

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 (SiO_2) – 19-23%

clay, loess, shale, sand, sandstone, quartzite, fly ash, rice-hull ash

alumina (Al_2O_3) – 2-6%

clay, loess, shale, bauxite, fly ash

iron oxide (Fe_2O_3) – 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 powder 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 kin, 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.

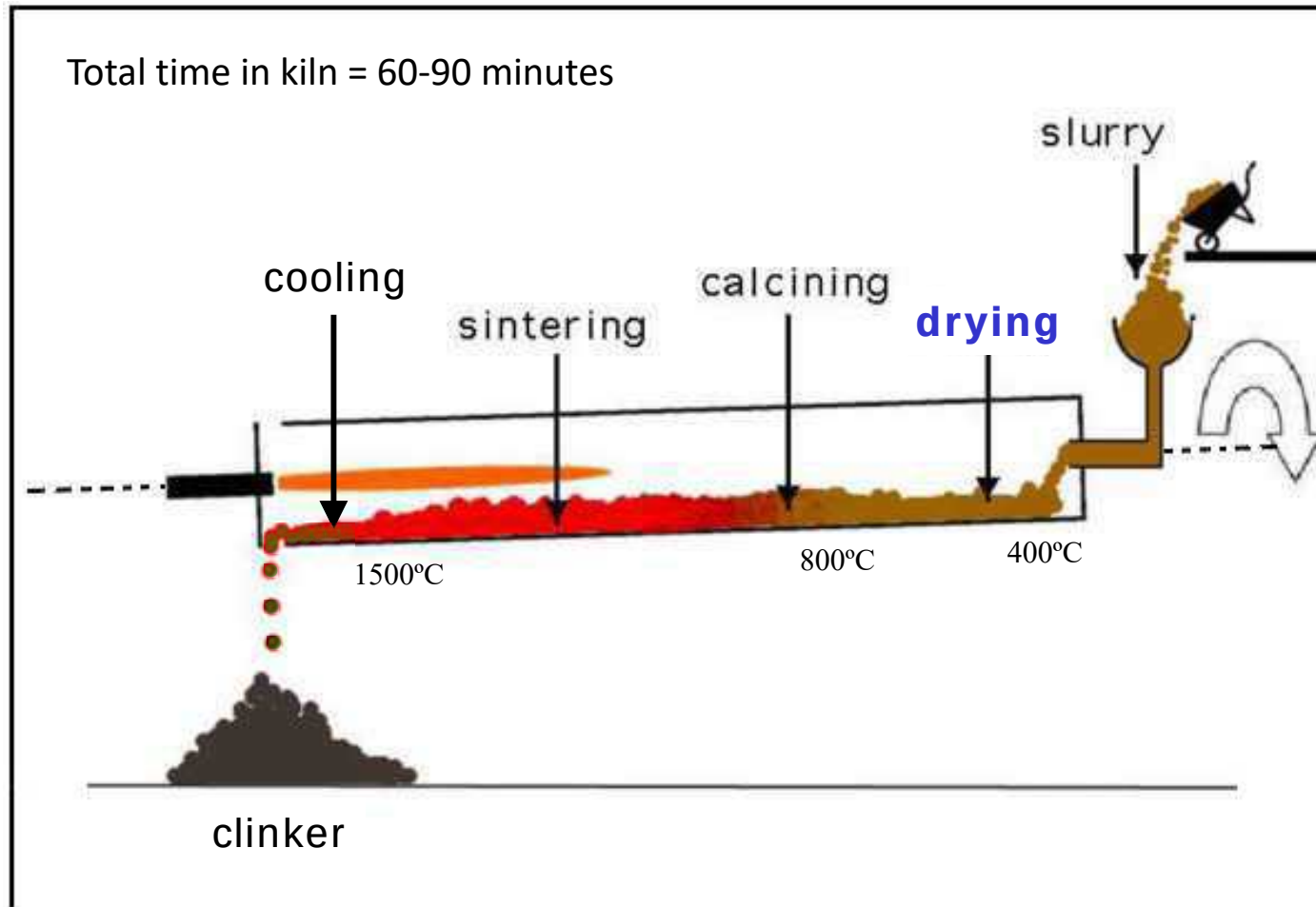
Cement Manufacture

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

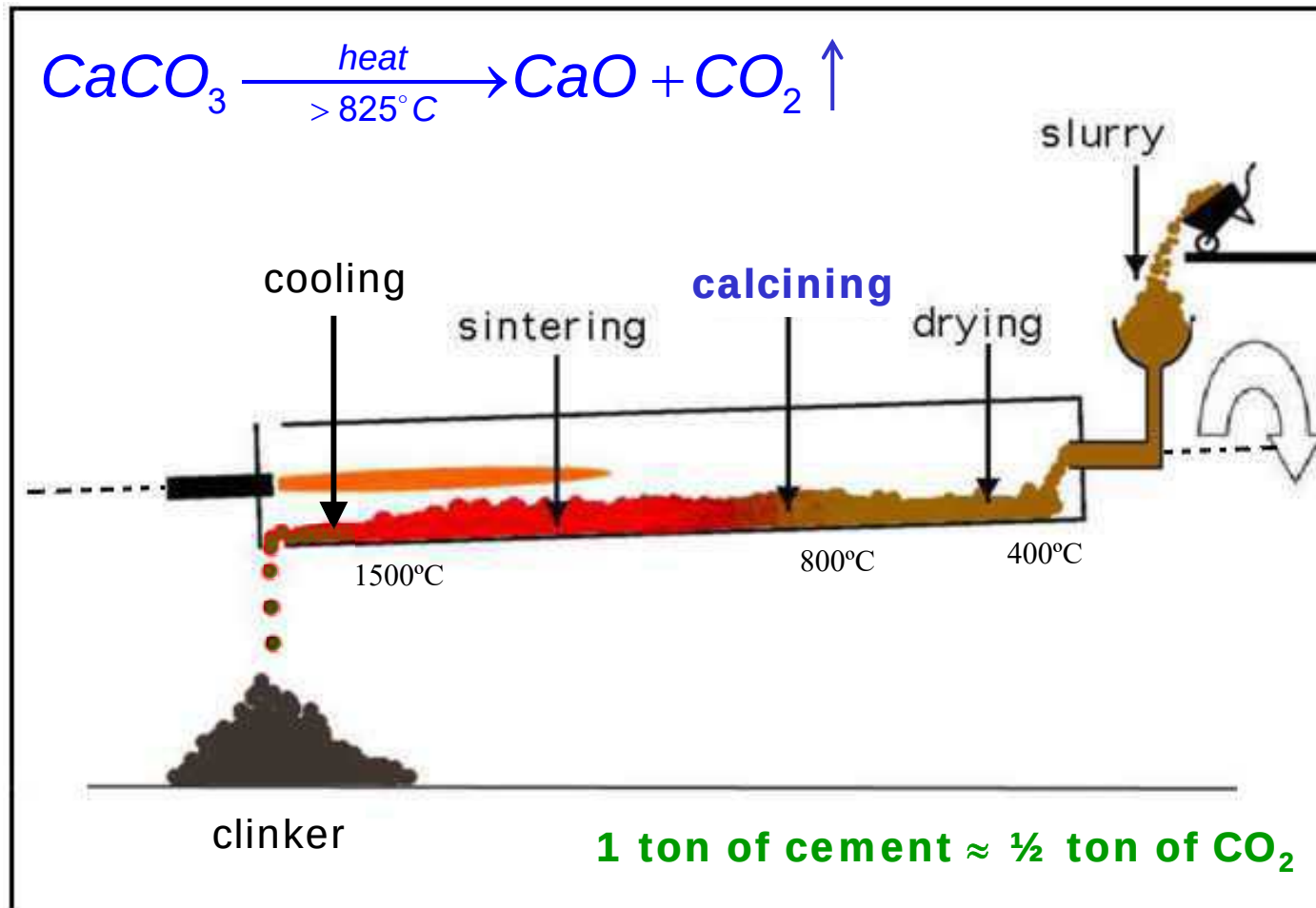
The clinker is then fed, along with a small amount (2% to 5%) of gypsum, into a grinding mill where it is reduced to a fine, gray-green powder.

During grinding, certain other materials such as fly ash can be added to enhance the cement's properties.

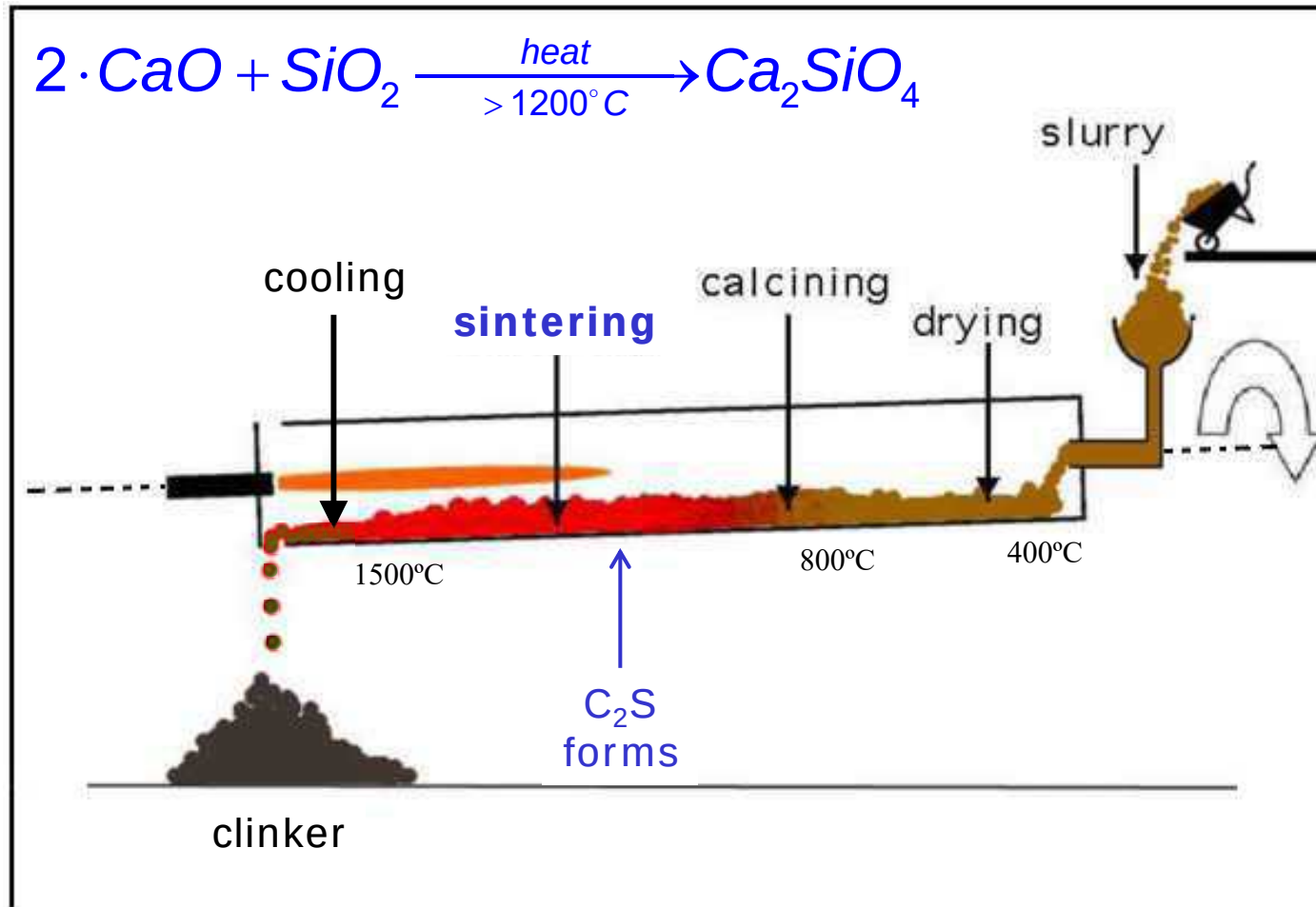
Inside a Cement Kiln



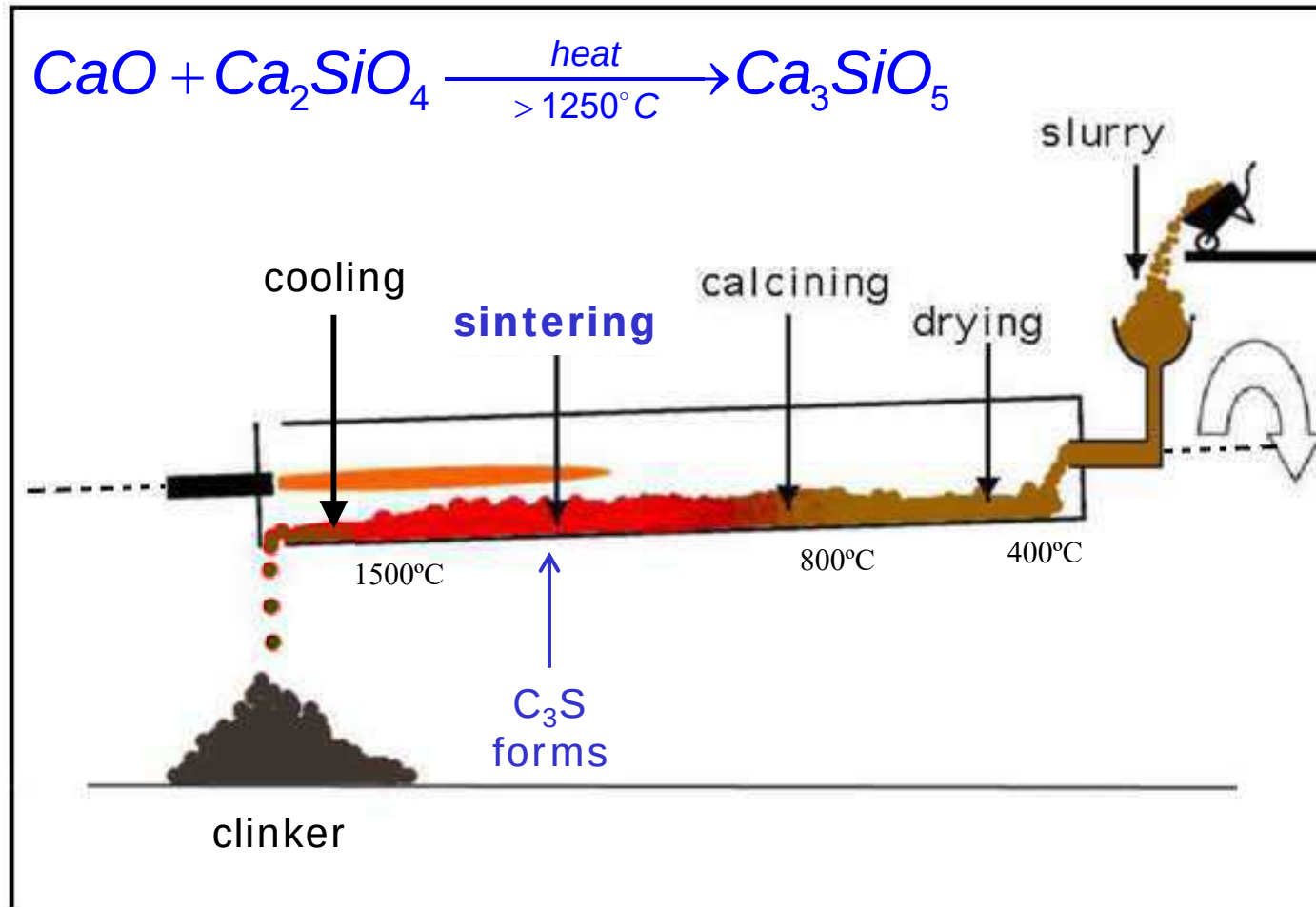
Inside a Cement Kiln



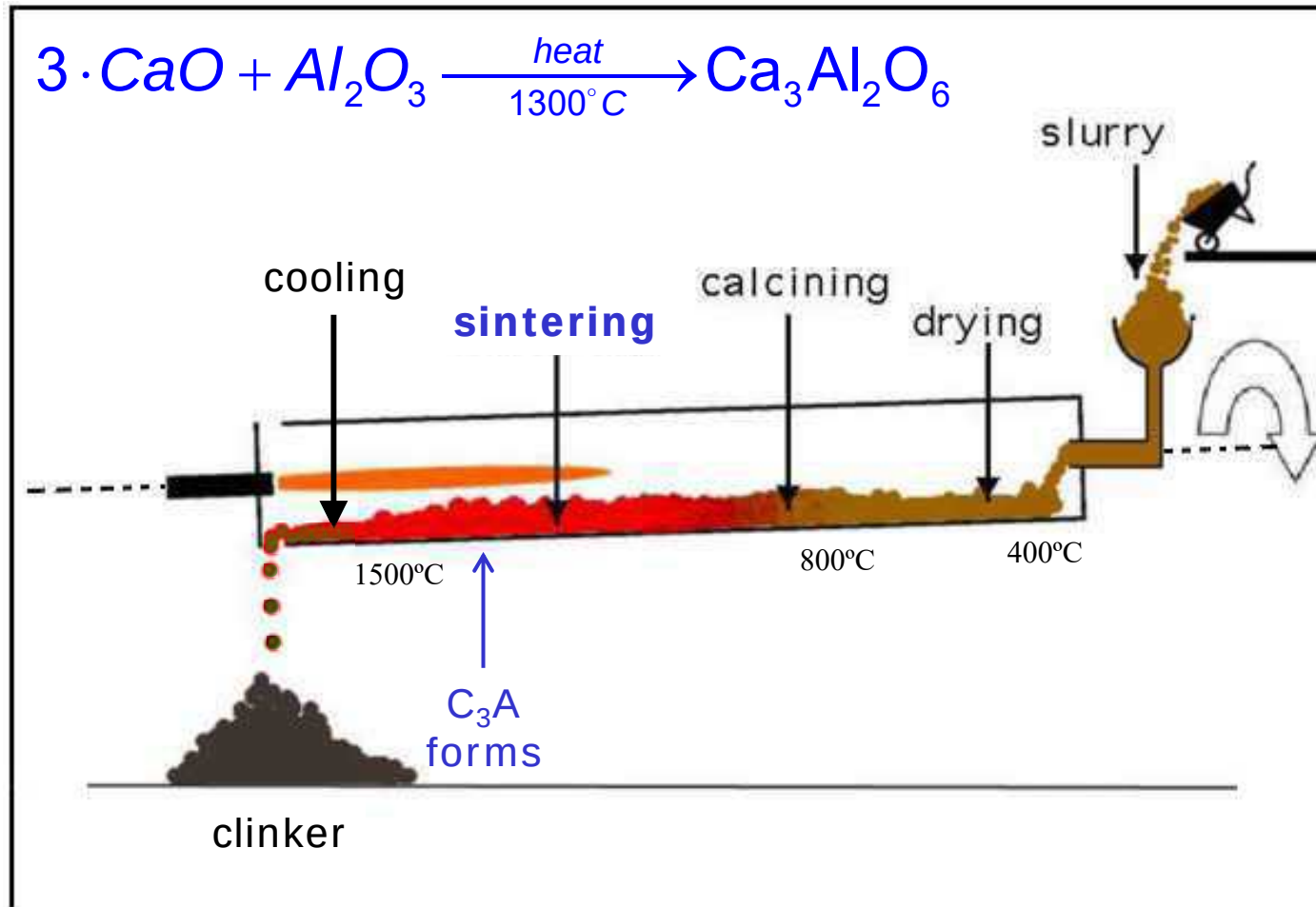
Inside a Cement Kiln



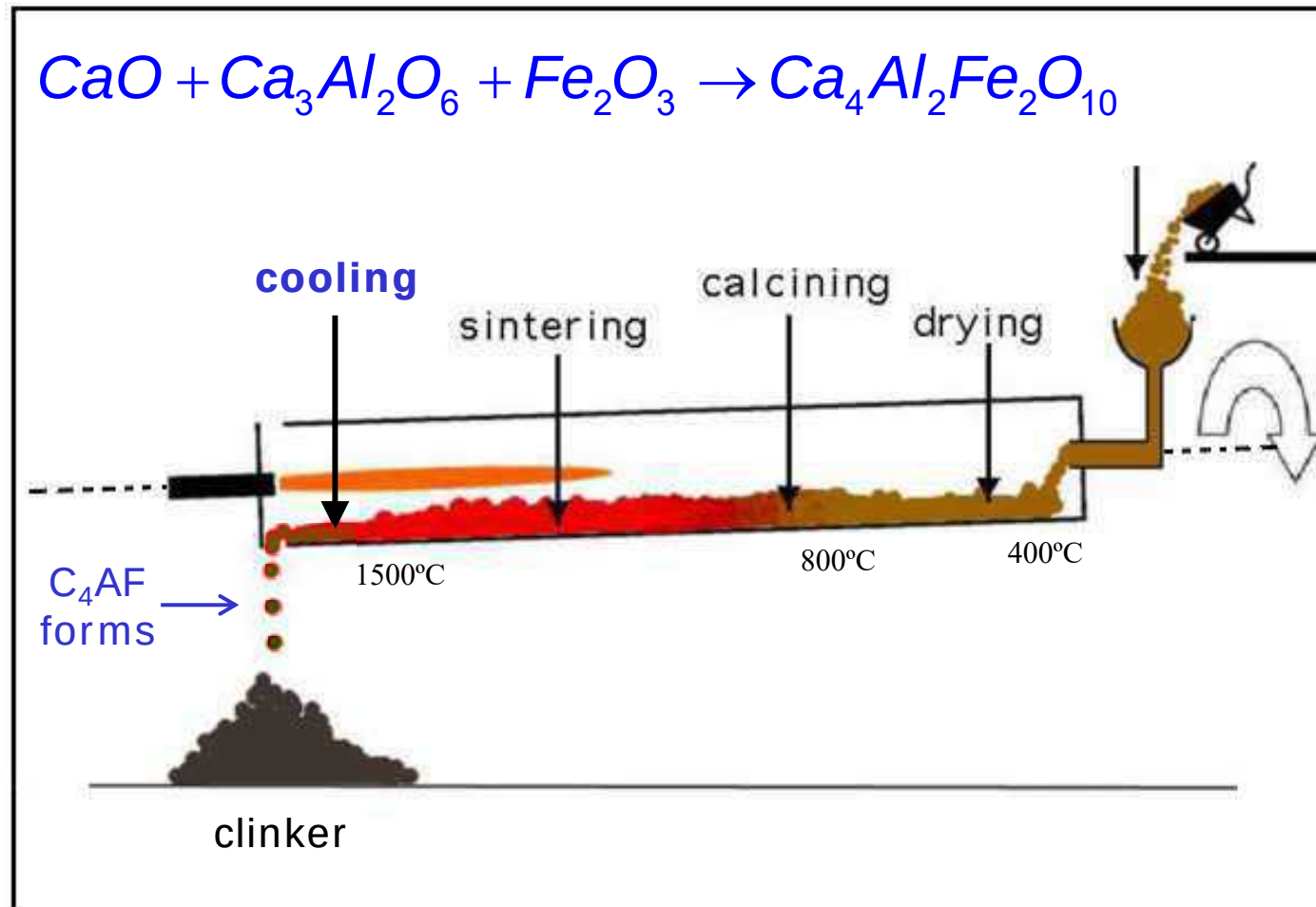
Inside a Cement Kiln



Inside a Cement Kiln



Inside a Cement Kiln



Cement Phases

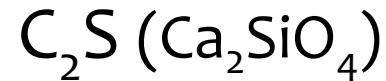
Portland cement is actually a chemically complex material composed of 4 major compounds (phases):

- Tricalcium silicate (Ca_3SiO_5)
- Dicalcium silicate (Ca_2SiO_4)
- Tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$)
- Tetracalcium aluminoferrite ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$)

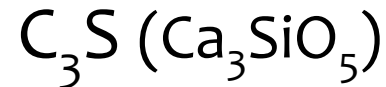
Each contributes different properties to the cement.

Cement Phases

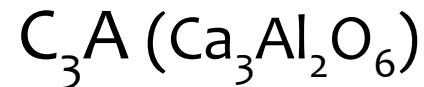
Dicalcium silicate



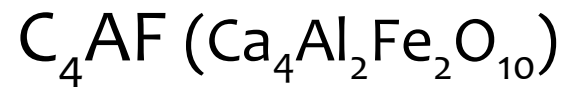
Tricalcium silicate



Tricalcium aluminate



Tetracalcium aluminoferrite



Cement Phases

Tricalcium silicate (C_3S) hydrates and hardens fairly quickly and is largely responsible for initial setting and early strength gain.

Dicalcium silicate (C_2S) hydrates and hardens slowly and is largely responsible for long-term strength gain.

Tricalcium aluminate (C_3A) 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 ($MgSO_4$ and $NaSO_4$ 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 aluminoferrite (C_4AF) 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)

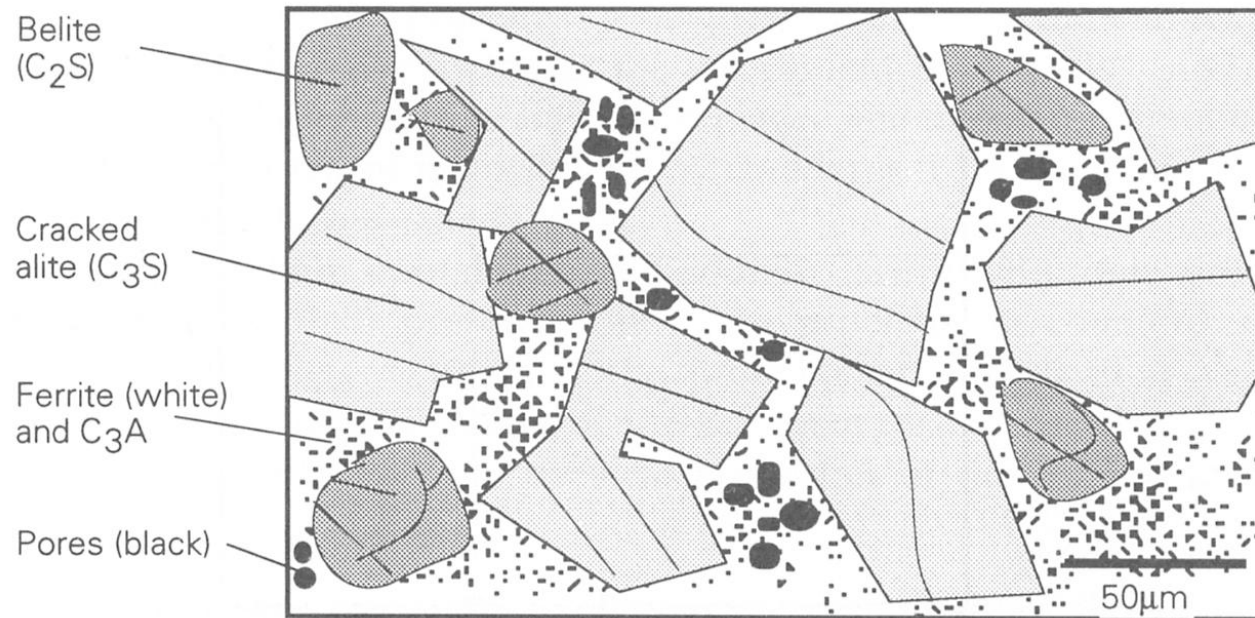


Figure 2.16 Microstructure of a commercial clinker. The alite crystals are light grey and the belite are the darker rounded crystals. The phases in between the alite and belite are ferrite (white) and C_3A (darker). The pores are black (redrawn from a micrograph from Scrivener, 1989)

Cement Phases

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

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

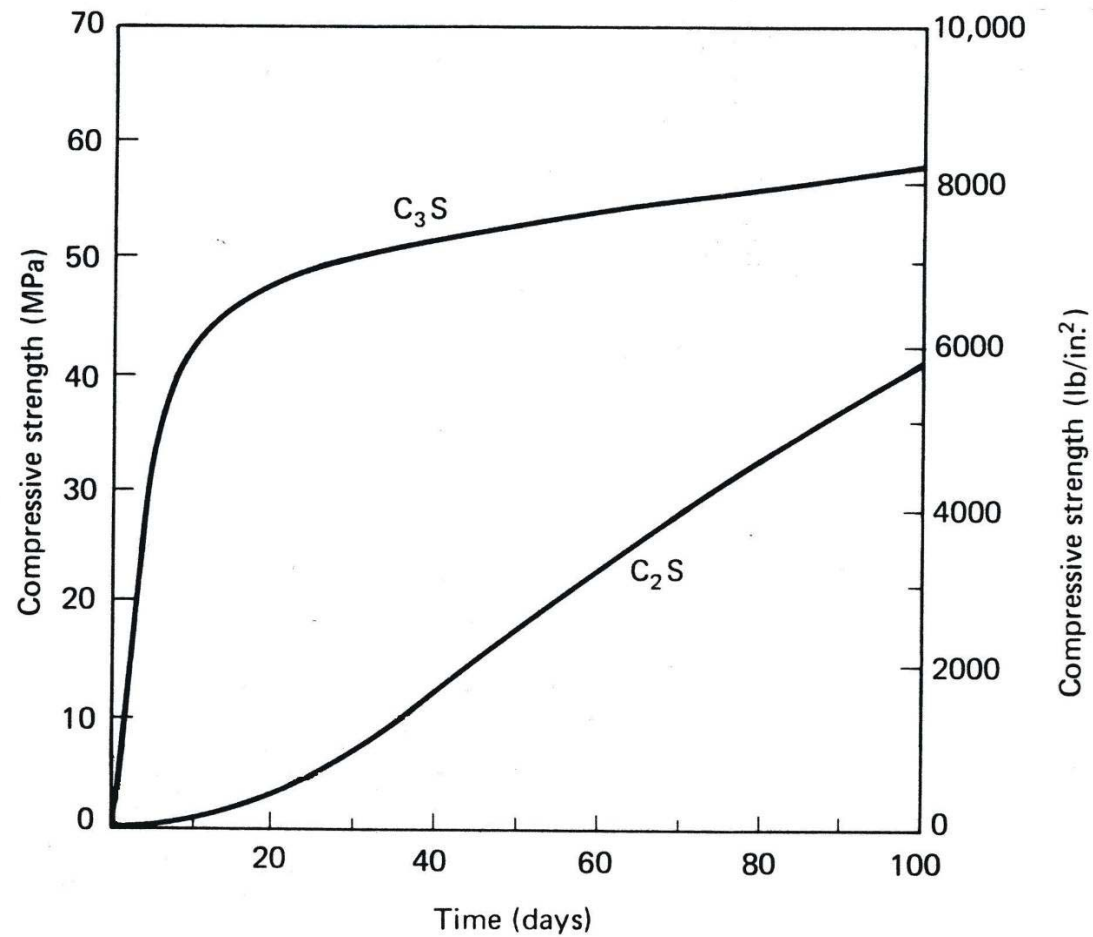
Characteristic	C_3S	C_2S	C_3A	C_4AF
Rate of hydration	Med	Slow	Fast	Fast
Heat of hydration	Med	Low	High	Low
Early strength	High	Low	Med	Low
Ultimate strength	High	High	Low	Low
Sulfate resistance	Good	Good	Poor	Good

Responsible
for
Short-term
Hardening

Responsible
for
Long-term
Hardening

Responsible
for
Initial
Setting

Rate of Strength Gain



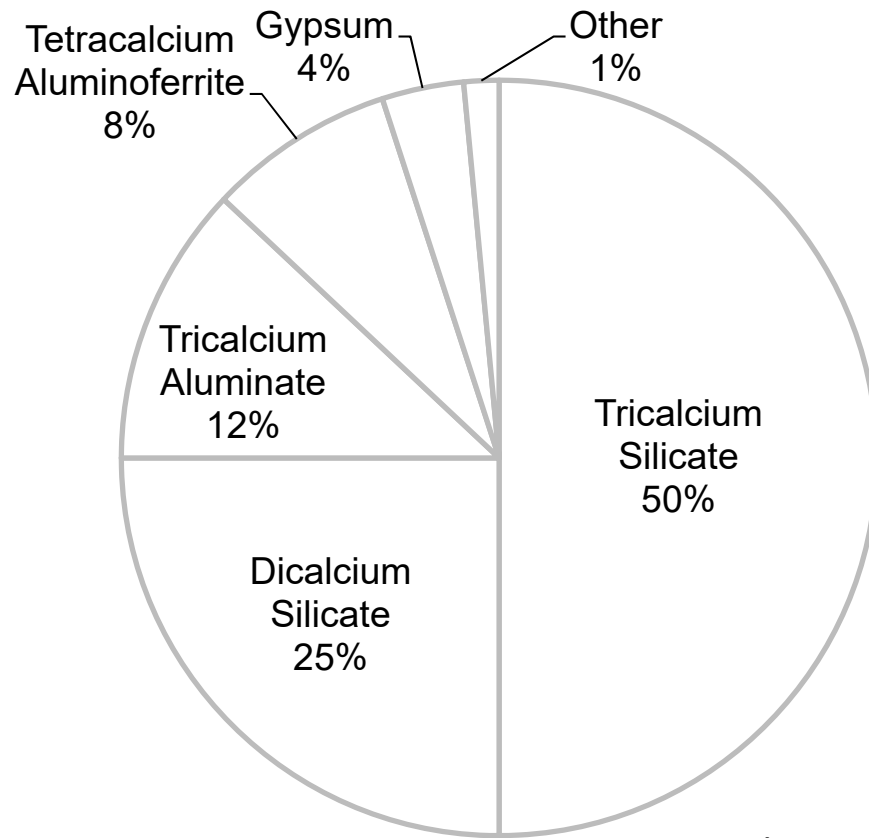
Cement Composition

A typical portland cement contains around 50% C_3S , 25% C_2S , 12% C_3A , 8% C_4AF , 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



Typical Percentages by Weight
(Mindess and Young, 1981)

Types of Portland Cement

Type	Name	Purpose
I	Normal	General-purpose cement suitable for most purposes.
IA	Normal-Air Entraining	An air-entraining modification of Type I.
II	Moderate Sulfate Resistance	Used as a precaution against moderate sulfate attack. It will usually generate less heat at a slower rate than Type I cement.
IIA	Moderate Sulfate Resistance-Air Entraining	An air-entraining modification of Type II.

Types of Portland Cement

Type	Name	Purpose
III	High Early Strength	Used when high early strength is needed. It 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.
IIIA	High Early Strength-Air Entraining	An air-entraining modification of Type III.
IV	Low Heat of Hydration	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.
V	High Sulfate Resistance	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.

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

Type	Name	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
I	Normal	50	24	11	8
II	Modified	42	33	5	13
III	High early	60	13	9	8
IV	Low heat	26	50	5	12
V	Sulfate-resistant	40	40	3.5	9

Responsible
for
Short-term
Hardening

Responsible
for
Long-term
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Responsible
for
Initial
Setting

Types of Portland Cement

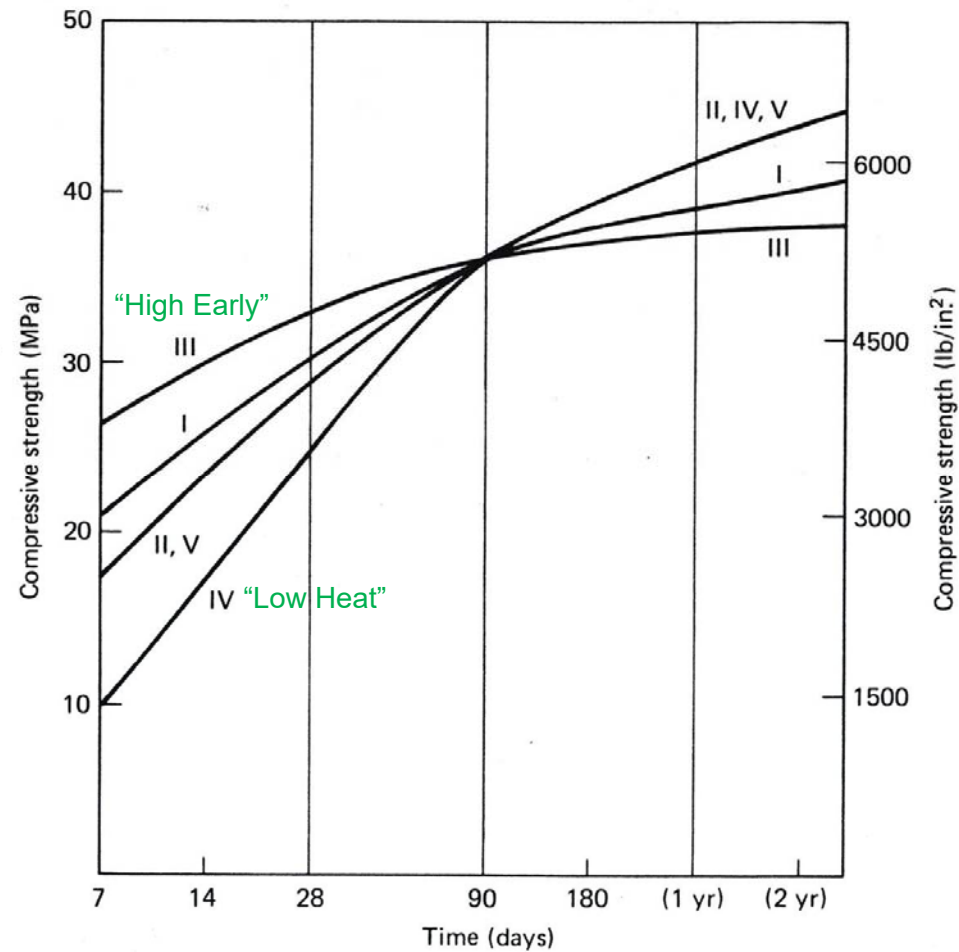
Changing the proportions of the various phases is a zero-sum game because they always total 100%.

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***.

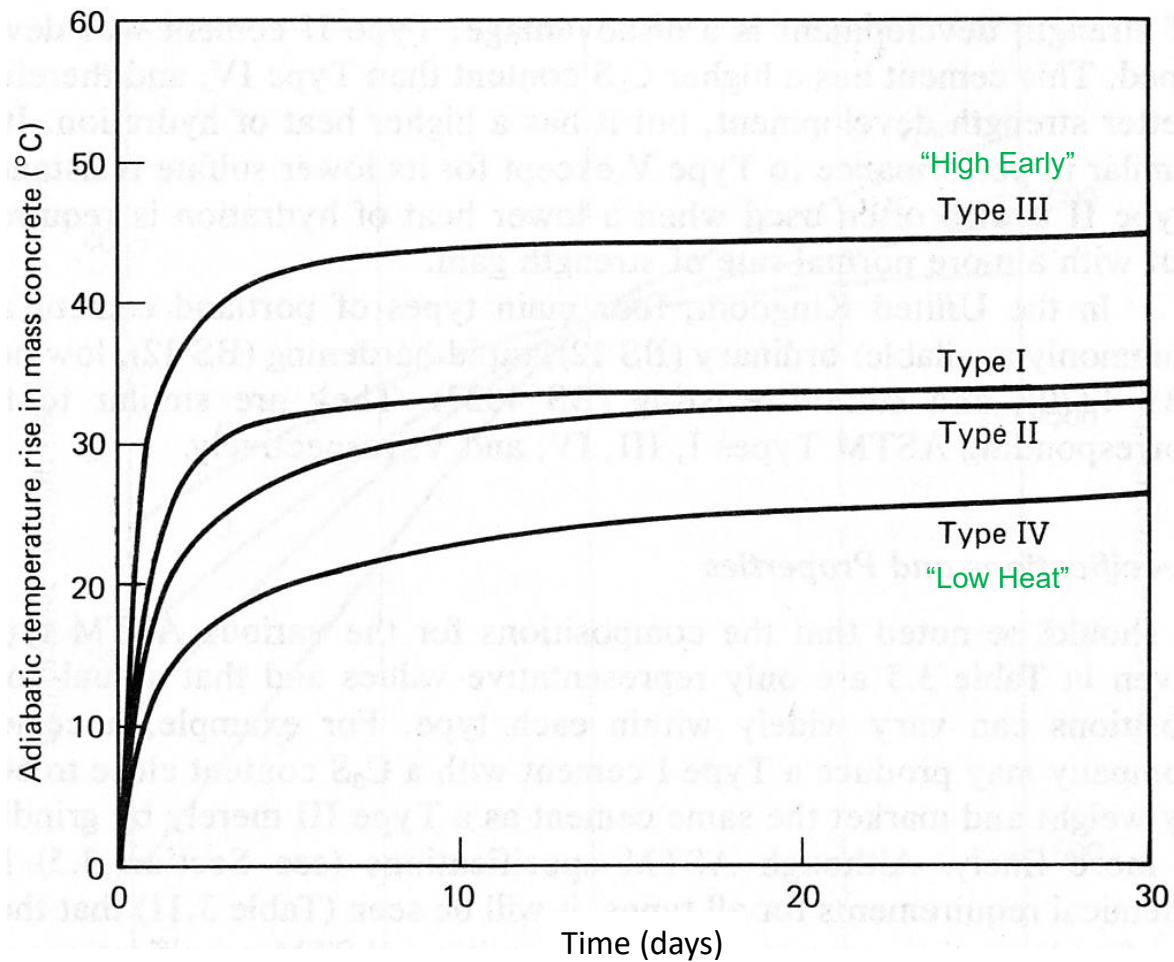
Types of Portland Cement

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



Rate of Heat Generation



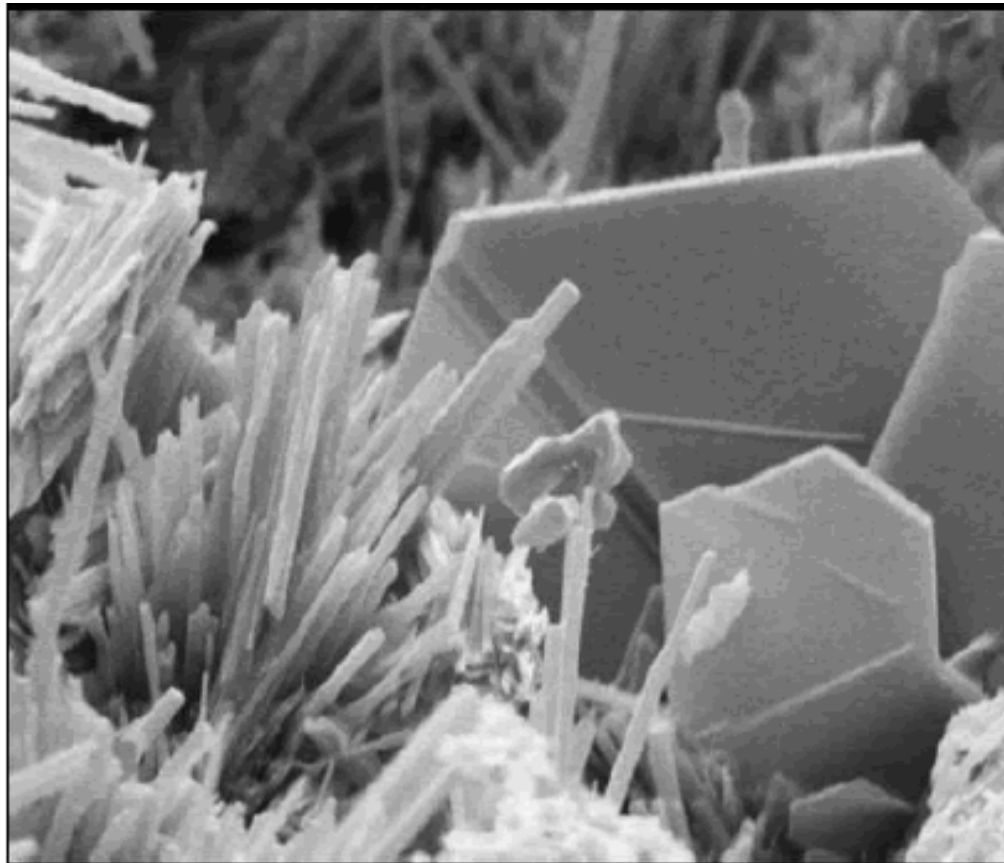
Cement Hydration

When cement comes into contact with water, an exothermic chemical reaction called ***hydration*** occurs.

The hydration of the C_3S and C_2S is responsible for the strength of concrete. When both compounds are mixed with water, they create ***calcium silicate hydrate*** gel (CSH) and ***calcium hydroxide*** crystals (CH). The CSH is what glues the aggregate particles together to form concrete.

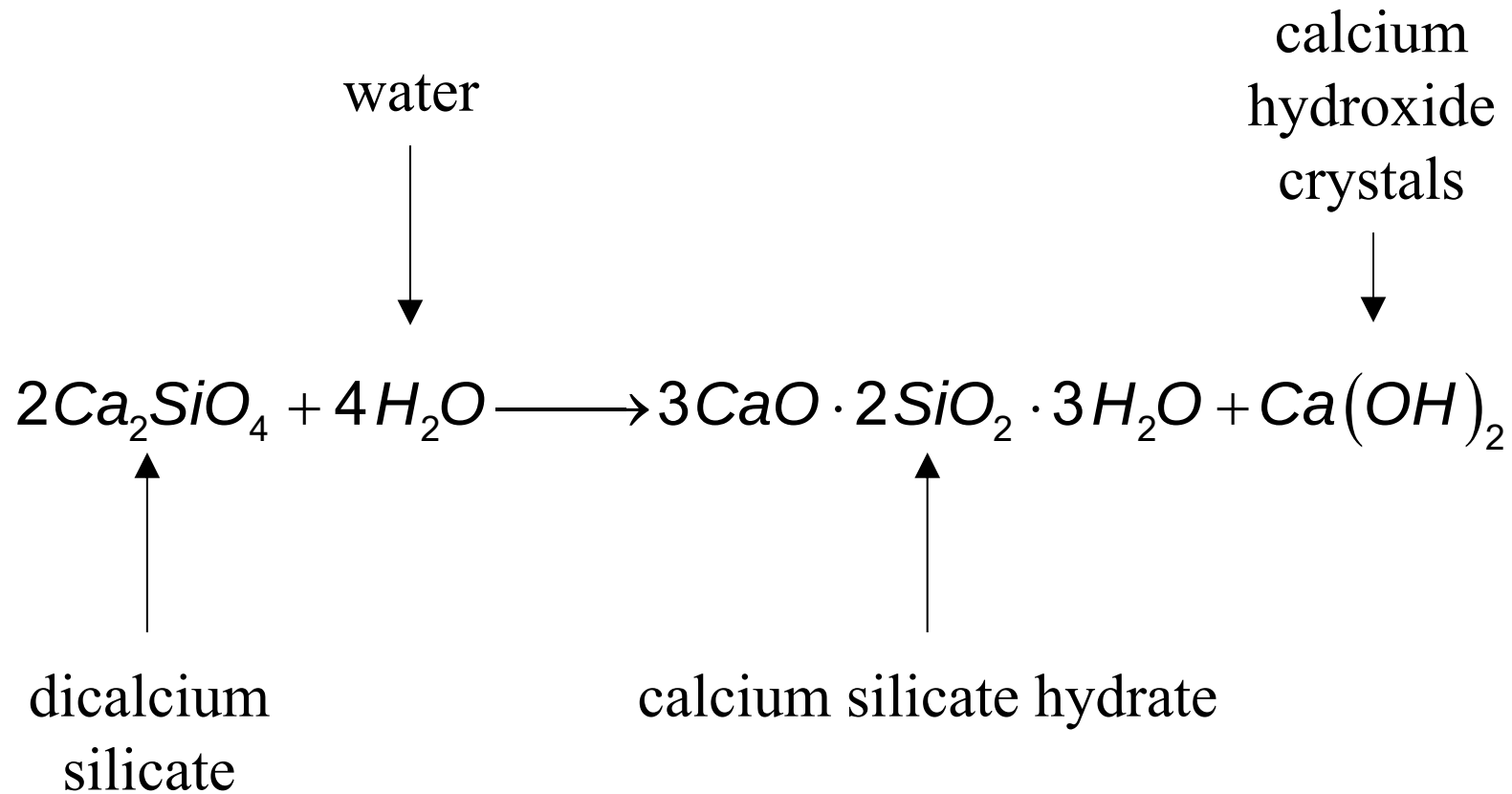
Hydration Chemistry

C-S-H

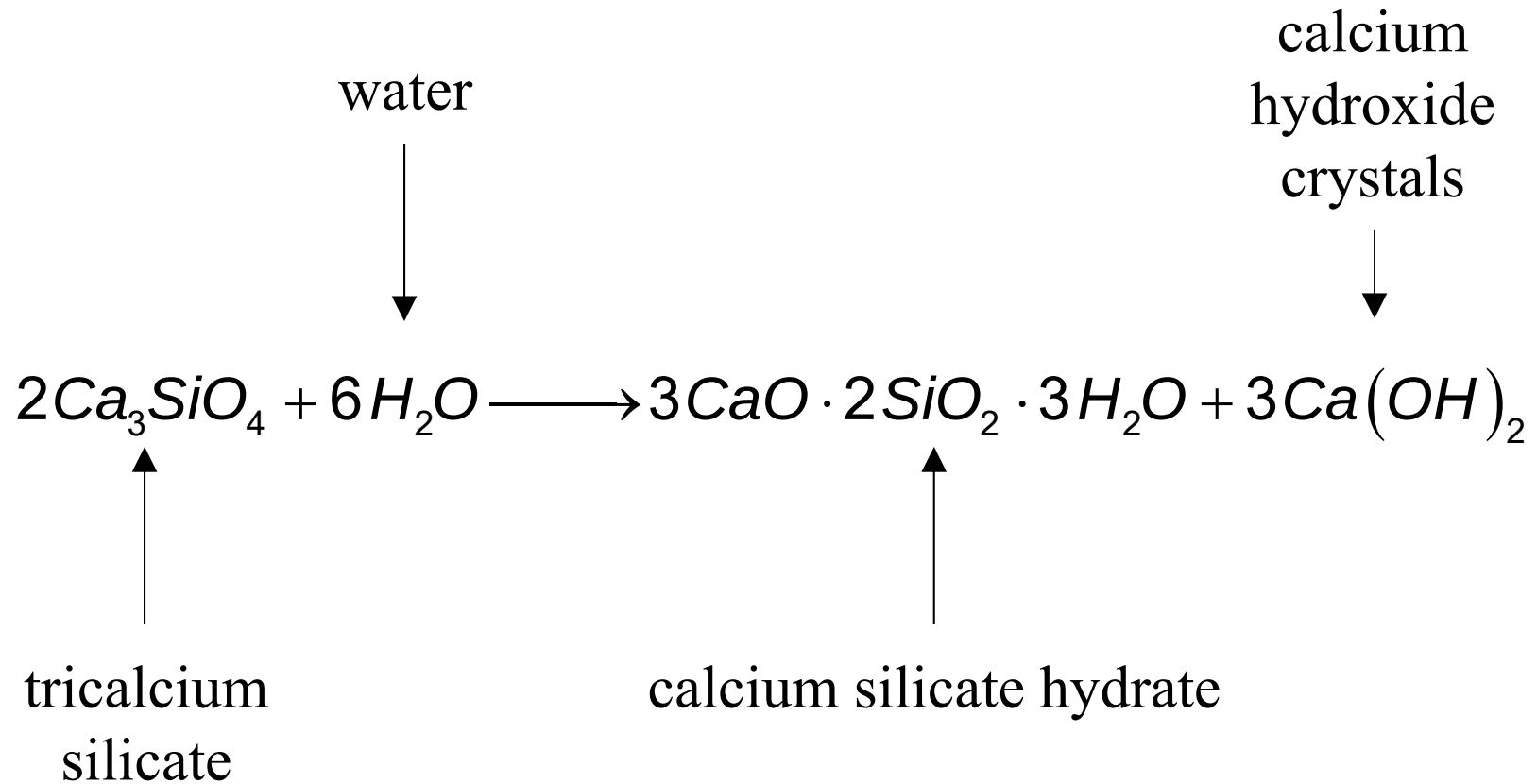


CH

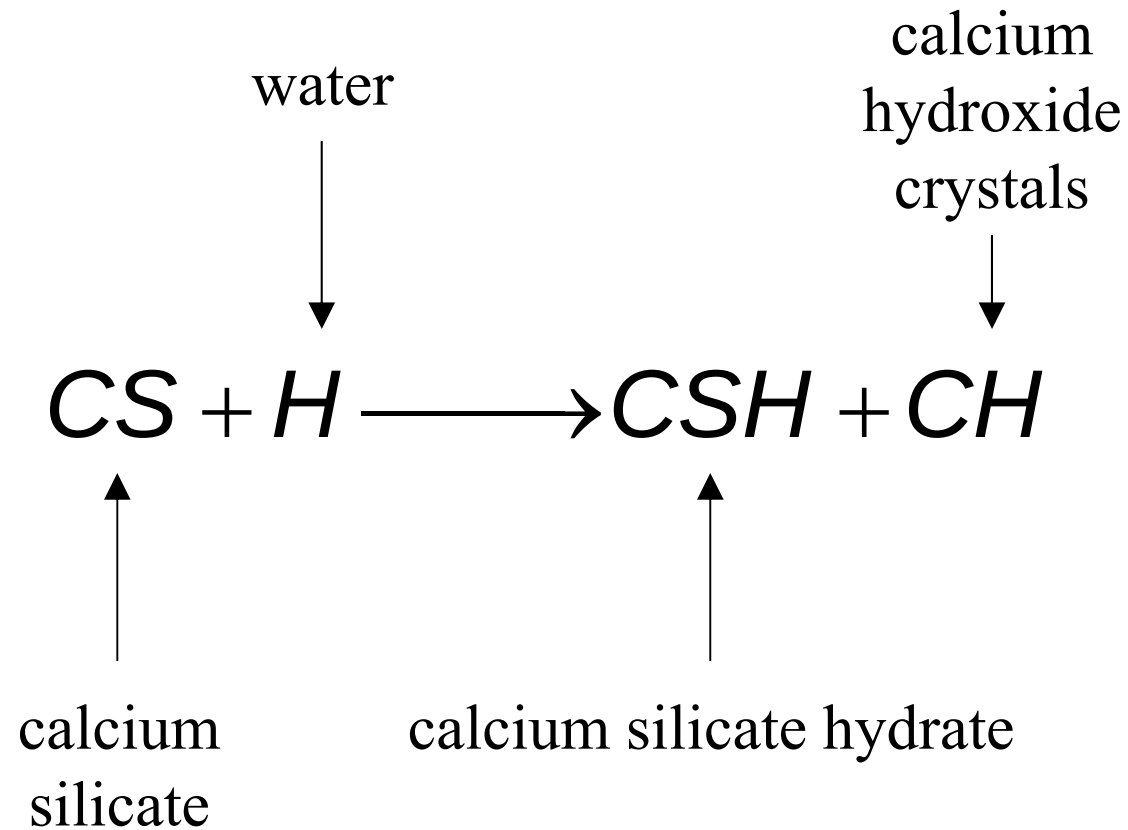
Hydration Chemistry



Hydration Chemistry



Hydration Chemistry



Cement Hydration

The hydration process is actually quite complex.

Soon after mixing, the C_3A 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 C_3A 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_3S and C_2S 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.

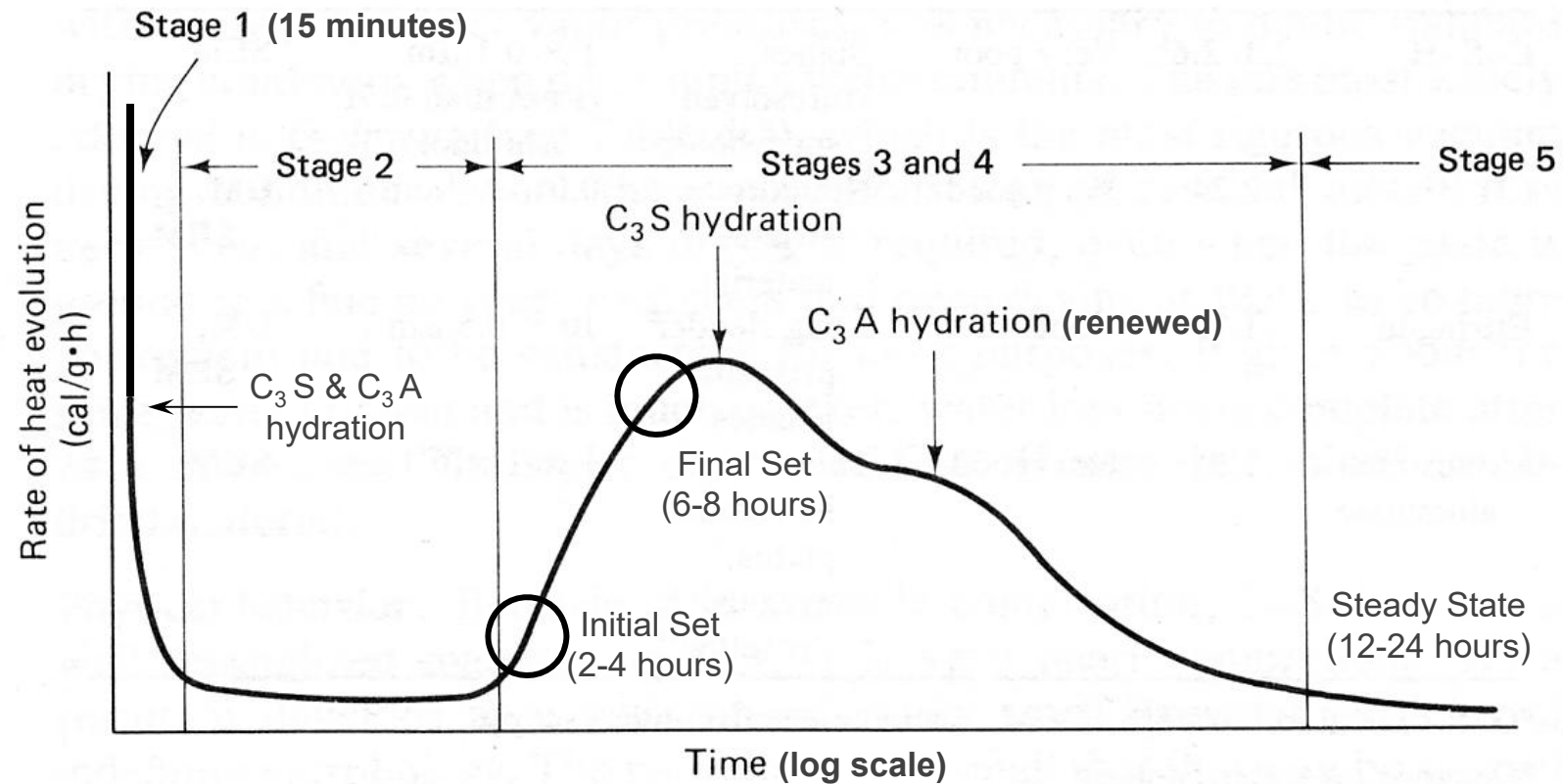
Cement Hydration

During the next stage (Stage IV) the reaction rate slows as the C_3S continues to hydrate and the concrete gains more strength.

As the individual cement grains hydrate from the surface inward, C_3A 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



Initial and Final Set

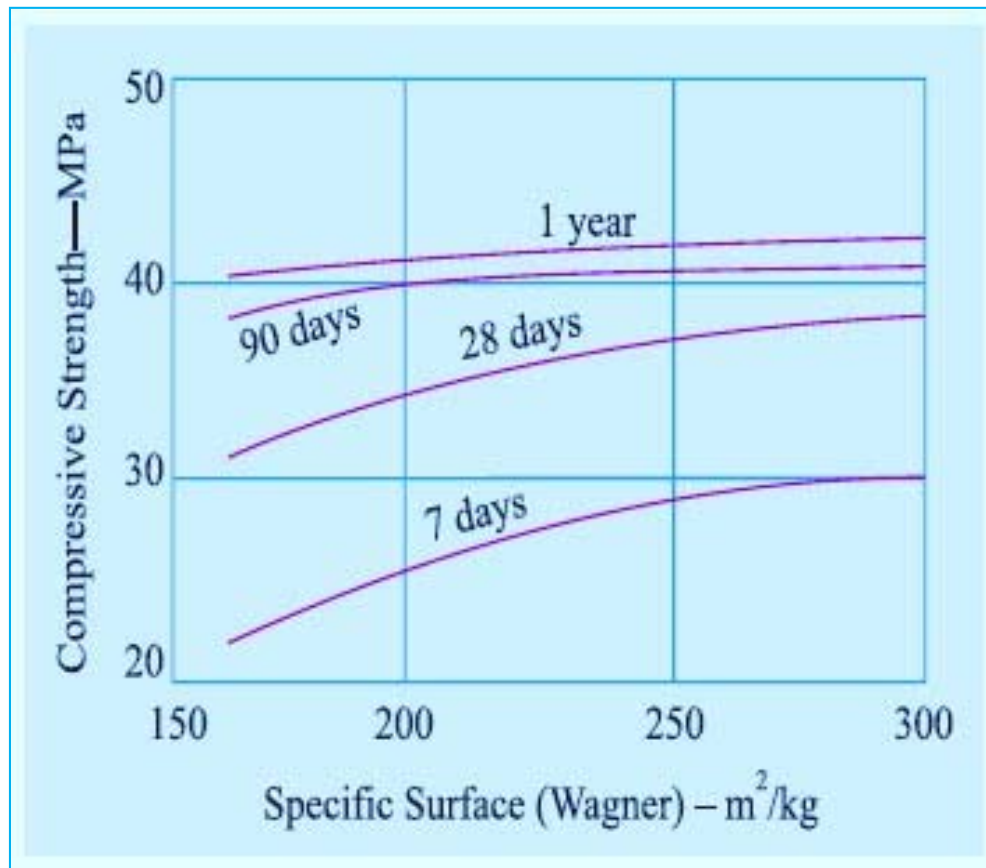
Shortly after the end of Stage II, the concrete reaches ***initial set***. Up until this point, the concrete is actually a gel and, if remixed, will return to its original fluid consistency. This is known as ***thixotropy***. It is the reason why ready-mix trucks have revolving drums: they keep the concrete 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

amount of C_3A
amount of $CaSO_4$
cement fineness

} cement type

Effects of Fineness



Source: www.theconstructioncivil.com

Setting Time Factors

amount of C_3A
amount of $CaSO_4$
cement fineness

}

cement type

amount of mixing water
amount of sun/wind
ambient temperature

}

placing conditions

Hardening Factors

amount of C_3S } cement type
amount of C_2S }

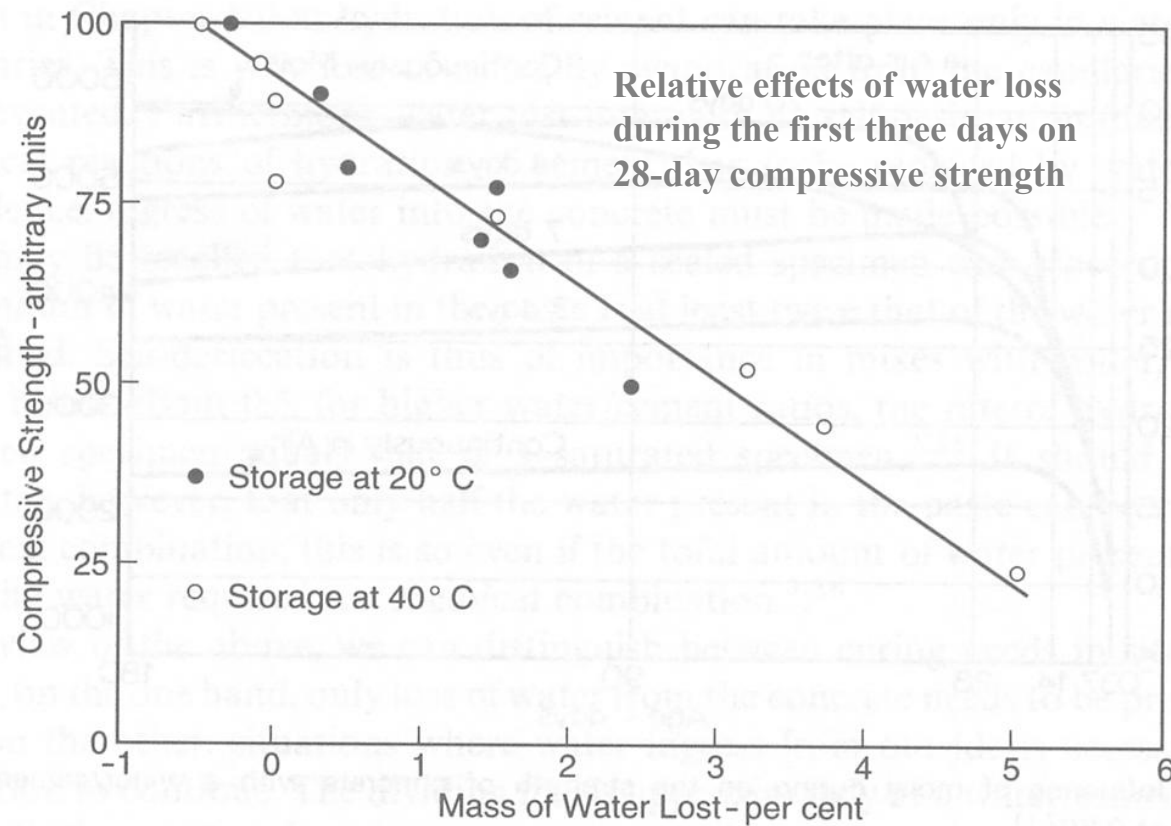
ambient temperature } curing conditions
ambient humidity }

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



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.

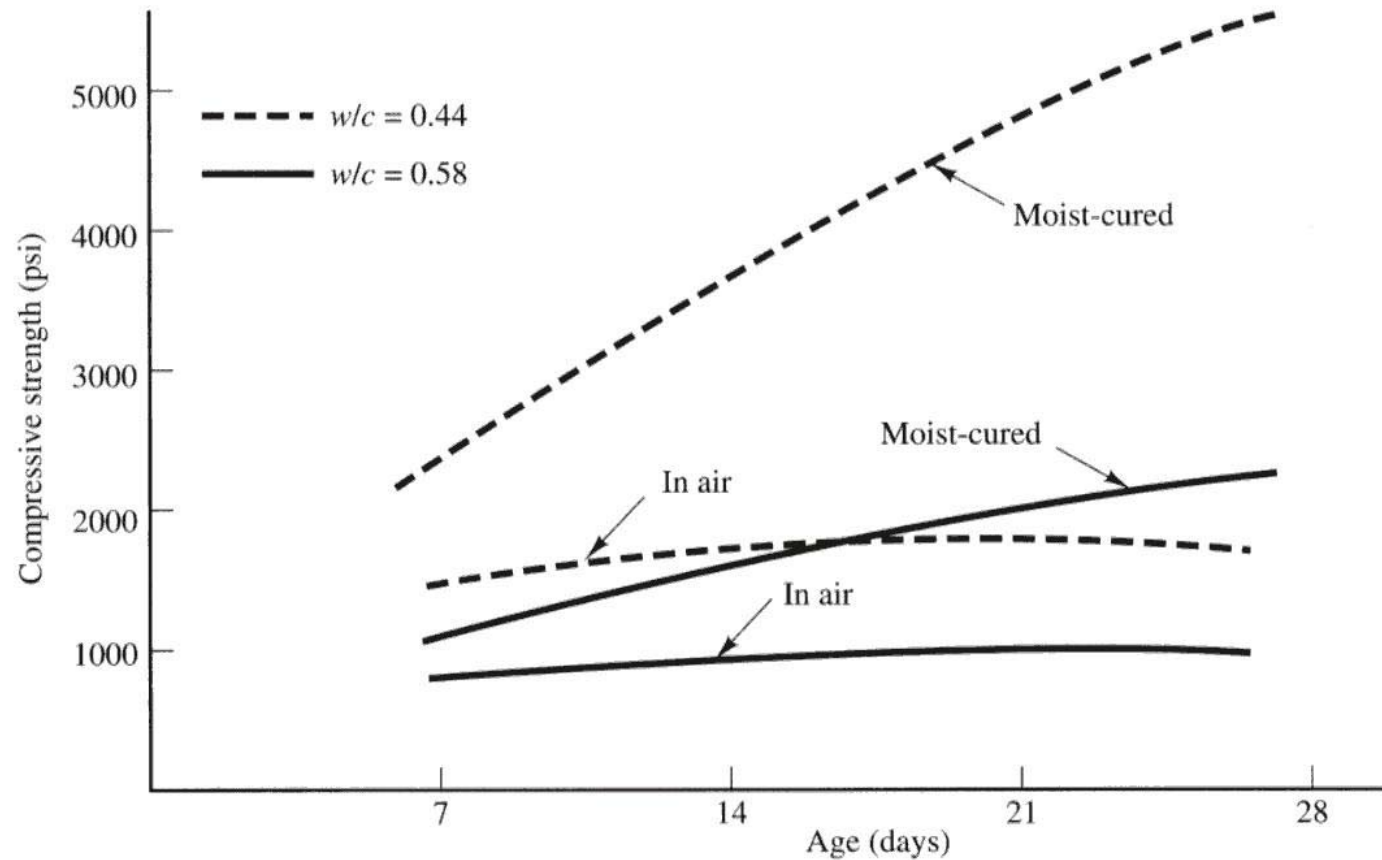
In the laboratory, concrete specimens can be put into water baths or stored in a humid room that keeps the relative humidity around the concrete near 90%.

Effects of Water Loss

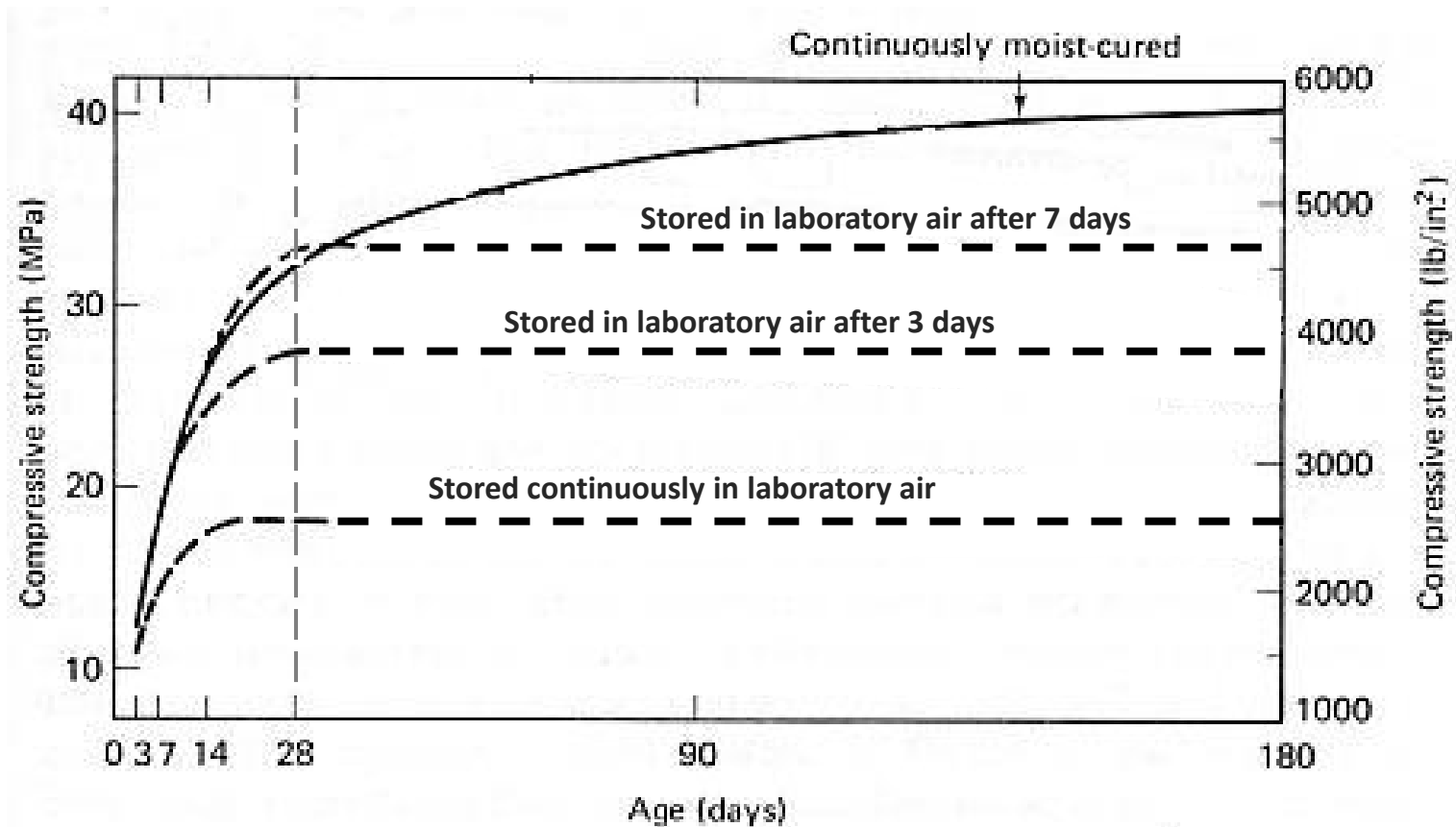
Concrete that has a high water/cement ratio is less susceptible to strength loss from improper curing because the amount of water is more than is needed for hydration.

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



Effects of Water Loss

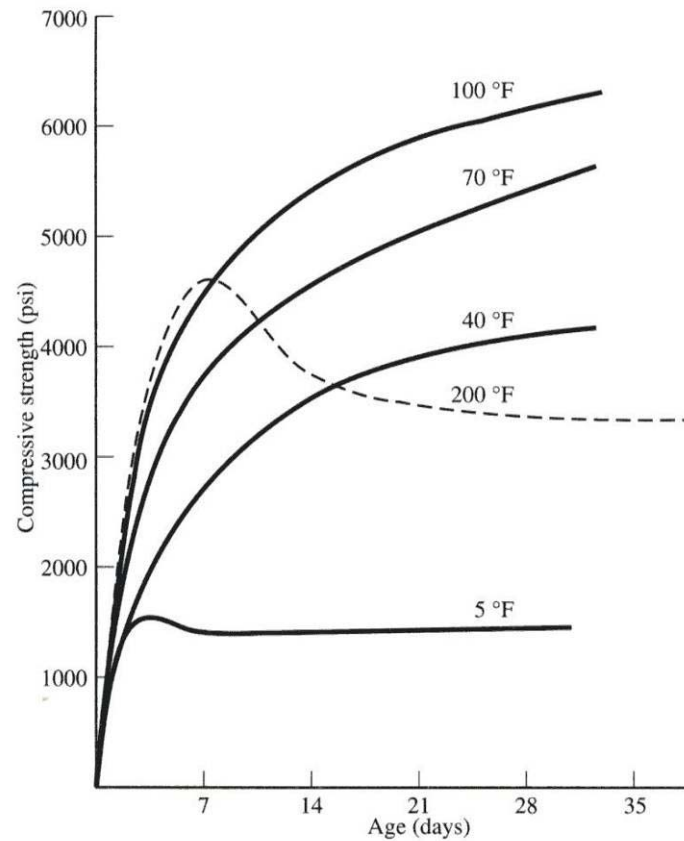


Effects of Temperature

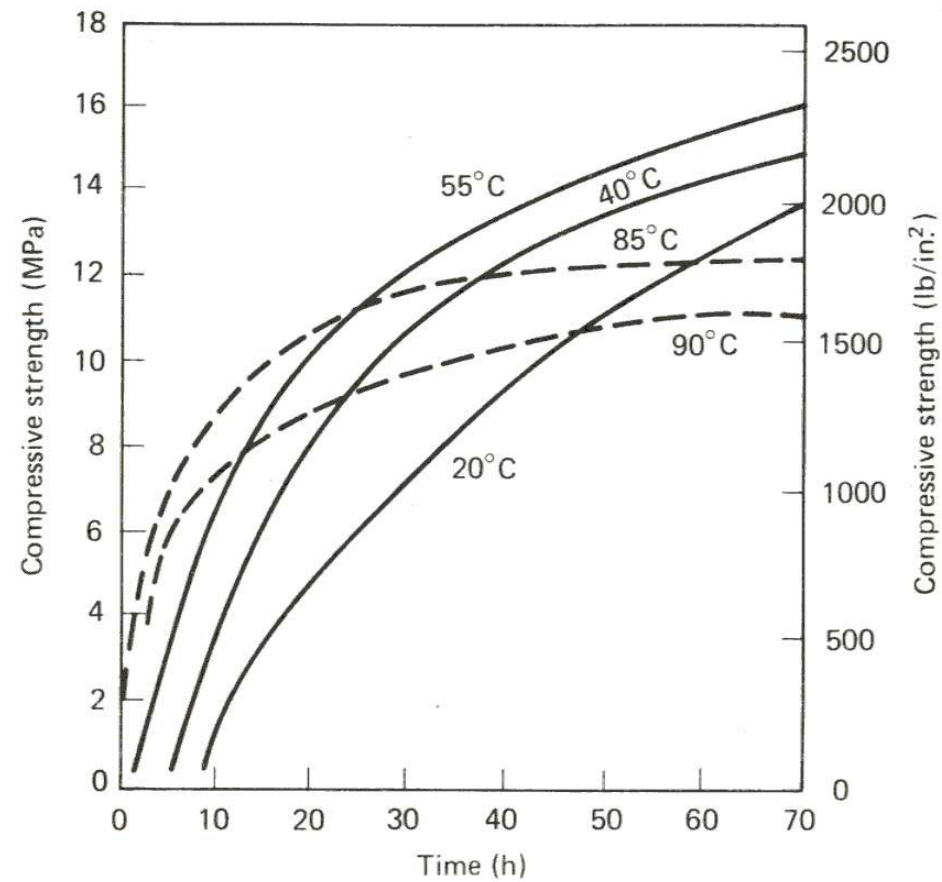
Like many chemical reactions, ambient temperature will affect the speed of the hydration reaction. Up to a point, the rate of hydration (and therefore strength gain) increases with increasing temperature. Beyond about 60°C (140°F), though, increasing temperatures hurt the strength.

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

