to both supply and demand reasons:

- Increase in Chinese Export Licenses
- Slow recovery in the world ex-China steel production

During 2009 and 2010, EFM EFM price increased significantly mainly due to increased export restrictions and energy costs in China.

Source: Industrial Minerals Price Data Base.

Chinese prices have long been a recognized benchmark of magnesia pricing as they influence DBM/EFM prices worldwide.
Impact of Financial Crisis in Steel production

Iron and steel production and performance is the primary factor influencing demand and prices for EFM.

Source: CRU Group
Facing the challenging scenario

Raw Material Challenges

- Large Crystal EFM have been increasingly rare in China.

- Refractory producers with captive EFM sources have a great competitive advantage as they are able to supply high performance products.

- Those who depend on Chinese imports must be highly aware on shipments unstable quality levels.

- Raw Material Integration is still in the plans of most refractory producers, seeking lower costs and less risk of raw material shortage and quality issues.

- Single Step EFM have been consumed in “commodity” type products, such as MgO-C.
Facing the challenging scenario

Consumer Market Challenges

- Refractory producers are seeking to increase presence in emerging markets, with expectation of higher growth.

- Shift of production volumes to lower cost countries is also being a strategy of major player in the market.

- Some producers are also investing in R&D in order to produce high performance products attending to steelmakers producing top quality steel.

- True partnership with customers, with excellence post sales and technical assistance services.

Global players in the refractory industry have been struggling to find ways to keep profitability and seek growth pools
Conclusion

- MgO bricks continue to be the best option for steelmaking processes (BOF, EAF and ladle)

- High grade MgO bricks (mainly MgO-C) have been intensively used for the production of high grade steels, which is processed under severe operating conditions

- MgO as a fused grain is the most important raw materials for the steel refining process due to its excellent corrosion resistance. Great preference has been done for high purity and large crystal materials.

- MgO-Cr$_2$O$_3$ remains the best option for secondary refining process (RH degassing and VOD).

- MgO spinel and MgO-Cr$_2$O$_3$ materials also remains the best option for cement and lime kilns and non-ferrous industry respectively.
Conclusion

- Dolomite bricks are the best option for stainless steel and silicon deoxidizing agent due to $C_2S$ formation in the hot face of the lining.

- It seems a scarce source of high grade sintered MgO and fused MgO in China where the manufactures have a tendency to produce commodities (mainly MgO-C).

- In order to keep the existing market share as well as increase sales some producers have invested in R&D to improve refractory performance as well as to reduce the refractory specific cost.

- Very close relationship with the customers and a strong technical approach have been adopted by some producers with the aim to increase equipment availability as well as refractory performance and specific cost.