Cement chemistry and processing


Basic cement chemistry

Chemical Formulæ

Cement chemistry shorthand used:

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>Fe₂O₃</td>
<td>H₂O</td>
</tr>
<tr>
<td>C</td>
<td>S</td>
<td>A</td>
<td>F</td>
<td>H</td>
</tr>
</tbody>
</table>

Examples:

- C₃S for Ca₃O·SiO₅ Alite Early Strength
- C₂S for Ca₂O·SiO₄ Belite Late Strength
- C₃A for Ca₃Al₂O₆ Aluminate
- C₄AF for Ca₄Al₂Fe₂O₁₀ Ferrite

Mineralogical Composition

Composition of material, expressed in the weight percent for each species

<table>
<thead>
<tr>
<th></th>
<th>Calcite</th>
<th>CaCO₃</th>
<th>90%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dolomite</td>
<td>CaMg (CO₃)₂</td>
<td>&lt;3%</td>
</tr>
<tr>
<td></td>
<td>Quartz</td>
<td>SiO₂</td>
<td>~7%</td>
</tr>
<tr>
<td></td>
<td>Alumina</td>
<td>AlSi</td>
<td>~3%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Alite</th>
<th>C₃S</th>
<th>58%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Belite</td>
<td>C₂S</td>
<td>23%</td>
</tr>
<tr>
<td></td>
<td>Aluminate</td>
<td>C₃A</td>
<td>9%</td>
</tr>
<tr>
<td></td>
<td>Ferrite</td>
<td>C₄AF</td>
<td>7%</td>
</tr>
<tr>
<td></td>
<td>Periclase</td>
<td>MgO</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td>Arcanite</td>
<td>K₂SO₄</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td>Free lime</td>
<td>CaO</td>
<td>1%</td>
</tr>
</tbody>
</table>

Significance of clinker minerals for cement properties

- **C₃S - Alite**
  - Contributes primarily to early strengths and later late strength (1 day - ...)
  - Increases heat of hydration

- **C₂S – Belite**
  - Contributes to late strength (28 days - ...)

- **C₃A – Aluminate**
  - Contributes to early strength (1-3 days ...)
  - Increases heat of hydration
  - Impairs resistance to sulfate attack
C₄AF – Ferrite  Little effect

Non-hydraulic cement

Does not dry in wet conditions as hydraulic does; forms/hardens when exposed to atmospheric CO₂ over a period of time.

CaCO₃ (limestone) burned to remove C (carbon) temperature 1517°F, 825°C

CaCO₃ > CaO + CO₂ (calcination)

CaO + H₂O > Ca(OH)₂ (slacking)

Ca(OH)₂ + CO₂ > CaCO₃ + H₂O (setting); when exposed to air hardens but cannot be used in applications that are exposed to water (on the surface or under water).

The Preheater-pre-calcining-kiln system is shown below.

https://www.cementequipment.org/

Drying
The cement components—limestone, silica, aluminum and iron—are mixed in a mixing shed with a raw material system of stackers and a reclaimer conveyor belt ahead of the preheater-precalcining-kiln system with less than 5% of moisture present. From the mixing shed, the components are transferred to the top of the preheater. The first cyclone in the preheater tower is the final drying to “bone dry.” The mixture contains virtually no moisture at this point of the process stream and the CaCO₃ is converted to CaO and CO₂.

Preheating

The most common preheater towers have five cyclone stages with a few systems having four or six stages. The selection is related to higher capital cost to reduce operating costs or vice versa. Experience in designs and operations indicated that introduction of auxiliary heat in the pre-heater tower and eventually heat added to calciner section was more efficient than losing heat at the exit end of the kiln.

Precalcining

The pre-calcining section improved energy utilization and reduced CO₂ within the pre-heater and precalcining section. The current estimated fuel consumption in the calciners section is estimated to be 55% to 60% of total fuel consumption. The high temperature zone in a rotary kiln where the melting of the clinker components takes place is from 1300°C to 1450°C (2372°F to 2606°F).
Rotary kiln mechanism

The current design with enlarged drying, calcining and burning zones has a size that is adjusted depending on limestone quality, fuel heat (BTU/ton of clinker), preheater and calcining design and atmospheric conditions (air pressure and local humidity).

System Auxiliary Equipment

Crushing and Roller Grinding Mills

Mined limestone from 1 cm to 1 m (.4 inches to 30 inch) in diameter is fed to a primary gyratory or impact crusher and then a secondary hammer crusher produces a crushed size feed size of 10 mm. This raw feed goes to the vertical roller mill. A vertical roller mill typically has three wheels positioned from vertical to 45 degrees and is attached with hydraulic rods to a center rod. The wheels rotate against the table and grind to a fine size.

The roller mill reduces to sizes from 230 mesh (0.063 mm) to 325 mesh (0.044 mm). The control of the crusher and grinding system uses a measuring device to adjust the incoming limestone raw mill feed as it is transported to the mixing shed where the silica (sand), aluminum from clays and iron are blended with the limestone.

Separate roller mills are also used to crush and grind the coal fuel to a size feeding to the calciner fuel system and rotary kiln. The raw mix sizing from the roller mill in 200-300 mesh size.

Coal for fuel is also reduced in a vertical roller mill to produce a smaller coal size fire in the kiln. Coal is fed to the roller mill at smaller than 110 mm then crushed to 0.09 mm in the roller mill. An open-air version reduces collection of methane inside the grinding chamber.
Fuels

The primary fuels in cement processing are coal and natural gas. Common auxiliary fuels in cement processing are diesel fuel and petroleum coke. Diesel fuel is substituted for natural gas when natural gas prices increase rapidly when compared to diesel prices on a BTU basis. Petroleum coke has been substituted for coal where availability of petroleum coke can replace coal.

The use and energy recovery of rubber in cement rotary kilns is a common. Use of tires decreases the carbon dioxide created in the kiln which, in turn, allows room for additional oxygen to be used in the kiln. The shredded tires without the steel belting can be introduced at the riser duct to the fourth stage preheater vessel. Shredded rubber tires with belting are fed at the low temperatures end of the kiln to supplement additional sources of iron going into the rotary kiln.

Clinker cooling

The clinker grate cooler adjacent to the hot end of the rotary kiln allows the clinker to be air quenched to produce alite form $3\text{CaO} \cdot \text{SiO}_2$ which is the desirable high strength cement glass form. Slow cooling allows a lesser amount of formation of the low strength glass from belite $\text{Ca}_2\text{SiO}_4$. The final clinker is a balance of alite and belite.

The concrete does not dry but sets and hardens. The cement is a hydraulic binder whose hydration requires water. Water is essential to its hardening and water losses must be minimized at the early setting stage to avoid the development of cracks. The step of poured
concrete minimizes desiccation (loss of water) by evaporation in the curing. Upon addition of water, clinker minerals react to form different types of hydrates and "set" (harden) as the hydrated cement paste and aggregate becomes concrete. The calcium silicate hydrates of alite and belite mineral represent the main "glue" components of the concrete. After initial setting, the concrete continues to harden and to develop its mechanical strength. The first 28 days are the most critical for the hardening.

From clinker cooler, the clinker is conveyed to a clinker storage bin adjacent to a gypsum storage bin. A mixture of clinker and gypsum, approximately 95-5 ratio, is transferred to a ball mill for final sizing. The ball mill is typically divided into at least two chambers allowing the use of different sizes of grinding media. Large balls are used at the inlet to crush clinker nodules down to 25 mm in diameter. Ball diameters are in the range of 60–80 mm. In the two-chamber mill, the balls in the second chamber are typically 15–40 mm. The final particle size of the mixture of Portland cement is typically 3 mm (0.12 in) to 25 mm (0.98 in) in diameter.

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1 Cement – Heat of hydration - The chemical reaction that takes place between the cement and water is an exothermic reaction (gives off heat) and the cement (in concrete) hardens.
4 Cement Rotary Kiln Design | Key Factors in Rotary Kiln Shell Design (cementplantsupplier.com)
5 Wikipedia
6 Gypsum is a sulfate mineral composed of calcium sulfate dihydrate, chemical formula CaSO₄·2H₂O
7 Wikipedia