Portland Cement
ACI Definition

**Portland cement** (*n.*) a cementitious product made by heating raw materials containing oxides of aluminum, silicon, and calcium to temperatures approaching 1500°C, then pulverizing the end product with a small amount of gypsum.
Origins

In 1824, bricklayer Joseph Aspdin patented a material he called “Portland cement” because it had a color similar to that of a popular building stone quarried on the Isle of Portland off the coast of England. This was strictly a marketing move!

He made his cement by grinding up local limestone, adding water and clay to make a slurry, drying it, heating it in a kiln (a process called clinkering) and then grinding the fired product into a fine powder.
Limestone Quarry
Isle of Portland
Origins

Joseph’s portland cement was mixed with water to create a mortar that could be used to stucco buildings. When the mortar cured, it has a color very similar to Portland stone.

Unfortunately, Aspdin’s product wasn’t really much better than other products in use at the time. Joseph’s son William was actually the one who perfected the process for creating what we know today as portland cement.
William Aspdin

https://en.wikipedia.org/wiki/William_Aspdin
Primary Ingredients

lime (CaO) — 61-67%
  limestone, marble, chalk, marl, calcite, seashells, blast furnace slag

silica (SiO₂) — 19-23%
  clay, loess, shale, sand, sandstone, quartzite, fly ash, rice-hull ash

alumina (Al₂O₃) — 2-6%
  clay, loess, shale, bauxite, fly ash

iron oxide (Fe₂O₃) — 0-6%
  clay, shale, iron ore, pyrite, blast furnace flue dust
Cement Manufacture

Today, there are two general methods used to make portland cement: the dry process and the wet process.

In the dry process, the raw materials are crushed to a nominal size of $\frac{3}{4}$" then fed into a grinding mill. The resulting powder is fed into silos where the various ingredients are proportioned and blended by adding compressed air to “fluidize” the power so it can be intimately mixed. The powder is then fed into the kiln where it is transformed into *clinker*. 
Cement Manufacture

In the wet process, hard materials like limestone are first crushed, then fed into a ball mill along with clay dispersed in water to form a slurry. This allows the ingredients to be intimately blended into a uniform mixture that is then fed directly into the kiln.

Compared to the dry process, the wet process is a simpler operation, produces much less dust, blends the ingredients better to produce a higher quality end product, but uses more energy to drive off the water.
Cement Manufacture

After the raw materials enter the kiln, they go through a series of transformations as they travel along the length of the kiln, getting ever closer to the burner end of the kiln where the temperatures reach 1500°C.

First, water is driven off to dry the material. Next, the limestone is *calcined* to produce lime and carbon dioxide. Then *sintering* occurs. This is where the ingredients partially melt and recombine into the minerals responsible for cement’s properties.
Cement Manufacture

As the semi-molten material approaches the end of the kiln, it cools into roughly golf-ball-sized, dark green lumps of clinker.

The clinker is then fed, along with a small amount (2% to 5%) of gypsum, into a grinding mill where it is reduced to a fine, gray-green powder.

During grinding, certain other materials such as fly ash can be added to enhance the cement’s properties.
Inside a Cement Kiln

Total time in kiln = 60-90 minutes

- 1500°C: sintering
- 800°C: calcining
- 400°C: drying
- Cooling

clinker
Inside a Cement Kiln

\[
\text{CaCO}_3 \xrightarrow{\text{heat} > 825^\circ \text{C}} \text{CaO} + \text{CO}_2
\]

1 ton of cement \( \approx \frac{1}{2} \) ton of \( \text{CO}_2 \)
Inside a Cement Kiln

\[ 2 \cdot CaO + SiO_2 \xrightarrow{heat > 1200^\circ C} Ca_2SiO_4 \]

Clinker forms at 400–800°C, then sintering occurs at 800–1200°C, leading to the formation of C\textsubscript{2}S.
Inside a Cement Kiln

\[ CaO + Ca_2SiO_4 \xrightarrow{\text{heat} > 1250^\circ C} Ca_3SiO_5 \]

- **sintering**
- **calcining**
- **drying**
- **cooling**

- **C\textsubscript{3}S** forms
- Clinker

[Diagram of cement kiln process with temperature and material flow highlighted]
Inside a Cement Kiln

$$3 \cdot CaO + Al_2O_3 \xrightarrow{heat\ 1300^\circ C} Ca_3Al_2O_6$$

- **Sintering**
- **Calcining**
- **Cooling**
- **Drying**

Clinker forms $C_3A$ at $1500^\circ C$. $C_3A$ forms during the sintering process.
Inside a Cement Kiln

\[ CaO + Ca_3Al_2O_6 + Fe_2O_3 \rightarrow Ca_4Al_2Fe_2O_{10} \]
Cement Phases

Portland cement is actually a chemically complex material composed of 4 major compounds (phases):

• Tricalcium silicate ($\text{Ca}_3\text{SiO}_5$)
• Dicalcium silicate ($\text{Ca}_2\text{SiO}_4$)
• Tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$)
• Tetracalcium aluminoferrite ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$)

Each contributes different properties to the cement.
Cement Phases

Dicalcium silicate  
$C_2S$ ($Ca_2SiO_4$)

Tricalcium silicate  
$C_3S$ ($Ca_3SiO_5$)

Tricalcium aluminate  
$C_3A$ ($Ca_3Al_2O_6$)

Tetracalcium aluminoferrite  
$C_4AF$ ($Ca_4Al_2Fe_2O_{10}$)
Cement Phases

Tricalcium silicate (C$_3$S) hydrates and hardens fairly quickly and is largely responsible for initial setting and early strength gain.

Dicalcium silicate (C$_2$S) hydrates and hardens slowly and is largely responsible for long-term strength gain.

Tricalcium aluminate (C$_3$A) hydrates and hardens the quickest, liberating a large amount of heat in the process. It is primarily responsible for setting.
Cement Phases

Gypsum is added to portland cement to retard $C_3A$ hydration. Without the gypsum, $C_3A$ hydration would cause the portland cement to set almost immediately after adding water.

$C_3A$ reacts poorly when exposed to sulfates ($\text{MgSO}_4$ and $\text{NaSO}_4$ salts) that naturally occur in groundwater, seawater, and some clayey soils. The reaction causes the concrete to expand and crack. Sulfate resistance cement has a low $C_3A$ concentration.
Cement Phases

Tetracalcium aluminoferite (C₄AF) hydrates rapidly but contributes very little to setting or strength gain. Its presence allows for lower kiln temperatures in the manufacturing process, which is why ferrous materials are added to the raw ingredients.
Cement Phases

(Taken from Cement and Concrete by M.S.J. Gani)

Figure 2.16 Microstructure of a commercial clinker. The alite crystals are light grey and the belite are the darker rounded crystals. The phases in between the alite and belite are ferrite (white) and $\text{C}_3\text{A}$ (darker). The pores are black (redrawn from a micrograph from Scrivener, 1989)
## Cement Phases

Setting = transformation of cement paste from fluid to gel to solid

Hardening = gain in strength after concrete gel has become a solid

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>$C_3S$</th>
<th>$C_2S$</th>
<th>$C_3A$</th>
<th>$C_4AF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate of hydration</td>
<td>Med</td>
<td>Slow</td>
<td>Fast</td>
<td>Fast</td>
</tr>
<tr>
<td>Heat of hydration</td>
<td>Med</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Early strength</td>
<td>High</td>
<td>Low</td>
<td>Med</td>
<td>Low</td>
</tr>
<tr>
<td>Ultimate strength</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Sulfate resistance</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
<td>Good</td>
</tr>
</tbody>
</table>

Responsible for Short-term Hardening

Responsible for Long-term Hardening

Responsible for Initial Setting
Rate of Strength Gain

![Graph showing the rate of strength gain for C\textsubscript{3}S and C\textsubscript{2}S over time in days. The graph plots compressive strength (MPa) and compressive strength (lb/in\textsuperscript{2}) against time (days).]
A typical portland cement contains around 50% C$_3$S, 25% C$_2$S, 12% C$_3$A, 8% C$_4$AF, 4% gypsum, and 1% other compounds.

By varying the proportions of the raw ingredients and things like the temperatures and dwell times in the various areas of the kiln, we can create portland cements with different properties.

ASTM C150 recognizes eight basic types of portland cement: Types I, IA, II, IIA, III, IIIA, IV, and V.
Cement Composition

- Tricalcium Silicate: 50%
- Dicalcium Silicate: 25%
- Tricalcium Aluminate: 12%
- Tetracalcium Aluminoferrite: 8%
- Gypsum: 4%
- Other: 1%

Typical Percentages by Weight (Mindess and Young, 1981)
# Types of Portland Cement

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Normal</td>
<td>General-purpose cement suitable for most purposes.</td>
</tr>
<tr>
<td>IA</td>
<td>Normal-Air Entraining</td>
<td>An air-entraining modification of Type I.</td>
</tr>
<tr>
<td>II</td>
<td>Moderate Sulfate Resistance</td>
<td>Used as a precaution against moderate sulfate attack. It will usually generate less heat at a slower rate than Type I cement.</td>
</tr>
<tr>
<td>IIA</td>
<td>Moderate Sulfate Resistance-Air Entraining</td>
<td>An air-entraining modification of Type II.</td>
</tr>
</tbody>
</table>
## Types of Portland Cement

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>High Early Strength</td>
<td>Used when high early strength is needed. It is has more C3S than Type I cement and has been ground finer to provide a higher surface-to-volume ratio, both of which speed hydration. Strength gain is double that of Type I cement in the first 24 hours.</td>
</tr>
<tr>
<td>IIIA</td>
<td>High Early Strength-Air Entrainning</td>
<td>An air-entraining modification of Type III.</td>
</tr>
<tr>
<td>IV</td>
<td>Low Heat of Hydration</td>
<td>Used when hydration heat must be minimized in large volume applications such as gravity dams. Contains about half the C3S and C3A and double the C2S of Type I cement.</td>
</tr>
<tr>
<td>V</td>
<td>High Sulfate Resistance</td>
<td>Used as a precaution against severe sulfate action – principally where soils or groundwaters have a high sulfate content. It gains strength at a slower rate than Type I cement. High sulfate resistance is attributable to low C3A content.</td>
</tr>
</tbody>
</table>
# Types of Portland Cement

Setting = transformation of cement paste from fluid to gel to solid
Hardening = gain in strength after concrete gel has become a solid

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>$C_3S$</th>
<th>$C_2S$</th>
<th>$C_3A$</th>
<th>$C_4AF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Normal</td>
<td>50</td>
<td>24</td>
<td>11</td>
<td>8</td>
</tr>
<tr>
<td>II</td>
<td>Modified</td>
<td>42</td>
<td>33</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>III</td>
<td>High early</td>
<td>60</td>
<td>13</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>IV</td>
<td>Low heat</td>
<td>26</td>
<td>50</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>V</td>
<td>Sulfate-resistant</td>
<td>40</td>
<td>40</td>
<td>3.5</td>
<td>9</td>
</tr>
</tbody>
</table>

- **Type I** is responsible for short-term hardening.
- **Type II** is responsible for long-term hardening.
- **Type III** is responsible for initial setting.

CIVL 3137
Types of Portland Cement

Changing the proportions of the various phases is a zero-sum game because they always total 100%.

For example, if you increase the $C_3A$ and $C_3S$ to increase the early strength gain, there will be less $C_2S$ available to provide late strength gain. As a result, Type III cement gains a lot of strength in the first few days, but then the strength gain slows to a crawl. Also, because $C_3A$ and $C_3S$ hydrate rapidly, Type III cement produces more heat of hydration.
Types of Portland Cement

If you want to produce low-heat cement, you need to limit the phases with the highest heat of hydration ($C_3A$ and $C_3S$), but those phases are responsible for setting and early strength gain, so Type IV cement develops strength more slowly than the other types. However, removing $C_3A$ and $C_3S$ means the $C_2S$ is more prevalent, leading to better long-term strength development.
Rate of Strength Gain

![Diagram showing the rate of strength gain over time with different designations: "High Early", "Low Heat", II, IV, V, I, III.](image)
Rate of Heat Generation

![Graph showing the rate of heat generation over time for different types of concrete. The graph indicates the temperature rise in degrees Celsius over time in days. The types are labeled as "High Early", "Low Heat", and "Type I", "Type II", "Type III", "Type IV".](image)
Cement Hydration

When cement comes into contact with water, an exothermic chemical reaction called \textit{hydration} occurs.

The hydration of the C\textsubscript{3}S and C\textsubscript{2}S is responsible for the strength of concrete. When both compounds are mixed with water, they create \textit{calcium silicate hydrate} gel (CSH) and \textit{calcium hydroxide} crystals (CH). The CSH is what glues the aggregate particles together to form concrete.
Hydration Chemistry

C-S-H

CH
Hydration Chemistry

\[ 2\text{Ca}_2\text{SiO}_4 + 4\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + \text{Ca(OH)}_2 \]

dicalcium silicate

water

crystals

calcium silicate hydrate
Hydration Chemistry

$$2\text{Ca}_3\text{SiO}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2$$
Hydration Chemistry

\[
CS + H \rightarrow CSH + CH
\]

- Calcium silicate
- Water
- Calcium silicate hydrate
- Calcium hydroxide crystals
Cement Hydration

The hydration process is actually quite complex.

Soon after mixing, the $\text{C}_3\text{A}$ reacts with the water to form an aluminate-rich gel (Stage I). The gel reacts with sulfate in solution to form small needle-like crystals of ettringite. The $\text{C}_3\text{A}$ reaction with water is strongly exothermic but does not last long, typically only a few minutes, and is followed by a period of a few hours of relatively low heat generation (Stage II).
Cement Hydration

The first half of the dormant period corresponds to when concrete can be placed. After that, the paste becomes too stiff to be workable.

At the end of the dormant period, the C$_3$S and C$_2$S start to react, forming calcium silicate hydrate and calcium hydroxide (Stage III). This stage is when the concrete turns from a paste into a solid and starts to gain strength.
Cement Hydration

During the next stage (Stage IV) the reaction rate slows as the C₃S continues to hydrate and the concrete gains more strength.

As the individual cement grains hydrate from the surface inward, C₃A hydration also resumes as fresh crystals become exposed to water.

After about 12-24 hours, the rate of heat generation tapers off to a low steady state (Stage V).
Cement Hydration

Stage 1 (15 minutes)

Stage 2

Stage 3 and 4

Stage 5

C$_3$S & C$_3$A hydration

C$_3$S hydration

C$_3$ A hydration (renewed)

Initial Set (2-4 hours)

Final Set (6-8 hours)

Steady State (12-24 hours)
Initial and Final Set

Shortly after the end of Stage II, the concrete reaches *initial set*. Up until this point, the concrete is actually a gel and, if remixed, will return to its original fluid consistency. This is known as *thixotropy*. It is the reason why ready-mix trucks have revolving drums: they keep the concrete fluid until it is ready to be placed. Several hours later (near the end of Stage III) the concrete reaches *final set*. At this point it is solid enough to resist penetration, but it doesn’t have any appreciable structural strength.
Setting Time Factors

\[
\begin{align*}
\text{amount of } C_3A & \\
\text{amount of } CaSO_4 & \\
\text{cement fineness} & \\
\end{align*}
\]

\{ cement type \}
Effects of Fineness

Source: www.theconstructioncivil.com
Setting Time Factors

\[
\begin{align*}
\text{amount of } \ce{C_3A} & \quad \text{amount of CaSO}_4 \\
\text{cement fineness} & \quad \text{cement type} \\
\text{amount of mixing water} & \quad \text{amount of sun/wind} \\
\text{ambient temperature} & \quad \text{placing conditions}
\end{align*}
\]
Hardening Factors

- amount of $C_3S$
- amount of $C_2S$
- ambient temperature
- ambient humidity

Cement Type

Curing Conditions
Effects of Water Loss

If there is not enough water present for the hydration reaction to occur, or the cement is robbed of water during hydration, the concrete may gain little or no strength.

It takes roughly 25 g of water to completely hydrate 100 g of cement. For each 1% decrease in the water available to hydrate the cement, there is a 15% loss in the 28-day compressive strength.
Effects of Water Loss

Relative effects of water loss during the first three days on 28-day compressive strength
Effects of Water Loss

That’s why it’s important to make sure the concrete doesn’t lose water while it is curing. In the field, this is accomplished by doing things like covering the concrete with plastic sheeting or wax-based spray-on coatings, or spraying it with water, or ponding water on top of the concrete.

In the laboratory, concrete specimens can be put into water baths or stored in a humid room that keeps the relative humidity around the concrete near 90%.
Effects of Water Loss

Concrete that has a high water/cement ratio is less susceptible to strength loss from improper curing because the amount of water is more than is needed for hydration.

Every day the concrete spends protected from water loss adds to the final strength of the concrete. If you can keep the concrete covered for at least 7 days, you can achieve the 28-day compressive strength called for in the specifications.
Effects of Water Loss

![Graph showing the effects of water loss on compressive strength over time for different w/c ratios.](image)
Effects of Water Loss

![Graph showing the effects of water loss on compressive strength over age.]
Effects of Temperature

Like many chemical reactions, ambient temperature will affect the speed of the hydration reaction. Up to a point, the rate of hydration (and therefore strength gain) increases with increasing temperature. Beyond about 60°C (140°F), though, increasing temperatures hurt the strength.

On the other end of the scale, at low temperatures, the hydration reaction slows to a crawl, making winter concreting difficult.
Effects of Temperature
Effects of Steam-Curing
Effects of Steam-Curing

Age of Concrete:

- 28 Days
- 1 Day

Compressive Strength - MPa

Curing Temperature - °C