Concrete

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Concrete: composite material composed of coarse granular materials (the aggregate or filler) embedded in a hard matrix of material (cement or binder) that fills the space between the aggregate particles and glues them together.

Gravity base structure for the Hibernia offshore oil platform (Hoff Consulting, LLC)
# Concrete

## Definitions for Concrete

<table>
<thead>
<tr>
<th>Concrete</th>
<th>Filler</th>
<th>Binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland cement concrete</td>
<td>Aggregate (fine and coarse)</td>
<td>Portland cement paste</td>
</tr>
<tr>
<td>Mortar</td>
<td>Fine aggregate</td>
<td>Paste</td>
</tr>
<tr>
<td>Paste</td>
<td>Cement</td>
<td>Water</td>
</tr>
</tbody>
</table>

## Quantities of Materials Used in U.S. Construction, 2000

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10^6 m³</td>
<td>10^6 ft³</td>
</tr>
<tr>
<td>Timber</td>
<td>107</td>
<td>3780</td>
</tr>
<tr>
<td>Concrete</td>
<td>275</td>
<td>9700</td>
</tr>
<tr>
<td>Cement</td>
<td>33</td>
<td>1180</td>
</tr>
<tr>
<td>Steel</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>Brick and clay products</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Building stone</td>
<td>0.3</td>
<td>12</td>
</tr>
<tr>
<td>Nonferrous metals</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Asphalt</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Concrete

Advantages and Disadvantages of Concrete as a Construction Material

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ability to be cast</td>
<td>Low tensile strength</td>
</tr>
<tr>
<td>Economical</td>
<td>Low ductility</td>
</tr>
<tr>
<td>Durable</td>
<td>Volume instability</td>
</tr>
<tr>
<td>Fire resistant</td>
<td>Low strength-to-weight ratio</td>
</tr>
<tr>
<td>Energy efficient</td>
<td></td>
</tr>
<tr>
<td>On-site fabrication</td>
<td></td>
</tr>
<tr>
<td>Aesthetic properties</td>
<td></td>
</tr>
</tbody>
</table>

Concrete

Typical Engineering Properties of Structural Concrete

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength</td>
<td>35 MPa (5000 lb/in.²)</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>6 MPa (800 lb/in.²)</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>3 MPa (400 lb/in.²)</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>28 GPa (4 × 10⁹ lb/in.²)</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.18</td>
</tr>
<tr>
<td>Tensile strain at failure</td>
<td>0.001</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>10 × 10⁻⁶°C (5.5 × 10⁻⁹°F)</td>
</tr>
<tr>
<td>Ultimate shrinkage strain</td>
<td>0.05–0.1%</td>
</tr>
<tr>
<td>Density</td>
<td>Normal weight = 2300 kg/m³ (145 lb/ft³)</td>
</tr>
<tr>
<td></td>
<td>Lightweight = 1800 kg/m³ (110 lb/ft³)</td>
</tr>
</tbody>
</table>
Concrete

**Typical Properties of Construction Materials:**

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg/m³)</th>
<th>Tensile Strength (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Coefficient of Thermal Expansion (10⁻⁶/°C)</th>
<th>Thermal Conductivity (W/m·K)</th>
<th>Energy Requirement (GJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Pure</td>
<td>2800</td>
<td>100</td>
<td>70</td>
<td>23</td>
<td>220</td>
<td>360</td>
</tr>
<tr>
<td>Alloy</td>
<td>2800</td>
<td>300</td>
<td>70</td>
<td>23</td>
<td>125</td>
<td>360</td>
</tr>
<tr>
<td>Steel Mild</td>
<td>7800</td>
<td>400</td>
<td>210</td>
<td>12</td>
<td>50</td>
<td>300</td>
</tr>
<tr>
<td>High strength</td>
<td>7800</td>
<td>1900</td>
<td>210</td>
<td>12</td>
<td>50</td>
<td>300</td>
</tr>
<tr>
<td>Glass</td>
<td>2500</td>
<td>60</td>
<td>65</td>
<td>6</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>Wood Soft</td>
<td>350</td>
<td>50</td>
<td>5.5</td>
<td>—</td>
<td>0.2–0.6</td>
<td>—</td>
</tr>
<tr>
<td>Hard</td>
<td>700</td>
<td>100</td>
<td>10</td>
<td>—</td>
<td>0.2–0.6</td>
<td>—</td>
</tr>
<tr>
<td>Plastic (polystyrene)</td>
<td>1000</td>
<td>~30</td>
<td>~3</td>
<td>72</td>
<td>0.1</td>
<td>—</td>
</tr>
<tr>
<td>Rock (granite)</td>
<td>2600</td>
<td>~20 (~25°)</td>
<td>~50</td>
<td>7–9</td>
<td>3</td>
<td>—</td>
</tr>
<tr>
<td>Concrete</td>
<td>2300</td>
<td>3 (35°)</td>
<td>~25</td>
<td>10</td>
<td>3</td>
<td>3.4</td>
</tr>
</tbody>
</table>

*Conversion factors: kg/m³ × 0.062 = lb/ft³; MPa × 145 = lb/in²; GPa × 0.145 = 10⁶ lb/in²; 10⁻⁶°C × 0.556 = 10⁻⁶°F; W/m·K × 0.578 = Btu/ft·h·°F; GJ/m³ × 26.9 = Btu/ft³.*

*In compression.*

---

Concrete

- **Strength!**
- Durability
- Workability
Concrete

- Strength
- Durability!
- Workability
Concrete

- The history of concrete can be traced back to the ancient Egypt era. In this period of time, Nonhydraulic cements that could only work in very dry climates, such as unburnt bricks and clay, were developed. These materials had no resistance to water.

Concrete

- The first calcareous materials to be used as cements in mortars were gypsum and lime

- Gypsum-based mortars (e.g. in the Pyramid of Cheops ~3000B.C.)

\[ 2\text{CaSO}_4\cdot2\text{H}_2\text{O} \rightarrow (\text{heat } \approx 130^\circ\text{C}) \]
\[ 2\text{CaSO}_4\cdot\frac{1}{2}\text{H}_2\text{O} + 3\text{H}_2\text{O} \]
Concrete

- Lime-based mortars were used in Crete, Cyprus, Greece, and the Middle East (~6000-12,000 B.C.)

- **Calcining limestone**
  \[ 2\text{CaCO}_3 \rightarrow (\text{heat } \sim 1000\degree \text{C}) \rightarrow \text{CaO + CO}_2 \]
  Hardening in air (air mortar)
  \[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \rightarrow (\text{with CO}_2) \text{CaCO}_3 + \text{H}_2\text{O} \]

Similar to portland cement:
- Decomposition of limestone, and restoring its strength with water

Concrete

- **Hydraulic limes**

  By calcining limestones containing argillaceous (clayey – volcanic ash; *pozzolana*) impurities, hydraulic limes could be produced with higher strength and water resistance, which was known by Greeks, Romans, and Chinese (~1000 B.C.)

  This technique was almost lost in Europe in the Middle Ages. The application of the pozzolans was reintroduced not until the 14th century.
Concrete

- **Pozzolan**: An inert silicious material which in the presence of water will combine with lime to produce a cementitious matter with excellent structural properties.
- Improved workability
  - Economy
  - Reduced alkali-aggregate reaction
  - Increased sulfate resistance

In 1756, John Smeaton, the first person who style himself a “civil engineer”, rebuilt the Eddystone Lighthouse off the coast of Cornwall, England. He carried out a series of experiments focusing on different limestones and pozzolans to improve the water resistance. The lighthouse stood for 126 years before it was replaced by a more modern structure (Kenneth Spencer Research Library).
Concrete

After Smeaton’s work, a number of researches were carried out.

- “Roman” cement (James Parker, England, 1796) – calcining nodules of impure limestone containing clay
- Vicat (France), 1813 – calcining synthetic mixtures of limestone and clay
- James Frost (England), 1822 – calcining synthetic mixtures of limestone and clay

Concrete

- The name of “Portland” was from the Isle of Portland, where the popular, naturally occurring limestone quarried was used in many 18th and 19th century buildings in southern England.
Concrete

- Portland cement: calcining finely ground limestone then mixing this with finely divided clay, and calcining the mixture in a kiln until the CO₂ was driven off.
- Isaac Johnson developed modern Portland cement in 1845 by increasing the temperature of the processing.

Concrete

- In 1886, Ransome first developed rotary kiln to replace the vertical kiln, which must be completely discharged before a new batch of cement could be made.
- In 1909, Thomas Edison was issued a series of patents for rotary kilns, most of which are still being used today.
**Concrete**

Cement Production in the United States and Canada (Metric Tons).

<table>
<thead>
<tr>
<th>Year</th>
<th>United States</th>
<th>Canada</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Natural Cement</td>
<td>Portland Cement</td>
<td>Natural Cement</td>
</tr>
<tr>
<td></td>
<td>Imported</td>
<td>Domestic</td>
<td>Imported</td>
</tr>
<tr>
<td>1880</td>
<td>450,000</td>
<td>18,000</td>
<td>4,500</td>
</tr>
<tr>
<td>1890</td>
<td>1,270,000</td>
<td>360,000</td>
<td>54,000</td>
</tr>
<tr>
<td>1900</td>
<td>1,850,000</td>
<td>270,000</td>
<td>1,540,000</td>
</tr>
<tr>
<td>1915</td>
<td>90,000</td>
<td>~ 900</td>
<td>14,100,000</td>
</tr>
<tr>
<td>1930</td>
<td>N.A.</td>
<td>N.A.</td>
<td>30,500,000</td>
</tr>
<tr>
<td>1950</td>
<td>540,000</td>
<td>41,000</td>
<td>42,100,000</td>
</tr>
<tr>
<td>1975</td>
<td>–</td>
<td>943,000</td>
<td>59,000,000</td>
</tr>
<tr>
<td>2000</td>
<td>–</td>
<td>21,200,000</td>
<td>88,800,000</td>
</tr>
</tbody>
</table>

*Both natural and portland cement*

*N.A., not available*
Portland Cement

- Dark gray powder
- Chemical combination of:
  - calcium carbonate
  - silica
  - alumina
  - iron oxide
  - calcium sulfate, gypsum

Manufacture of Portland Cement

- Fabrication of portland cement is, basically, quite simple and relies on the use of abundant raw materials.
- Heating of mixtures of limestone and clay particles in a kiln to 1400-1600°C to form calcium silicates.
- In reality, a number of issues need to be considered due to the large material volume and the quality control.
Manufacture of Portland Cement

- Mixing limestone and clay, heating in a kiln
  - limestone, lime chalk
  - clay, silt, shale
- Quarry, primary crusher, conveyer, second crusher
- Heating melts all components, drives the water out, and fuses the ingredients

A typical dry-process rotary kiln
Manufacture of Portland Cement

- Final processing:
  
The material that emerges from the kiln is known as clinker (dark-gray porous nodules 6-50mm large). Further processing consisting of grinding and intergrinding with gypsum is required to control the reaction of the tricalcium aluminate.

Environmental Concerns

Each year, 2-4 billion tons of portland cement is produced

- Emits ~1 ton CO₂ to produce 1 ton portland cement (~5% human produced greenhouse gas)
- Accounts for 5-8% industrial energy use
Greenhouse Gas

What we know about greenhouse gas effect:

1. Greenhouse gas effect is real

(Venus: The second planet from the Sun
Surface temperature 462 °C
Sulfuric acid cloud layer
Ocean disappeared due to the runaway greenhouse gas effect)

Climate will change, if greenhouse gas concentration keeps increasing

Y. Qiao, UCSD (yqiao@ucsd.edu)

Pre-1750 | Current
---|---
CO₂ | 280,000 | 400,000
Methane | 700 | 1,800
Nitrous oxide | 270 | 322
Ozone | 25 | 34
CFC-12 | 0 | 0.5
HCFC-22 | 0 | 0.2
SF₆ | 0 | 0.007

(Unit: parts per billion)

Y. Qiao, UCSD (yqiao@ucsd.edu)

2. CO₂ is important
3. [CO₂] is rising
**Greenhouse Gas**

What we know about greenhouse gas effect:

<table>
<thead>
<tr>
<th></th>
<th>Pre-1750</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CO₂</strong></td>
<td>280,000</td>
<td>400,000</td>
</tr>
<tr>
<td>Methane</td>
<td>700</td>
<td>1,800</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>270</td>
<td>322</td>
</tr>
<tr>
<td>Ozone</td>
<td>25</td>
<td>34</td>
</tr>
<tr>
<td>CFC-12</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>SF₆</td>
<td>0</td>
<td>0.007</td>
</tr>
</tbody>
</table>

(Unit: parts per billion)

(IPCC Report, 2007)

What we don't know:

4. We are still safe…

Today's level

Permian-Triassic extinction

Ichthyostega showed up

(http://earthguide.ucsd.edu)
Portland Cement

Biologically induced climate changes happened before:

- The Great Oxygenation Event (2.3 billion years ago)
- Oceanic cyanobacteria have been producing oxygen through photosynthesis for 200 million years, prior to the GOE
- The oxygen greatly reduced greenhouse gas (e.g. methane)
- It led to the longest Snowball Earth period
- One of the most significant extinction events

Manufacture of Portland Cement

<table>
<thead>
<tr>
<th></th>
<th>Wet Process</th>
<th>Dry Process</th>
<th>All Plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Consumption</td>
<td>6.06 (5.74)</td>
<td>4.41 (4.18)</td>
<td>4.77 (4.52)</td>
</tr>
<tr>
<td>Power consumption*</td>
<td>142</td>
<td>156</td>
<td>153</td>
</tr>
<tr>
<td>Fuel + Power</td>
<td>6.56 (6.22)</td>
<td>4.97 (4.71)</td>
<td>5.32 (5.04)</td>
</tr>
</tbody>
</table>

* kWh/metric ton.
## Composition of Portland Cement

### Typical Composition of Ordinary Portland Cement

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Chemical Formula</th>
<th>Shorthand Notation</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate</td>
<td>3CaO · SiO₂</td>
<td>C₃S</td>
<td>55</td>
</tr>
<tr>
<td>Dicalcium silicate</td>
<td>2CaO · SiO₂</td>
<td>C₂S</td>
<td>18</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>3CaO · Al₂O₃</td>
<td>C₃A</td>
<td>10</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite</td>
<td>4CaO · Al₂O₃ · Fe₂O₃</td>
<td>C₄AF</td>
<td>8</td>
</tr>
<tr>
<td>Calcium sulfate dihydrate (gypsum)</td>
<td>CaSO₄ · 2H₂O</td>
<td>CSH₂</td>
<td>6</td>
</tr>
</tbody>
</table>

*See the section entitled “Specifications and Properties,” however, concerning cements produced in the western states.

### Typical Oxide Composition of a General-Purpose Portland Cement

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Shorthand Notation</th>
<th>Common Name</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>C</td>
<td>lime</td>
<td>64.67</td>
</tr>
<tr>
<td>SiO₂</td>
<td>S</td>
<td>silica</td>
<td>21.03</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>A</td>
<td>alumina</td>
<td>6.16</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>F</td>
<td>ferric oxide</td>
<td>2.58</td>
</tr>
<tr>
<td>MgO</td>
<td>M</td>
<td>magnesia</td>
<td>2.62</td>
</tr>
<tr>
<td>K₂O</td>
<td>K</td>
<td>alkalis</td>
<td>0.61</td>
</tr>
<tr>
<td>Na₂O</td>
<td>N</td>
<td></td>
<td>0.34</td>
</tr>
<tr>
<td>SO₃</td>
<td>S</td>
<td>sulfur trioxide</td>
<td>2.03</td>
</tr>
<tr>
<td>CO₂</td>
<td>C</td>
<td>carbon dioxide</td>
<td>–</td>
</tr>
<tr>
<td>H₂O</td>
<td>H</td>
<td>water</td>
<td>–</td>
</tr>
</tbody>
</table>
Composition of Portland Cement

- Bogue Calculation of the phases from the composition

Case A:  \( A/F \geq 0.64 \)
- \( C_3S = 4.071C - 7.600S - 6.718A - 1.430F - 2.852S \)
- \( C_2S = 2.867S - 0.7544C_3S \)
- \( C_3A = 2.650A - 1.692F \)
- \( C_4AF = 3.043F \)

Case B:  \( A/F < 0.64 \)
- \( C_3S = 4.071C - 7.600S - 4.479A - 2.859F - 2.852S \)
- \( C_2S = 2.867S - 0.7544C_3S \)
- \( C_3A = 0 \)
- \( C_4AF = 2.100A + 1.702F \)

Hydration of Cement

- When portland cement is mixed with water its constituent compounds undergo a series of chemical reactions that are responsible for the eventual hardening of concrete. Reactions with water are designated as hydration, and the new solids formed on hydration are collectively referred as hydration products.

- The hydration process can be described by reaction stoichiometries, rates of reaction, and heats of reaction.

- \( C_3A \) and \( C_3S \) are the most reactive compounds, whereas \( C_2S \) reacts much more slowly.
Hydration of Cement

Characteristics of Hydration of the Cement Compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Reaction Rate</th>
<th>Amount of Heat Liberated</th>
<th>Contribution to Cement Heat Liberation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>Moderate</td>
<td>Moderate</td>
<td>High</td>
</tr>
<tr>
<td>C₂S</td>
<td>Slow</td>
<td>Low</td>
<td>Low initially, high later</td>
</tr>
<tr>
<td>C₄AF + C₃AH₉</td>
<td>Fast</td>
<td>Very high</td>
<td>Low</td>
</tr>
<tr>
<td>C₄AF + C₃SH₉</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Very high</td>
</tr>
</tbody>
</table>

Hydration of Cement

Reaction rates in pure compounds

Reaction rates in cement paste
**Hydration of Cement**

- Rates of reaction have direct relation to strength development;
- Calcium silicates provide most the strength;
- C$_3$S provides most of the early strength;
- C$_3$S and C$_2$S contribute about equally to ultimate strength.

**Types of Portland Cement**

- **Type I**: general purpose
- **Type II**: moderate sulfate resistance and moderate heat of hydration
- **Type III**: high early strength
- **Type IV**: low heat of hydration
- **Type V**: sulfate resistance
## Types of Portland Cement

### Typical Chemical Composition and Properties of Portland Cements, ASTM Types I to V

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3S$</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>42</td>
<td>55</td>
</tr>
<tr>
<td>$C_2S$</td>
<td>18</td>
<td>19</td>
<td>17</td>
<td>12</td>
<td>22</td>
</tr>
<tr>
<td>$C_A$</td>
<td>10</td>
<td>6</td>
<td>10</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$C_AF$</td>
<td>8</td>
<td>11</td>
<td>8</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>$C_SH_2$</td>
<td>6</td>
<td>5</td>
<td>6</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Fineness (Blaine, $m^2/kg$)</td>
<td>365</td>
<td>375</td>
<td><strong>550</strong></td>
<td>340</td>
<td>380</td>
</tr>
<tr>
<td>Compressive strength$^b$ [1 day, MPa (lb/in.$^2$)]</td>
<td>15</td>
<td>14</td>
<td>24</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>Heat of hydration (7 days, J/g)</td>
<td>2200</td>
<td>2000</td>
<td>3500</td>
<td>600</td>
<td>1750</td>
</tr>
</tbody>
</table>

$^a$ CSA designations are 10, 20, 30, 40, and 50, respectively.
$^b$ ASTM C 109 50 mm mortar cubes.

### Types of Portland Cement

**Type III: high early strength**

- High $C_3S$ content, fine particles (high reaction rate)
- High rate of heat evolution. The temperature rise can be very large. The associated thermal stresses may cause tensile cracking in the interior after a few days when the cement is no longer plastic, especially when the size of the structure is large.
- Should not be used in thick (>0.5m) concrete sections.
Types of Portland Cement

Type IV: low heat of hydration
- Reduced volume fraction of C₃S and C₃A that are responsible for most of the early liberation of heat produced.
- Thermal cracking can be eliminated but low ultimate/early strength.

Type V: high sulfate resistance
- High sulfate resistance is required to avoid the deterioration of portland cement when exposed to waters or soils containing sulfates, e.g. seawater, many groundwaters.
- Sulfate attacks involve interactions between the hydration products formed from C₃A.
- Reducing the content of C₃A by converting it to C₄AF is quite helpful to combat sulfate attacks.
Types of Portland Cement

• All the cements contain the same compounds, although in different proportions.
• In all five types the sum total of the $C_3S$ and $C_2S$ contents is about the same: 75% by weight. Thus, the ultimate strengths are quite similar while the rates to achieve them can be very different.
Types of Portland Cement

Blended Cements (ASTM C595)

- Pozzolans or blast furnace slag can be blended with portland cement to adjust reaction rates, to improve durability and other properties not controlled by the five types.
- In US, since mineral admixtures are usually added at the concrete mixer, blended cements are uncommonly used.
Modified Portland Cements

Expansive Cements

- Drying shrinkage of portland cement can cause serious cracking.
- Special cements have been developed to enhance the early expansion. They are also called “shrinkage compensation cements”.

Hydration
Hydration of Portland Cement

- The setting and hardening of concrete are the result of chemical and physical processes that take place between cement and water.
- The hydration of the cement can be decomposed as the hydration reactions of the cement compounds. It is usually assumed that the hydration of each compound takes place independently of the others that are present in portland cement.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium Silicate</td>
<td>$2\text{C}_3\text{S} + 11\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_8 + 3\text{CH}$</td>
</tr>
<tr>
<td>Dicalcium Silicate</td>
<td>$2\text{C}_2\text{S} + 9\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_8 + \text{CH}$</td>
</tr>
</tbody>
</table>
Hydration of Portland Cement

- The principal hydration product is a calcium silicate hydrate (C-S-H), which is a poorly crystalline material that forms extremely small particles in the size range of colloidal matter (less than 1 micron) in any dimension.
- Both of the reactions are exothermic, which means that heat is released as the reaction progresses, leading to the temperature rise of the concrete unless quickly released to the surroundings.
- The heat evolution reflects the degree and the rate of the hydration reactions, and can be conveniently measured in lab by using calorimeter.

The calorimetric curve of C₃S
Hydration of Portland Cement

Stage 1: *period of rapid evolution of heat*
- Ceases within about 15 minutes
- Calcium ions and hydroxide ions are rapidly released from the surface of each C₃S grain
- PH rises to over 12 within a few minutes, which indicates a very alkaline solution
- When the calcium and hydroxide concentration reach a critical value, the hydration products, CH and C-S-H, start to crystallize from solution and the reaction of C₃S again proceed rapidly.

Stage 2: *induction or dormant period*
- The reason why portland cement concrete remains in the plastic state for several hours.
- Caused by the need to achieve a certain concentration of ions in solution before crystal nuclei form from which the hydration products grow.
Hydration of Portland Cement

Stage 3: acceleration period
- Initial set occurs in 2 to 4 hours
- C₃S has begun to react again with renewed vigor
- Final set has been passed and early hardening has begun.
- CH crystallizes from solution.
- C-S-H apparently develops at the surface of the C₃S and forms a coating covering the grain.
- C₂S hydrates in a similar matter but is much slower.

Stage 4: deceleration period
- As hydration continues, the thickness of the hydrate layer (C-S-H) increases and forms a barrier through which water must flow to reach the unhydrated C₃S and through which ions must diffuse to reach the growing crystals.
- Mass transport through the C-S-H layer determines the rate of reaction, and the hydration becomes diffusion controlled.

Stage 5: steady-state.
Hydration of Portland Cement

Sequence of Hydration of the Calcium Silicates

<table>
<thead>
<tr>
<th>Reaction Stage</th>
<th>Kinetics of Reaction</th>
<th>Chemical Processes</th>
<th>Relevance to Concrete Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Initial hydrolysis</td>
<td>Chemical control; rapid</td>
<td>Initial hydrolysis; dissolution of ions</td>
<td>Determines initial set</td>
</tr>
<tr>
<td>2 Induction period</td>
<td>Nucleation control; slow</td>
<td>Continued dissolution of ions</td>
<td>Determines final set and rate of initial hardening</td>
</tr>
<tr>
<td>3 Acceleration</td>
<td>Chemical control; rapid</td>
<td>Initial formation of hydration products</td>
<td>Determines rate of early strength gain</td>
</tr>
<tr>
<td>4 Deceleration</td>
<td>Chemical and diffusion control; slow</td>
<td>Continued formation of hydration products</td>
<td>Determines rate of later strength gain</td>
</tr>
<tr>
<td>5 Steady state</td>
<td>Diffusion control; slow</td>
<td>Slow formation of hydration products</td>
<td></td>
</tr>
</tbody>
</table>

Properties of Hydration Products

C-S-H

- Compositional variations – C-S-H is not a well-defined compound. The formula C₃S₂H₈ is only an approximate description, as the stoichiometry is quite variable.
- The C/S ratio is generally higher than 1.5, varying in the range of 1.5-2.0, depending on the age of the paste, the temperature of hydration, the w/c ratio, the amount and kind of impurity oxides, etc.
- The water content varies even more drastically and depends on the extent of drying as well as the above factors.
- The loss of water is continuous as the relative humidity is lowered from 100% to strong drying in vacuum or on heating.
Properties of Hydration Products

- C-S-H is not a well crystallized material. It is essentially amorphous and develops as a mass of extremely small irregular particles of indefinite morphology.
- C-S-H has very high surface areas ~400m²/g. Such high surface areas are characteristics of colloids.
- Due to its amorphous character, compositional variability, and poorly resolved morphology, interpretation of experimental data of C-S-H is still a subject of active debate.
- C-S-H can be considered to have a degenerate clay structure (quasi-layered structure).
- There are three kinds of pores in C-S-H: interlayer pores (I), micropores (M), and isolated capillary pores (P).
Properties of Hydration Products

Calcium Hydroxide
- It is a well-crystallized material with a definite stoichiometry.
- Crystals can be large enough to be seen by naked eyes.
- Does not form homogeneous crystals in a cement paste.

Calcium Sulfoaluminate
- Ettringite crystallizes as hexagonal crystals, but in a form of needles with a much greater aspect ratio.
- Crystal masses of ettringite can frequently be observed filling in cracks or voids in mature concretes.
- Monosulfoaluminate tends to form clusters (rosettes) of irregular plates first, then grow into well-developed, but very thin, hexagonal plates that are very small.
Properties of Hydration Products

- Needle-like ettringite crystals
- C-S-H particles
- CH crystals

Monosulfoaluminate formed from C₃A
Properties of Hydration Products

(a) Initial mix
(b) 7 days
(c) 28 days
(d) 90 days

Fracture surface of paste with less than 3 days’ hydration (NIST).
Needle-like ettringite in water-filled pores
Platey crystals of CH
C-S-H with indeterminate morphology
Properties of Hydration Products

Polished surface of a 28-day-old paste (NIST)
Large bright unhydrated cores of large grains surrounded by darker C-S-H
Light-gray CH
Black capillary pores

Properties of Hydrated Pastes

- The hardened cement paste more closely resembles ceramic materials dominated by ionic-covalent bonding than it does organic polymers dominated by van der Waal’s bonding.
- The presence of flaws lower the tensile strength of the pastes significantly.
- Increasing of the compressive strength increases with gel/space ratio, $X$, regardless of age, original w/c ratio, or identity of cement. Note that $X$ reflects capillary porosity in terms of w/c and $\alpha$. 
Properties of Hydrated Pastes

- As long as there is enough water, the ultimate porosity is independent to w/c and only related to the degree of hydration.
- The normal range of water is 0.44-0.55.
- Large pores can act as crack initiators; Macropores control the transport of water or dissolved ions through the paste (permeability).
- The permeability of a paste with low w/c ratio can be higher than that of a paste with high w/c ratio by three orders of magnitude, since the large pores are isolated.

Properties of Hydrated Pastes

- CH contributes to strength since it reduces pore volume, but it has a detrimental effect on durability since it is more soluble than C-S-H. On the other hand, it can slow down acid attack and protect reinforcing steel.
- Calcium sulfoaluminate slow down sulfate attack, but promotes expansion. Although ettringite contributes to the early strength, it is not important to the ultimate strength.
- Water in the micropores can result in considerable internal pressure. Removal of the water is the primary mechanism of cement creep.
Aggregates generally occupy 70-80% of the volume of concrete. They are granular materials, derived for the most part from natural rock (crushed stone, or natural gravels) and sands, often hard and strong, free of undesirable impurities, and chemically stable. Synthetic materials such as slags and expanded clay or shale are also used to some extent, mostly in lightweight concrete. They are used as economical filler, and for better dimensional stability and wear resistance, as well as higher stiffness. Usually the strength of concrete is independent of the composition of aggregates, which does affect durability. Aggregates are classified based on specific gravity, not mineralogy (ASTM C294, C33).
Properties of Aggregates

Shape and Texture
- Aggregate shape and texture affect the workability of fresh concrete through their influence on cement paste requirements. Sufficient paste is required to coat the aggregates and to provide lubrication. Spherical aggregates with low surface/volume ratio (most natural sands and gravels) are desired.
- The shape and texture also affect the mechanical properties by affecting the mechanical bond and the degree of stress concentration. Note that usually fracture occurs first at the paste-aggregate interface.

Size Gradation
- The particle size distribution or grading of an aggregate supply is important because it determines the paste requirement for a workable concrete, which affects cost, strength, and durability.
- Void space between particles (paste requirement) of rough particles > uniform-sized spherical particles > nonuniform-sized particles > when the maximum aggregate size is larger.
- However, the size gradation leading to the minimum void space does not result in workable concrete. Trade-off between economy and workability must be considered.
- The grading of an aggregate supply is determined by a sieve analysis using a stack of sieves arranged in order of decreasing size of the openings of the sieves.
Properties of Aggregates

(a) Uniform size
(b) Continuous grading
(c) Replacement of small sizes by large sizes
(d) Gap-graded aggregate
(e) No-fines grading

Moisture Contents

- Water can be absorbed into the body of porous aggregates, and retained on the surface as a film of moisture.
- If the aggregates tend to absorb water, water will be removed from the paste so the the w/c ratio is effectively lowered and the workability decreases, vice versa.
- There are four moisture states:
  (1) oven dry (OD)
  (2) Air dry (AD)
  (3) Saturated surface dry (SSD): “field” state
  (4) Wet.
Properties of Aggregates

- To calculate the amount of water that aggregate will add to or subtract from the paste, we need to define three quantities: absorption capacity (A), effective absorption (EA), and surface moisture (SM).
- A represents the maximum amount of water the aggregate can absorb. It is calculated from the difference between the SSD and OD states
  \[ A = (SSD - OD)/OD \]
  Usually A ~ 1-2%. The absorption of water in the first 30 minutes is essential. After that, the absorption is slow.
- EA represents the amount of water required to bring an aggregate from AD to SSD state.
  \[ EA = (SSD - AD)/SSD \]
- SM = (Wet – SSD)/SSD
- The moisture content (MC) can be estimated as
  \[ MC = (W_{stock} – SSD)/SSD \]
Properties of Aggregates

(a) Dry; (b) partially saturated (menisci formation); (c) fully saturated; (d) increase in volume as a function of surface moisture.

Specific Gravity

- The density of the aggregates is required in mix proportioning to establish weight-volume relationships. The density is usually expressed as specific gravity (SG)

\[ \text{SG} = \frac{\text{density of solid}}{\text{density of water}} \]

- If we take the impermeable pores (not connected to the surface) as part of the solid, we get apparent specific gravity (ASG). Otherwise we get bulk specific gravity (BSG) with all the pores excluded from the solid.

\[ \text{ASG} = \frac{\text{weight of aggregate (solid only)}}{\text{volume of aggregate (solid only)}} \times \frac{\text{density of water}}{\text{density of water}} \]

\[ \text{BSG} = \frac{\text{weight of aggregate (solid+pores)}}{\text{volume of aggregate (solid+pores)}} \times \frac{\text{density of water}}{\text{weight of water displaced}} \]
Properties of Aggregates

- The BSG value is the realistic one to use.
- ASG > BSG_{SSD} > BSG_{OD}
- For most of rocks since MC~1-2%, all the above values are about the same. Usually BSG ~2.5-2.8.
- For lightweight aggregates, BSG value strongly depends on the moisture content.
- BSG measurement method is specified in ASTM C127 and C128.
- Measurement of moisture content is discussed in ASTM C70.

Properties of Aggregates

Unit Weight

- Unit weight (UW) can be defined as the weight of a given volume of graded aggregate, which is also known as bulk density. Note it is very different from BSG.
- UW includes both the particles and the voids between them.
- The measurement of UW is discussed in ASTM C29.
- The void space that must be filled with mortar $V_v$ is $V_v = 1 - \frac{UW}{BSG \times \rho_{water}}$
  Thus, percent of voids $= \left( BSG \times \rho_{water} - UW \right) / \left( BSG \times \rho_{water} \right)$
Properties of Aggregates

Durability of Aggregates

- Since aggregates make up the bulk of concrete, its durability is important.
- In US, this problem is less serious compared with other areas.
- Testing of aggregate durability is discussed in ASTM C702 and D75.
Admixtures

A material other than water, aggregates, hydraulic cement and fiber reinforcement that is used as an ingredient of concrete or mortar and is added to the batch immediately before or during its mixing (ASTM C125).
Mineral Admixtures

- The addition of finely ground solid materials (mineral admixtures or supplementary cementing materials) to concrete is an established practice in modern concrete technology.
- Admixtures are added to replace cement (cost-performance balance), to improve the workability of fresh concrete, and to enhance the durability of hardened concrete.
- Usually mineral admixtures are not water soluble.
- They can be divided into three main categories:
  - Pozzolanic materials
  - Cementitious materials
  - Non-reactive materials (workability aids): finely divided materials (such as ground limestone, silica flour, hydrated lime, etc.);
  - masonry cements with improved workability and water retention.

Pozzolanic Materials

- The addition of naturally occurring materials of volcanic origin to hydraulic limes was known to the Greeks.
- The Romans adopted this technique. The name of "pozzolan" is from "Pozzuoli", a town in the Bay of Naples that was the source of a highly prized deposit of weathered ash (tuff) from Mt. Vesuvius.
- Natural pozzolans were widely used before 1940s. The first modern use of pozzolans in the US dates back to the early construction of the Los Angeles aqueduct in 1910-1912.
- Now, pozzolanic materials indicate any reactive aluminosilicate material, of either natural or industrial origin.
- The material must either occur in finely divided state or be ground to cement fineness.
Pozzolanic Materials

- A good pozzolan should have a high fraction of reactive glassy (formed by rapid cooling) or amorphous material.
- Good quality silica fume contains 98% of amorphous silica.
- Fly ash and natural pozzolans contain significant portion of inert crystalline phases, which can be detected through x-ray diffraction.
- Class F fly ashes have 70-90% glass, with quartz, mullite, hematite, and magnetite as the principal phases that crystallize from the glass on cooling.
- Class C fly ashes contain quartz, free lime (uncombined CaO), and anhydrite (CaSO₄). These crystals undergo complicated reactions. In general, class C fly ash should not be used to avoid problems with high water demand, early stiffing, or rapid setting.
- Many pozzolans also contain alkali oxides (alkalis) in the form of soluble salts that have been deliberately added to improve the efficiency of the electrostatic precipitators, and they may influence the rate of setting and the alkali-aggregate reactions.
Blast Furnace Slag

Effects of Mineral Admixtures on Concrete

Heat of Hydration
- Mineral admixtures reduce the overall heat of hydration and particularly the rate of heat liberation, which controls the temperature rise in hardening concrete.
- The use of mineral admixtures is equivalent to increase C_2S content and effectively turn type I cement into type II or IV cement.

Workability
- Mineral admixtures increase the cementitious material content, which increases the workability of harsh mixes (e.g., concretes made with coarse or angular sands, or short fiber reinforced concretes).
- Due to the spherical shape, fly ash and silica fume are particularly beneficial (ball bearing effect). W/C ratio can be reduced to <0.35 with fly ash additions of up to 25wt%, leading to the high ultimate strength.
- Use of silica fume also makes it effective in eliminating bleeding and segregation, and improve the paste-aggregate bonding (“sticky”).
Effects of Mineral Admixtures on Concrete

**Air Entrainment**
- Concretes containing mineral admixtures must be air entrained for frost resistance, unless the w/c ratio is below 0.24.
- The proportioning of air-entraining agents should be changed.
- The residual carbon in fly ash or rice husk ash strongly inhibits air entrainment, but even carbon-free pozzolan can affect air entrainment.

**Microstructure**
- The increased fraction of C-S-H leads to a more amorphous microstructure.
- Residual CH crystals are small and of altered amorphous.
- The overall porosity is decreased significantly, so is pore size. However, this requires extensive pozzolanic reaction in prolonged moist curing. The reduction of the porosity is also attributed to the reduction of w/c ratio, as well as the filling of the small pozzolan particles, which is beneficial to strength, durability, and permeability.

Effects of Mineral Admixtures on Concrete

**Strength Development**
- Develop very good ultimate strength over time, while the early strength is usually lower.
- Reduction of early strength can be offset by lowering the w/c ratio with the concomitant use of a water-reducing admixture.
- Some highly reactive materials, such as silica fume, calcined clay or rice husk ash, can actually lower the setting time and contributes to early strength.

**Drying Shrinkage and Creep**
- Adding mineral admixtures does not affect drying shrinkage significantly.
- However, if volume change is critical, tests should be made to determine the secondary effect.
- Theoretically, the volume change may increase due to the increased fraction of C-S-H and the finer pore structure.
Effects of Mineral Admixtures on Concrete

Durability
- Better sulfate resistance, control of the alkali-silica reaction, decreased chloride diffusion, and reduction of leaching and efflorescence.
- The mechanisms include: reduction in calcium hydroxide, which is the most soluble of the hydration products; changes in pore structure; reductions in the w/c ratio.
- Pozzolans reduce the amount of ettringite: (1) they reduce the permeability and inhibit the ingress of soluble sulfates; (2) they reduce the amount of CH, thereby limiting the formation of gypsum from soluble sulfates; (3) they reduce the effective C₃A content.
- Reduction of CH is important since CH can leach out over time thus increases the permeability and porosity.

- Not all pozzolans improve sulfate resistance to the same extent.
- Those with high alumina contents can form C-A-H compounds that will increase the potential ettringite formation.
- Also, the increased CaO contents in class C fly ashes will reduce the consumption of calcium hydroxide in the pozzolanic reactions.
- Resistance factor \( R = (\text{CaO}-5)/\text{Fe}_2\text{O}_3 \). Note that Al₂O₃ content is related to CaO and Fe₂O₃. Fly ashes with low \( R \) values give better sulfate resistance.
- Mineral admixtures also reduce expansion due to the alkali-silica reaction, primarily due to the reduction of the alkali content of the cementitious blend and the reduction in pH of the pore solution. Also, the C-S-H formed from pozzolans can absorb alkali ions to a greater extent than that formed by hydration of calcium silicates alone.
- The improvement of durability is also related to the reduction in transport properties, water permeability, and ionic diffusion, which are the rate-limiting factors in chemical attack.
Potential Issues of Mineral Admixtures in Concrete

- Difficulty in mixing and setting (e.g. high CaO content)
- Slow hardening rate
- High content of irregular, weak inclusions
- Distributed damages: hard to retrofit if there is any problem

Chemical Admixtures

- The water soluble materials added in concrete before or during mixing are collectively called chemical admixtures.
- There are three main categories of admixtures:
  (1) Air-entraining agents (ASTM C260) are added primarily to improve the resistance of concrete to freezing and thawing;
  (2) Set-controlling admixtures (ASTM C494) are added to control setting or to induce early hardening;
  (3) Plasticizing admixtures (ASTM C494 and C1017) are water-soluble polymers designed to enhance workability by increasing slump; particularly in excess of 195mm (ASTM C1018) or to reduce the water requirement for a desired workability (ASTM C494).
Use of Admixtures

To avoid surprises:

- Require admixtures to conform to relevant ASTM specifications, where applicable. The supply data from the manufacturer should include:
  1. the main effect of the admixture on concrete performance
  2. any additional influences
  3. physical properties
  4. the concentration of the active ingredient
  5. the presence of any potentially detrimental substances such as chlorides, sulfates, sulfides, nitrates, or ammonia
  6. pH
  7. potential occupational hazards for users
  8. conditions for storage and recommended shelf life
  9. preparation of admixture and procedures for introducing it into the concrete mix, and
  10. recommended dosage under identified conditions, recommended maximum dosage, and effect of overdosing.

---

### Beneficial Effects of Chemical Admixtures on Concrete Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Admixture Type</th>
<th>ASTM Spec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Workability</td>
<td>Water-reducing admixtures</td>
<td>C 494</td>
</tr>
<tr>
<td></td>
<td>Plasticizers</td>
<td>C 1017</td>
</tr>
<tr>
<td></td>
<td>Air-entraining admixtures</td>
<td>C 260</td>
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<tr>
<td></td>
<td>Pumping aids</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Anti-washout admixtures</td>
<td>–</td>
</tr>
<tr>
<td>Set Control</td>
<td>Set-accelerating admixtures</td>
<td>C 494</td>
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<tr>
<td></td>
<td>Set-retarding admixtures</td>
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<tr>
<td></td>
<td>Extended-set admixtures</td>
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<tr>
<td>Strength</td>
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<td>Durability</td>
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<td>C 260</td>
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<tr>
<td></td>
<td>Water-reducing admixtures</td>
<td>C 494</td>
</tr>
<tr>
<td></td>
<td>Corrosion inhibitors</td>
<td>–</td>
</tr>
</tbody>
</table>
Use of Admixtures

- Follow the manufacturer’s instructions regarding dosage, but make relevant tests to check that the desired effects are obtained. It is important to run tests using job material under job-site conditions: cement composition, aggregate characteristics and impurities, mix proportions, presence of other admixtures, type and length of mixing, time of addition, concrete temperature, and environmental conditions.
- Ensure that reliable procedures are established for accurate batching of the admixture, especially for air-entraining admixtures with the typical dosages below 0.1wt%.
- The effects that the admixture may have on other concrete properties should be taken into consideration, particularly if these effects may be unfavorable.

Air-Entraining Admixtures

- To reduce the damage during freezing-thawing cycles by increasing the amount of air that is incorporated into concrete during mixing.
- The volume of air giving optimum frost resistance is 9% by volume.
- In practice, the air content must be in the range of 2-8% by volume of concrete for satisfactory frost protection.
- Intentionally entrained air increase the total volume of air voids by 3-4% of the volume of the concrete and is distributed in the paste as very fine bubbles.
Air-Entraining Admixtures

Morphology of air-entrained concrete (PCA)

An air-entraining agent should always be tested under field condition.

Increasing dose will invariably increase air content, decrease bubble size, and decrease the spacing factor.
Air-Entraining Admixtures

Effect on Fresh Concrete

- Improves the workability and cohesiveness, at both high and low slumps. The bubbles behave as low-friction, elastic, fine aggregate that reduces interactions between conventional solid aggregates.
- Bleeding and segregation are considerably reduced in wet mix during handling and transportation.
- Addition of 3-4% entrained air (total air content 4-7%) will increase the slump about 35-50mm.
- To maintain the same slump, the sand and water content can be decreased significantly, which partially offset the strength loss due to the high air content.

Effect on Hardened Concrete

- The strength loss of 10-20% is common in air-entrained concrete (1% entrained air → 5% strength loss).
- If air content is very high, usually there are large bubbles that lead to poor durability.
Water-Reducing Admixtures

- A water-reducing admixture lowers the water required to attain a given slump, which improves strength, impermeability (water-tightness), and durability.
- Or, the desired slump can be reached without changing w/c ratio by lowering the cement content, which is done for both economic reasons and technical reasons (lowering the heat of hydration).
- Or, it can be used to increase slump without increasing cement and water contents, to facilitate difficult placements. When used this way, it is sometimes called a plasticizer.
- An admixture can be classified in this category if the water reduction is higher than 5%. Many air-entraining agents could also be classed as water-reducing admixtures.

- Water-reducing admixtures are negatively charged organic molecules that adsorb primarily at the solid-water interface.
- In ordinary cement, particles may have opposing charges that can exert considerable electrostatic attractions, causing the particles to flocculate, with a considerable amount of water tied up in these agglomerates and adsorbed on the solid surfaces, leaving less water available to reduce the viscosity.
- The water-reducing admixture molecules make the charges on the solids particles uniform. Thus, most of the water is released.
Water-Reducing Admixtures

- Regular water-reducer can be divided into three types:
  1. lignosulfonates;
  2. hydroxy-carboxylic acids and their salts; and
  3. hydroxylated polymers derived from hydrolyzed starch.
- Most superplasticizers are low molecular weight synthetic polymers containing oxyacid groups attached to the carbon backbone.
- Most of the commercial admixtures belongs to one of the following:
  1. sulfonated naphthalene-formaldehyde;
  2. sulfonated melamine-formaldehyde condensates;
  3. lignosulfonates; and
  4. carboxylated acrylic ester copolymers.

(a) Flocculated paste
(b) Dispersed paste
Water-Reducing Admixtures

Effect on Fresh Concrete

- Concrete with very high slumps can be used for difficult placement, e.g. sections with very congested reinforcing steel, or to improve the ease of placement, e.g. pumping.
- Slumps exceeding 150mm can be achieved with conventional water reducer only by using oversanded mixes with high cement contents. Use of superplasticizer is desirable, which prevents excessive segregation and bleeding.
- If the superplasticizer content is overdosed, the concrete is so fluid that segregation can be serious. Then mixing becomes important.
- A rapid slump loss can be a problem. A second dose should be added if necessary.

Water-Reducing Admixtures

- The admixtures may not improve cohesiveness. Thus, bleeding can be problem.
- Any water-reducing admixture will reduce the amount of an air-entraining admixture required to attain a given air content, due to its own air-entraining ability and the fact that the air-entraining admixture is no longer adsorbed on the solid surface.
- Many water-reducing admixtures will retard the setting. If it is not acceptable, an accelerating admixture must be used.
Water-Reducing Admixtures

Effect on Hardened Concrete

- Lower w/c ratio leads to higher compressive strength. However, the strength increase is usually 25% higher than would be anticipated from the decrease in w/c ratio alone. This is due to the development of more uniform microstructure, which also lowers the permeability and improves durability.
- Very high strengths can be achieved when w/c ratios are lowered below 0.40. Superplasticizer must be used to do this economically and without excessive generation of heat by keeping the cement content at normal level.
- Water-reducing admixtures can increase drying shrinkage. The reason is still unknown.
- The spacing factor required is higher than that of ordinary concrete.

Admixtures for Set Control

Set-Retarding Admixtures

- Retarders can be used to avoid large temperature rise or allow delay of the placement.
- Retarders can be classified as:
  (1) lignosulfonic acids and their salts;
  (2) hydroxycarboxylic acids and their salts;
  (3) sugars and their derivatives;
  (4) phosphates and organic phosphonate salts; and
  (5) salts of amphoteric metals, such as zinc, lead, and tin.
- Retarders slow down the early hydration of C₃S by extending the induction period.
- Organic retarders can be adsorbed on CH surface and inhibit them from growing into large crystals.
Admixtures for Set Control

- Many retarders have air-entraining ability, especially when they are also water-reducing agents.
- Retarders can also increase the rate of workability (slump) loss.
- Whenever a retarding admixture is used, some reduction in the one-day strength should be anticipated, unless there is a concomitant reduction in w/c ratio.
- The ultimate strength can be improved.
- The rate drying shrinkage is slightly increased, while the ultimate value remains about the same.

Set-Accelerating Admixtures

- Quick setting admixtures (soluble carbonates, aluminates, fluorides, and ferric salts) provide setting times of only a few minutes and are used in shotcreting applications for plugging leaks while under hydraulic pressure and for emergency repair.
- Regular accelerators are used to speed construction by permitting earlier finishing of flatwork and earlier attainment of sufficient strength. They are beneficial in winter in dealing with the relatively low temperature rise due to the slow hydration process associated with the low temperature.
- Accelerators can be classified as:
  1. Soluble inorganic salts, e.g., calcium salts (calcium chloride, calcium nitride – which should be used in reinforced concrete to prevent corrosion),
  2. Soluble organic compounds, e.g., triethanolamine, calcium formate; and
  3. Miscellaneous solid materials, e.g., calcium sulfoaluminate and calcium fluoroaluminate that can serve as “seeds” in the hydration process.
Admixtures for Set Control

- Accelerators shorten the induction period, and increase the hydration rate in stage III and stage IV.
- Accelerators may or may not have effects on air entrainment. Special tests should be performed to check this if necessary.
- Accelerators can increase the water required.
- They can increase one-day strength. 2 wt% of calcium chloride can double the one-day strength.
- Later strength (>28 days) is likely to be lower. This effect is profound when the setting time is very short.
- They increase the rate of drying shrinkage, but not the ultimate value.
- Use of calcium chloride reduces resistance to sulfate attack and aggravates the alkali-aggregate reaction.
- They increase the corrosion rate of reinforcement agents considerably!

Miscellaneous Admixtures

- Viscosity Modifiers: high molecular weight, water soluble polymers; reduce the tendency of bleeding and segregate.
- Antifreezing Admixtures: high-molecular-weight alcohols, high concentration of chlorides, nitrates, nitrites…; used under cold weather; lower freezing point of water and increase heat evolution of hydration; not used widely in the US; popular in Russia.
- Expansion-producing Admixtures
- Gas-Forming Admixtures
- Expansive Hydrates
- Corrosion Inhibitors
- Alkali-Aggregate Reaction Inhibiting Admixtures
- Shrinkage-Reducing Admixtures
## Miscellaneous Admixtures

<table>
<thead>
<tr>
<th>Category</th>
<th>Example</th>
<th>Addition</th>
<th>Mode of Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodic inhibitors</td>
<td>Calcium nitrite</td>
<td>0.5-2</td>
<td>Promotes formation of a protective passive film.</td>
</tr>
<tr>
<td></td>
<td>Sodium chromate</td>
<td>2-4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium benzoate</td>
<td>6-8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stannous chloride</td>
<td>2-4</td>
<td></td>
</tr>
<tr>
<td>Cathodic inhibitors</td>
<td>NaOH or Na₂CO₃</td>
<td>2-4</td>
<td>Increases pH and lowers solubility of Fe⁺³.</td>
</tr>
<tr>
<td></td>
<td>Aniline derivatives</td>
<td></td>
<td>Proton acceptors that adsorb on the cathode.</td>
</tr>
<tr>
<td></td>
<td>(Aminobenzene)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed inhibitor</td>
<td>Aminobenzeneethiol</td>
<td></td>
<td>Adsorbs at both anodic and cathodic sites.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Amino group adsorbs at cathode, thiol group at anode.)</td>
</tr>
</tbody>
</table>

*% of cement mass.