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Calcined Dolomite for Refractories

(and other uses)

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Dolomite raw material

- Total production of dolomite very large ~ 100 million tonnes annually
- By far the largest use is in construction as an aggregate representing 80% or more of demand
- Distinct mineral entity $\text{CaCO}_3 \cdot \text{MgCO}_3$ NOT a mixture of calcite and magnesite
- Theoretical composition 21.7% MgO 30.4% CaO and 47.8% CO_2
- Whole range of intermediate compositions calcitic dolomites, dolomitic calcites, magnesian limestones etc



Applications

- **Construction -- aggregates, asphalt filler**
- **Agriculture -- soil conditioner, animal feed**
- **Metallurgical fluxes -- iron and steel**
- **Refractories -- sintered/dead-burned dolomite (doloma)**
- **Chemicals -- magnesia chemicals**
- **Environmental -- water & sewage treatment, FGD, etc**
- **Glass -- flat, container, and domestic**
- **Ceramics -- tiles, porcelain**
- **White carbonate fillers -- paints, plastics, etc**



Construction

- Largest use
- Physical properties most important
 - shear strength
 - crushing resistance
 - polishing resistance
 - water absorption
 - porosity
- For Asphalt
 - either a 200 mesh powder or an 8 mesh granule is typical



Agriculture

- Ground dolomite or dolomitic limestone added as a dressing on soils to adjust pH
- Advantage on grazing pastures for dairy cattle –provides magnesia to combat magnesium deficiency disease – staggers
- Generally a minus 5mm grade used
- Small use in animal feed but magnesium additions tend to be via CCM
- Some use as an inert filler in fertilisers



Metallurgical Fluxes

- Dolomite used as a flux or slag conditioner in iron and steel
- In the blast furnace dolomite previously added directly as lumps
- Now more common as part of blast furnace sinter or iron ore pellets
- Olivine an alternative source of magnesia
- Dolomite preferred when high silica iron ore is used
- Specification generally requires high magnesium and calcium
- Silica typically below 0.75%
- Very low sulphur generally maximum 0.05%
- Relatively high iron up to 1-1.5% can be tolerated



Chemicals

- A variety of chemicals can be manufactured utilising dolomite
- Largest application in the manufacture of magnesia from brines or seawater
- Lime can be used but dolime adds magnesium and where it is readily available is the preferred material
- Some can be used in processing to magnesium metal



Environmental

- Dolomite or dolime may be used for neutralising effect in environmental applications
- High calcium lime more commonly used
- Where silica removal is required, dolime is preferred because of the reaction of silica with the magnesium component



Glass

- Dolomite the cheapest and most practical source of magnesia needed for glass batch, requires a high purity material
- Magnesia content reduces tendency for devitrification in flat glass and improves workability in pressed glass or fiberglass
- Iron content most important consideration

Type of glass	Fe ₂ O ₃ content
Coloured glass	0.25-0.35%
Flat glass -- regular	0.1-0.2%
Colourless containers	<0.05% can be acceptable <0.03% preferred
Flat glass -- white	<0.03%
Crystal glass	<0.02%



Ceramics

- Both limestone and dolomite are used in the body constituent of ceramics and glazes particularly in wall tiles
- Ground to minus 75 μ or minus 63 μ before use
- High specification typically

MgO 21.4% min

CaO 30.0% min

Al₂O₃ 0.2% max

Fe₂O₃ 0.03% max



Fillers

- Much less common as a white carbonate filler than limestone/marble
- Harder than CaCO_3 fillers so more abrasion on equipment
- Requires high whiteness/brightness
- Small market compared to other filler/extenders
- 10s of thousands of tonnes rather than in millions of tonnes
- Some niches where abrasion resistance is favoured



Refractories

- Dolomite in refractories is a specialised sector
- Volumes significant but much smaller than magnesia
- Few specialised suppliers
- Generally vertically integrated from raw material to product
- Higher specifications than the common fettling grades in the era of the open hearth
- Limited international trade in sintered dolomite



Raw Dolomite Specification for Refractories

	MgO	CaO	Fe₂O₃	Al₂O₃	SiO₂	LOI
Lhoist (Belgium)	21.5	29.9	0.3	0.1	0.2	48.0
Wulfrath (Germany)	20.2	31.5	0.4	0.4	0.5	47.0
Whitwell (UK)	20.8	30.1	0.5	0.2	0.5	47.2
Turkey	21.5	31.45	0.015	0.02	0.15	46.8
Calcinor	20		0.2		0.2	47



Sintered dolomite specifications

- Calcined at up to 1800°C
- Forms CaO.MgO a mixture of the two oxides rather than a specific mineral entity
- Magnesia content
 - typically 20-22% on a raw basis
 - Typically 36-41% after sintering
- Bulk density can be as high as 3.3g/cc but typically 3-3.2g/cc
- Low but predictable levels of impurities such as iron, silica, alumina and boron and very low alkalis



Typical sintered dolomite specifications

• CaO	58-62%
• MgO	36-41%
• SiO ₂	0.5-1.5%
• Fe ₂ O ₃	0.5-1.0%
• Al ₂ O ₃	0.2-0.8%
• MnO	0.1-0.2%
• Density	3.0-3.2 g/cm ³



Production of sintered dolomite

- Estimated world production ~ 850-950,000 tonnes annually
- About 550-600,000 for burned and tempered brick
- Of the order of 300-400,000 tonnes for monolithics
- Addition tonnages of magnesia/dolomite co-clinker
 - Especially in China
- Dolomite raw material requirement 1.7-1.9 million tonnes



Industry structure – Burnt Dolomite Brick

- Magnesita by far the largest producer after acquisition of LWB
- LWB had previously purchased Baker Refractories which had previously purchased Steetley
- Had to sell WRI (now owned by Resco) as a condition of the Baker purchase
- Few burnt brick producers
 - Magnesita by far largest
 - Resco in the USA and Tata in India the other much smaller players both previous direct or technology links to LWB
 - Qinghua in China, but based on magnesia/dolomite co-clinker



Industry structure Tempered Bricks

- Magnesita again the market leader
- RHI though its Italian operations second largest
- WRI and Tata again amongst the smaller producers
- Other producers include
 - Kelsen in Spain – part of the Calcinor Group
 - PMO in Krakow – Part of Arcelor-Mittal Refractories
 - Kumas in Turkey
 - Vardar Dolomit (owned by Haznedar of Turkey) in Macedonia
- All of them also supply sintered dolomite monolithics



The refractory applications examples steel

- Steel Ladle bricks – particularly for silicon killed steel because of slag chemistry
- EAF – monolithic bottoms
- Stainless steel
 - Greater proportion of dolomite refractories used
 - Burnt and tempered brick used in ladles
 - AOD converters, dolomite burnt brick
 - Tends to be silicon rich slags better tolerated by dolomite than magnesia
 - Alternatives are magnesia/dolomite co-clinker and magnesia/chrome
- Monolithics for maintenance



Applications – Cement/lime

- Dolomite used in the burning zone
- Competition with spinels as replacement for magnesia/chrome
- Chemistry helps produce a protective coating on the refractories
- Needs installation expertise, particularly regarding protecting against hydration of product before and during installation



Barriers to new entrants

- Needs either an internal or long term stable source of high quality dolomite
- No significant open market in sintered dolomite
- Significant capital investment needed for sintering operations
- Considerable expertise required for production and installation of burnt brick to control propensity for hydration
- Tempered brick (resin or pitch bonded) less problematical for hydration
- Existing producers long established with good technical backup



Questions

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