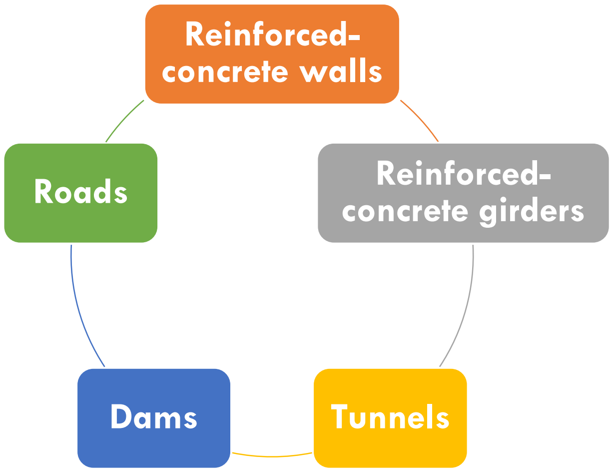
CEMENT

REFERENCE: SHREVE'S BOOK CH. 10, PP. 171-186
HTTPS://WWW.UNDERSTANDING-CEMENT.COM/ARTICLE-DIRECTORY.HTML (UP TO "CEMENT ANALYSIS")

What is common among these?



Reinforced-concrete walls

Reinforced-concrete girders

Tunnels

Dams

Roads

Concrete and Cement

- Concrete is composite material, meaning that it is made up of more than one type of material at the macroscopic scale.
- In its simplest view, concrete is divided into two components: the filler and the binder.
    - Cement is the binder component of concrete, the glue that holds the filler together to create a uniform, strong material.
    - The filler in concrete consists primarily of aggregate particles. The vast majority of aggregate is just sand, gravel, and rocks.

Basic Ingredients of Concrete

From left to right:
fine aggregate (sand),
coarse aggregate,
water, and cement.

Typical Concrete Mix Design		
Ingredient	**Percent by Volume**	**Percent by Weight**
Water	19.5	8.1
Cement	11.3	14.7
Coarse aggregate (1 inch max)	42	46.5
Fine aggregate	27.2	30.7
Total	**100**	**100**

Basic Definitions and Terminology

- Cement: The dry unreacted powder that comes in a sack
- Cement paste: Cement that has been mixed with water.
- Concrete: A mixture of sand, gravel, and rocks held together by cement paste.
- Aggregate: The inert filler material that makes up the bulk of concrete. Usually sand, gravel, and rocks.
- Mortar: A mixture of cement paste and sand used in thin layers to hold together bricks or stones. Technically, mortar is just a specific type of concrete with a small maximum aggregate size.

Basic Definitions and Terminology

- Fresh: Cement paste or concrete that has been recently mixed and is still fluid. This is what those big trucks with the rotating container on the back are full of. (These are often called "cement mixers" but now you know why they should be called "concrete mixers").
- Hardened: Cement paste or concrete that has gained enough strength to bear some load.
- Set: The transition from fresh cement paste to hardened cement paste. The terms "initial set" and "final set" refer to specific times when the paste becomes no longer workable and completely rigid, respectively. "Setting" is the process by which this occurs.

Basic Definitions and Terminology

- Curing/Hardening: Essentially interchangeable terms that mean the process of continued strength gain after the cement paste has set due to chemical reactions between cement and water.
- Young: Cement paste or concrete that has recently set and is now actively hardening. What constitutes "young" in terms of time is variable; the term implies that the paste has undergone a only fraction of its full reaction and is thus weak and vulnerable to damage. This could be anywhere from a few hours to weeks depending on the mix design and the temperature.
- Mature: Cement paste or concrete that has reached close to its full strength and is reacting very slowly, if at all. An age of 28 days is a very rough rule of thumb for reaching maturity.

Basic Definitions and Terminology

- Hydration: The chemical reactions between cement and water. Hydration is what causes cement paste to first set and then harden.
- Hydration products: The new solid phases that are formed by hydration.
- Heat of hydration: The hydration reactions between cement and water are exothermic. Large volumes of concrete can warm up considerably during the first few days after mixing when hydration is rapid. This is generally a bad thing, for reasons that will be discussed.

Basic Definitions and Terminology

- Placing: The process of transferring fresh concrete from the mixer to the formwork that defines its final location and shape.
- Segregation: An undesirable process of the aggregate particles becoming unevenly distributed within the fresh cement paste while the concrete is being placed or consolidated.
- Bleeding: An undesirable process of mix water separating from the fresh cement paste or concrete while it is being placed or consolidated.

What is Special about Cement?

Convenient

Cheap

Adaptible

Strong

Durable

Types of Hydraulic Cements

1. **Hydraulic lime**
   Only used in specialized mortars. Made from calcination of clay-rich limestones.
2. **Natural cement**
   Misleadingly called Roman. It is made from argillaceous limestones or interbedded limestone and clay or shale, with few raw materials. Because they were found to be inferior to Portland.
3. **Portland cement**
   Artificial cement. Made by the mixing clinker with gypsum in a 95:5 ratio.

Types of Hydraulic Cements

4. **Portland-limestone cement**
   Large amounts (6% to 35%) of ground limestone have been added as a filler to a Portland cement base.
5. **Pozzolan-lime cement**
   Original Roman cements. Mix of pozzolans (2 to 4 parts) with hydrated lime (1 part). Resist corrosive action of saline solution and seawater better than Portland cement.
6. **Blended cement**
   Mix of Portland cement with one or more supplementary cemetitious materials (SCM) like pozzolanic additives.

Types of Hydraulic Cements

7. **Aluminous cement**
   Limestone and bauxite (aluminum oxide) are the main raw materials. Used for refractory applications (such as cementing furnace bricks) and certain applications where very rapid hardening is required. More expensive than Portland. Superior resistance to seawater and sulfate-bearing water.
8. **Masonry cement**
   Portland cement where other materials have been added primarily to impart plasticity.

Abbreviations Used in Cement Industry

$CaO = C$	$MgO = M$	$CO_2 = \bar{C}$
$SiO_2 = S$	$SO_3 = \bar{S}$	$H_2O = H$
$Al_2O_3 = A$	$Na_2O = N$	
$Fe_2O_3 = F$	$K_2O = K$	

$$\mathbf{Ca_3SiO_5 = 3CaO.SiO_2 = C_3S}$$

Cement Minerals and Products

- Different ways to represent some cement minerals and products:

Oxide Formula	Chemical Name	Cement Notation	Mineral Name
$2CaO.SiO_2$	Di-calcium silicate	C_2S	Belite
$3CaO.SiO_2$	Tri-calcium silicate	C_3S	Alite
$3CaO.Al_2O_3$	Tri-calcium aluminate	C_3A	Aluminate
$4CaO.Al_2O_3.Fe_2O_3$	Tetracalcium aluminoferrite	C_4AF	Ferrite
$CaSO_4.2H_2O$	Calcium sulfate dihydrate	$C\bar{S}H_2$	Gypsum
$CaO.H_2O$	Calcium hydroxide	CH	Portlandite
CaO	Calcium oxide	C	Lime

Portland Cement Manufacturing

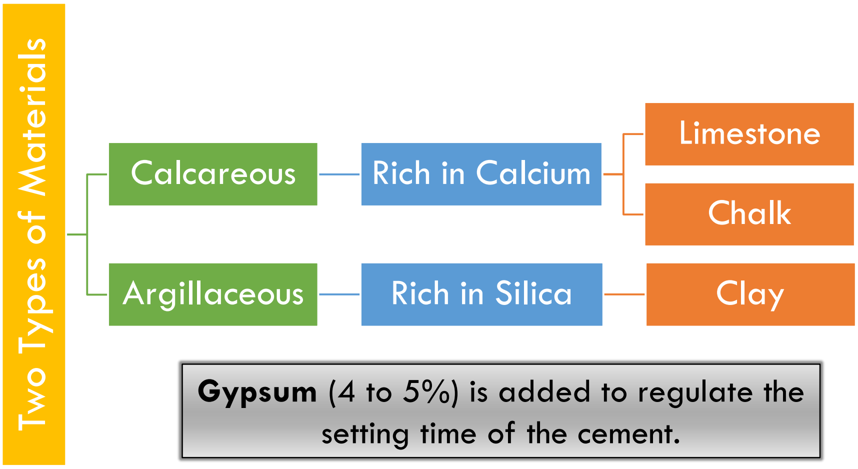
Preparation of Raw materials
- **Grinding & Mixing**

Burning in a Kiln
- **Forming Cement Clinker**

Final Processing

Quality Control

Raw Materials



Gypsum (4 to 5%) is added to regulate the setting time of the cement.

Raw Materials

- ☐ Limestone (calcium carbonate) is a common source of calcium oxide.
- ☐ Iron-bearing aluminosilicates are the most common source of silica.
- ☐ Aluminum and iron oxides act as fluxing agents, i.e. lower fusion temperature of part of the raw mix to a practical firing temperature

Raw Materials

- Grinding and blending prior to entering the kiln can be performed with the raw ingredients in the form of a slurry (the wet process) or in dry form (the dry process).
- The addition of water facilitates grinding. However, the water must then be removed by evaporation as the first step in the burning process, which requires additional energy.
- The wet process, which was once standard, has now been rendered obsolete by the development of efficient dry grinding equipment, and all modern cement plants use the dry process.
- When it is ready to enter the kiln, the dry raw mix has 85% of the particles less than 90 μm in size.

Portland Cement Manufacturing

Preparation of Raw materials
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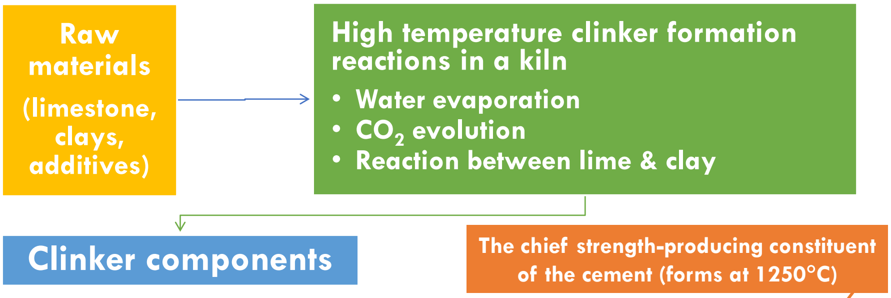
Clinker Formation and Compounds



Raw materials

(limestone, clays, additives)

High temperature clinker formation reactions in a kiln

- **Water evaporation**
- **CO_2 evolution**
- **Reaction between lime & clay**

Clinker components

The chief strength-producing constituent of the cement (forms at 1250°C)

$2CaO.SiO_2$	Di-calcium silicate	C_2S
$3CaO.SiO_2$	Tri-calcium silicate	C_3S
$3CaO.Al_2O_3$	Tri-calcium aluminate	C_3A
$4CaO.Al_2O_3.Fe_2O_3$	Tetracalcium aluminoferrite	C_4AF
MgO	Magnesium oxide in free state	M

Cement Rotary Kiln

- The rotary kiln is a tube up to 200 m long and perhaps 6 m in diameter, with a long flame at one end.
- The raw feed enters the kiln at the cool end and gradually passes down to the hot end, then falls out of the kiln and cools down.

Cement Rotary Kiln

- This long cylinder rotates about its axis once every minute or two.
- The axis is inclined at a slight angle, the end with the burner being lower.
- The rotation causes the raw meal to gradually pass along from where it enters at the cool end, to the hot end where it eventually drops out and cools.

Wet and Dry Process

- **Wet Process Kiln**
  - The original rotary cement kilns were called 'wet process' kilns. They were relatively simple compared with modern developments.
  - The raw meal was supplied at ambient temperature in the form of a slurry.
  - A wet process kiln may be up to 200m long and 6m in diameter. It has to be long because a lot of water has to be evaporated and the process of heat transfer is not very efficient.
  - The slurry may contain about 40% water. This takes a lot of energy to evaporate.

Wet and Dry Process

- **Wet Process Kiln**
  - Various developments of the wet process were aimed at reducing the water content of the raw meal.
  - An example of this is the 'filter press' - such adaptions were described as 'semi-wet' processes.
  - The wet process has survived for over a century because
    - many raw materials are suited to blending as a slurry
    - for many years, it was technically difficult to get dry powders to blend adequately.
  - New cement kilns are of the 'dry process' type.

Wet and Dry Process

- **Dry Process Kiln**
  - In a modern works, the blended raw material enters the kiln via the pre-heater tower. Here, hot gases from the kiln are used to heat the raw meal. As a result, the raw meal is already hot before it enters the kiln.
  - The dry process is much more thermally efficient than the wet process.
    - Firstly, and most obviously, this is because the meal is a dry powder and there is little or no water that has to be evaporated.
    - Secondly, and less obviously, the process of transferring heat is much more efficient in a dry process kiln.
    - An integral part of the process is a heat exchanger called a 'suspension preheater'.

Clinker: Reactions in the Kiln

- They can be considered under three broad headings:
  - Decomposition of raw materials - temperatures up to about 1300 °C.
  - Alite formation and other reactions at 1300 °C - 1450 °C in the burning zone.
  - Cooling of the clinker.

Clinker: Reactions in the Kiln

- **Decomposition of raw materials - temperatures up to about 1300 °C:**
  - This includes:
    - Water evaporation in the raw feed, if any. [up to 450 °C]
    - Loss of carbon dioxide from the limestone (i.e.: calcining) [450 °C – 900 °C].
    - Decomposition of the siliceous and aluminosilicate fractions of the feed [900 °C – 1300 °C].
    - Formation of a sulfate melt phase [900 °C – 1300 °C].
  - The decomposition products react with lime to form intermediate compounds which in turn form other compounds as clinkering proceeds.

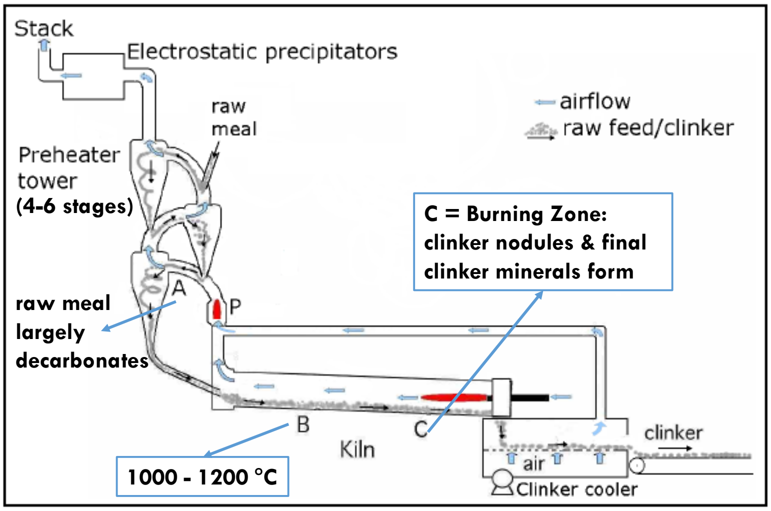
Clinker: Reactions in the Kiln

- **Alite (C_3S) formation and other reactions at 1300 °C - 1450 °C in the burning zone.**
  - In the burning zone, above about 1300 °C, reactions take place quickly. The clinker is in the burning zone for perhaps 10-20 minutes but in this time a lot happens:
    - The proportion of clinker liquid increases and nodules form.
    - Intermediate phases dissociate to form liquid and belite.
    - Belite reacts with free lime to form alite.
    - Some volatile phases evaporate.

Clinker: Reactions in the Kiln

- **Cooling of the clinker:**
  - As the clinker cools, the main liquid phase crystallizes to form aluminate (C_3A), ferrite (C_4AF) and a little belite.
  - Fast cooling of clinker is advantageous - it makes for more hydraulically-reactive silicates and lots of small, intergrown, aluminate and ferrite crystals.
  - Slow cooling gives less hydraulically-reactive silicates and produces coarse crystals of aluminate and ferrite. Over-large aluminate crystals can lead to erratic cement setting characteristics. Very slow cooling allows alite to decompose to belite and free lime.

Burning in a Kiln



C = Burning Zone: clinker nodules & final clinker minerals form

raw meal largely decarbonates

1000 - 1200 °C

Suspension Preheater

- A tower with a series of cyclones in which fast-moving hot gases keep the meal powder suspended in air.
- All the time, the meal gets hotter and the gas gets cooler until the meal is at almost the same temperature as the gas.
- The basic dry process system consists of the kiln and a suspension preheater. Raw materials are ground finely and blended to produce the raw meal. Raw meal is fed in at the top of the preheater tower and passes through the series of cyclones in the tower.

Suspension Preheater

- Hot gas from the kiln and, often, from the clinker cooler are blown through the cyclones. Heat is transferred efficiently from the hot gases to the raw meal.
- The heating process is efficient because
  - the meal particles have a very high surface area relative to their size,
  - there is a large temperature difference between hot gas and meal.
- Typically, 30%-40% of the meal is decarbonated before entering the kiln.

Wet and Dry Process

- Since meal enters the kiln at about 900 °C (compared with about 20 °C in the wet process), the kiln can be shorter and of smaller diameter for the same output.
- This reduces the capital costs of a new cement plant.
- A dry process kiln might be only 70 m long and 6 m wide but produce a similar quantity of clinker (usually measured in tonnes per day) as a wet process kiln of the same diameter but 200 m in length.
- For the same output, a dry process kiln without a precalciner would be shorter than a wet process kiln but longer than a dry process kiln with a precalciner.

Clinker Cooler

- The purpose of a cooler is, obviously, to cool the clinker. This is important for a several reasons:
  - From an engineering viewpoint, cooling is necessary to prevent damage to clinker handling equipment such as conveyors.
  - From both a process and chemical viewpoint, it is beneficial to minimize clinker temperature as it enters the cement mill. The milling process generates heat and excessive mill temperatures are undesirable. It is clearly helpful, therefore, if the clinker is cool as it enters the mill.
  - From an environmental and a cost viewpoint, the cooler reduces energy consumption by extracting heat from the clinker, enabling it to be used to heat the raw materials.
  - From a cement performance viewpoint, faster cooling of the clinker enhances silicate reactivity.

Clinker Cooler

- The cooled clinker is then conveyed either to the clinker store or directly to the clinker mill. The clinker store is usually capable of holding several weeks' supply of clinker, so that deliveries to customers can be maintained when the kiln is not operating.

Cement Mill

- Cement clinker is usually ground using a ball mill: a large rotating drum containing grinding media - normally steel balls.
  - As the drum rotates, the motion of the balls crushes the clinker. The drum rotates approximately once every couple of seconds.
  - The drum is generally divided into two or three chambers, with different size grinding media. As the clinker particles are ground down, smaller media are more efficient at reducing the particle size still further.
- Grinding systems are either 'open circuit' or 'closed circuit.'
  - In an open circuit system, the feed rate of incoming clinker is adjusted to achieve the desired fineness of the product.
  - In a closed circuit system, coarse particles are separated from the finer product and returned for further grinding.

Cement Mill

- Gypsum is interground with the clinker in order to control the setting properties of the cement. Clinker grinding uses a lot of energy and the cement becomes hot – this can result in the gypsum becoming dehydrated, with potentially undesirable results.

Potential Compound Composition of Some Typical Cements (%)

	C_3S	C_2S	C_3A	C_4AF
Type I	55	19	10	7
Type II	51	24	6	11
Type III	56	19	10	7
Type IV	28	49	4	12
Type V	38	43	4	9

Function of Tricalcium Silicate (C_3S)

- Hydration of C_3S gives cement paste most of its strength, particularly at early times.
- C_3S is highly reactive. It hardens rapidly and largely responsible for initial set and early strength.
- Increase in C_3S percentage causes the early strength (at 7 or 8 days) of Portland cement to be higher.
- A higher C_3S percentage produces higher heat of hydration and accounts for faster gain in strength.
- Responsible for final strength (at 1 year).

Function of Dicalcium Silicate (C_2S)

- Hardens slowly
- Its effect on strength gain occurs at ages beyond one week
- Responsible for long term final strength (at 1 year).

Function of Tricalcium Aluminate (C_3A)

- Highly reactive: contributes to strength development in the first few days because it is the first compound to hydrate
  - Causes set but needs retardation (by gypsum)
- It turns out higher heat of hydration and contributes to faster gain in strength.
- It results in poor sulfate resistance and increases the volumetric shrinkage upon drying.
- Cements with low C_3A contents usually generate less heat, develop higher strengths and show greater resistance to sulfate attacks.
- It has high heat generation and reactive with soils and water containing moderate to high sulfate concentrations.

Function of Tetracalcium Aluminoferrite (C_4AF)

- Assists in the manufacture of Portland Cement by allowing lower clinkering temperature.
- Acts as a filler.
- Contributes very little strength of concrete even though it hydrates very rapidly.
- Responsible for grey color of Ordinary Portland Cement (OPC).

Types of Portland Cement

Type	Description
I	*Regular portland cement* – Fairly high C_3S content for good early strength development, used for general construction purposes Other types: white (contains no C_4AF), oil-well cement, quick-setting cement
II	*Moderate-heat-of-hardening and sulfate-resisting portland cement* – Low C_3A content (<8%), used where moderate heat of hydration is required, or for general concrete construction exposed to soil or water containing sulfate ions
III	*High-early-strength (HES) cement* – contains higher lime to silica ratio, ground finer, and higher proportion of C_3S than type I cement→ quicker hardening and faster evolution of heat, used for roads for faster put into service and for cold weather concreting

Types of Portland Cement

Type	Description
IV	*Low-heat portland cement* – contains lower percentage of C_3S (<50%) and C_3A (and higher C_4AF) → has lower heat evolution, used when a low heat of hydration is desired (in massive structures like dams)
V	*Sulfate-resisting portland cement* – very low in C_3A (<5%) → higher content of C_4AF, used when high sulfate resistance is required.

Types of Portland Cement

Cement type	Use
IA	Type I cement containing an integral air-entraining agent
IIA	Type II cement containing an integral air-entraining agent
IIIA	Type III cement containing an integral air-entraining agent

Air-entraining agent increases the resistance of the hardened concrete to scaling from alternating freezing and thawing and the use of de-icers (such as $CaCl_2$).

White Portland cement is made from raw materials containing little or no iron or manganese, the substances that give conventional cement its gray color.

Analysis of Portland Cement (%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Alkali Oxides	SO_3
	Regular Cement						
Minimum	61.17	18.58	3.86	1.53	0.60	0.66	0.82
Maximum	66.92	23.26	7.44	6.18	5.24	2.9	2.26
Average	63.85	21.08	5.79	2.86	2.47	1.4	1.73
	High-Early-Strength: High C_3S						
Minimum	62.7	18.0	4.1	1.7	-	-	2.2
Maximum	67.5	22.9	7.5	4.2	-	-	2.7
Average	64.6	19.9	6.0	2.6	-	-	2.3
	Low-Heat-of-Hardening: Lower C_3S and C_3A, Higher C_2S and C_4AF						
Minimum	59.3	21.9	3.3	1.9	-	-	1.6
Maximum	61.5	26.4	5.4	5.7	-	-	1.9
Average	60.2	23.8	4.9	4.9	-	-	1.7

Cement Hydration

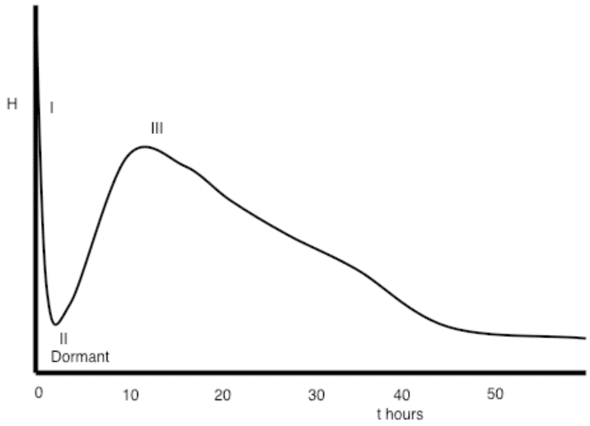
- By the process of **hydration** (reaction with water) Portland cement mixed with sand, gravel and water produces the synthetic rock we call ***concrete***.
- Concrete is as essential a part of the modern world as are electricity or computers.
- Clinker is anhydrous having come from a hot kiln. Cement powder is also anhydrous if we ignore the small amount of water in any gypsum added at the clinker grinding stage.
- **Hydration** involves many different reactions, often occurring at the same time.
  - As the reactions proceed, the hydration products gradually bond together the individual sand and gravel particles, and other components of the concrete, to form a solid mass.

The Hydration Process: Reactions

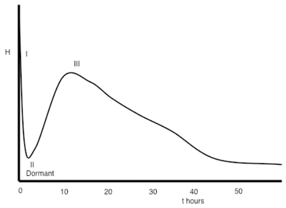
- In the anhydrous state, four main types of minerals are normally present: alite (C_3S), belite (C_2S), aluminate (C_3A) and a ferrite phase (C_4AF).
- Also present are small amounts of clinker sulfate (sulfates of sodium, potassium and calcium) and also gypsum, which was added when the clinker was ground up to produce the familiar grey powder.
- When water is added, the reactions which occur are mostly exothermic.
- We can get an indication of the rate at which the minerals are reacting by monitoring the rate at which heat is evolved using a technique called **conduction calorimetry**.

The Hydration Process: Reactions

- An illustrative example of the heat evolution curve produced is shown below.

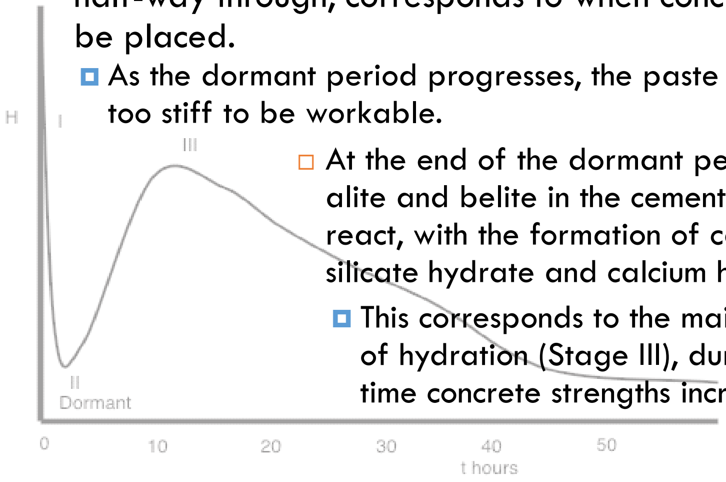


The Hydration Process: Reactions



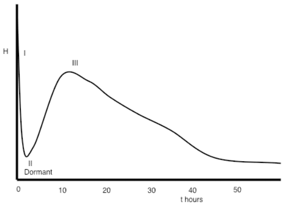
- Three principal reactions occur:
  - Almost immediately on adding water some of the clinker sulfates and gypsum dissolve producing an alkaline, sulfate-rich, solution.
  - Soon after mixing, the (C_3A) phase (the most reactive of the four main clinker minerals) reacts with the water to form an aluminate-rich gel (Stage I on the heat evolution curve).
  - The gel reacts with sulfate in solution to form small rod-like crystals of ettringite $[Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O]$.
  - (C_3A) reaction with water is strongly exothermic but does not last long, typically only few minutes, and is followed by a period of a few hours of relatively low heat evolution. This is called the dormant, or induction period (Stage II).

The Hydration Process: Reactions



- The first part of the dormant period, up to perhaps half-way through, corresponds to when concrete can be placed.
  - As the dormant period progresses, the paste becomes too stiff to be workable.
- At the end of the dormant period, the alite and belite in the cement start to react, with the formation of calcium silicate hydrate and calcium hydroxide.
  - This corresponds to the main period of hydration (Stage III), during which time concrete strengths increase.

The Hydration Process: Reactions



- The period of maximum heat evolution occurs typically between about 10 and 20 hours after mixing, and then gradually tails off.
  - In a mix containing PC only, most of the strength gain has occurred within about a month.
  - Where PC has been partly-replaced by other materials, such as fly ash, strength growth may occur more slowly and continue for several months or even a year.
- Ferrite reaction also starts quickly as water is added, but then slows down, probably because a layer of iron hydroxide gel forms, coating the ferrite and acting as a barrier, preventing further reaction.

Hydration Products

- The products of the reaction between cement and water are termed "hydration products."
- In concrete (or mortar or other cementitious materials) there are typically four main types:
  1. **Calcium silicate hydrate:** this is the main reaction product and the main source of concrete strength. It is often abbreviated to "C-S-H“. The Si/Ca ratio is somewhat variable but typically approximately 0.45-0.50 in hydrated Portland cement but up to perhaps about 0.6 if slag or fly ash or microsilica is present, depending on the proportions.

Hydration Products

2. **Calcium hydroxide:** (or Portlandite)- $Ca(OH)_2$, often abbreviated to 'CH.' CH is formed mainly from alite hydration. Alite has a Ca:Si ratio of 3:1 and C-S-H has a Ca/Si ratio of approximately 2:1, so excess lime is available to produce CH.
3. **AFm and AFt phases:** these are two groups of minerals that occur in cement, and elsewhere. One of the most common AFm phases in hydrated cement is monosulfate and by far the most common AFt phase is ettringite. Ettringite is an AFt phase because it contains three (t-tri) molecules of anhydrite when written as $C_3A.3CaSO_4.32H_2O$, and monosulfate is an AFm phase because it contains one (m-mono) molecule of anhydrite when written as $C_3A.CaSO_4.12H_2O$.

Hydration Products

- The most common AFt and AFm phases in hydrated cement are:
  - **Ettringite:** present as rod-like crystals in the early stages of reaction or sometimes as massive growths filling pores or cracks in mature concrete or mortar. The chemical formula for ettringite is $[Ca_3Al(OH)_6.12H_2O]_2.2H_2O]$ or, mixing notations, $C_3A.3CaSO_4.32H_2O$.
  - **Monosulfate:** tends to occur in the later stages of hydration, a day or two after mixing. The chemical formula for monosulfate is $C_3A.CaSO_4.12H_2O$. Note that both ettringite and monosulfate are compounds of C_3A, CaSO4 (anhydrite) and water, in different proportions.
  - **Monocarbonate:** the presence of fine limestone, whether interground with the cement or present as fine limestone aggregate, is likely to produce monocarbonate ($C_3A.CaCO_3.11H_2O$) as some of the limestone reacts with the cement pore fluid.

Hydration Products

- Some important points to note about AFm and AFt phases are that:
  - They contain a lot of water, especially AFt - principally ettringite in the context of cement.
  - AFm contains a higher ratio of Al/Ca compared with AFt.
  - The aluminium can be partly-replaced by iron in both AFm and AFt phases.
  - The sulfate ion in monosulfate AFm phase can be replaced by other anions; a one-for-one substitution if the anion is doubly-charged (e.g.: carbonate, CO_3^{2-}) or one-for-two if the substituent anion is singly-charged (e.g.: hydroxyl, OH^- or chloride, Cl^-).
  - The sulfate in ettringite can be replaced by carbonate or, probably, partly replaced by two hydroxyl ions, although in practice neither of these is often observed.