A. HYDRAULIC CEMENTS AND THEIR PROPERTIES

I. INTRODUCTION

- Inorganic materials which are mixed with water and used to bind other materials together are generally classified as “Cementitious” materials.

- Hydraulic cements have the special property of setting and hardening under water. The most common hydraulic cement is portland cement and will be the principal topic of discussion here.

- The definition of hydraulic cements is that they harden by reacting with water to form a water-resistant product.

- The definition of portland cement is given in ASTM C 150 as a hydraulic cement produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an interground addition.

- There are many other cementitious materials*, but none is more important than portland cement.

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*There are other examples of cementitious materials that are nonhydraulic such as lime (CaO) or plaster-of-paris (calcium sulfate CaSO₄ which is also known as Gypsum) which can both be mixed with water to bind other materials together or along to form a homogeneous solid but their hydration products are not resistant to water.
II. THE COMPONENT PHASES OF PORTLAND CEMENT

- Most portland cement is manufactured from limestone and clay by heating it in a rotary kiln which is schematically shown in Fig. 1.

![Diagram of a rotary cement kiln](image.png)

**Fig. 1** A Schematic outline of conditions and reactions in a typical rotary cement kiln (dry process).

- The limestone and clay are ground by mechanical grinders and either placed in a water-based slurry or are fed in dry powder form into the top of the kiln. The wet-process can require as much as 1400 kcal/kg of clinker, and thus it is generally being replaced by the dry-process in which the fuel requirements can be as low as 800 kcal/kg.

- The raw mix is transported along the kiln by the rotation of the entire structure which is usually consists of a steel tube that is lined with fire bricks. The kiln is heated by a burner.

- The physical and chemical processes are shown along the length of the kiln. The presence of $\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ in the clay causes a liquid melt to form in the feed materials and this causes a "balling up" of the solid particles into a snowball-like structure which is called a **clinker**. It is this physical process of a liquid melt binding solids together that allows the formation of the chemical compounds discussed below.

- The chemical reactions taking place in the cement kiln can be represented approximately by the following:
II. THE COMPONENT PHASES OF PORTLAND CEMENT (Continued...)

Limestone $\rightarrow$ CaO + CO$_2$

Clay $\rightarrow$ SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ + H$_2$O

$\begin{align*}
3\text{CaO} . \text{SiO}_2 & \quad (C_3S \text{- Tricalcium silicate}) \\
2\text{CaO} . \text{SiO}_2 & \quad (C_2S \text{- Dicalcium silicate}) \\
3\text{CaO} . \text{Al}_2\text{O}_3 & \quad (C_3A \text{- Tricalcium aluminate}) \\
4\text{CaO} . \text{Al}_2\text{O}_3 . \text{Fe}_2\text{O}_3 & \quad (C_4\text{AF} \text{- Tetracacium aluminate ferrite})
\end{align*}$

- In cement chemistry, the individual oxides and clincker compounds are expressed by their abbreviations.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Abbreviation</th>
<th>Compound</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>C</td>
<td>3 CaO . SiO$_2$</td>
<td>$C_3$S</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>S</td>
<td>2 CaO . SiO$_2$</td>
<td>$C_2$S</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>A</td>
<td>3 CaO . Al$_2$O$_3$</td>
<td>$C_3$A</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>F</td>
<td>4 CaO . Al$_2$O$_3$ . Fe$_2$O$_3$</td>
<td>$C_4$AF</td>
</tr>
<tr>
<td>MgO</td>
<td>M</td>
<td>4 CaO . Al$_2$O$_3$ . SO$_3$</td>
<td>$C_4$A$_3$S</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>$\bar{S}$</td>
<td>3 CaO . 2SiO$_2$ . 3H$_2$O</td>
<td>$C_3$S$_2$H$_3$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>H</td>
<td>CaSO$_4$ . 2H$_2$O</td>
<td>$C\bar{S}$H$_2$</td>
</tr>
</tbody>
</table>

($C_3S$ = Tricalcium Silicate; $C_2S$ = Dicalcium Silicate)

B. PORTLAND CEMENT PASTE AND CONCRETE

I. INTRODUCTION

- In principal measure of structural quality of concrete is its compressive strength. This property is usually measured in the United States on 6 by 12-in. cylinders which have been moist-cured for a specific length of time (e.g., 3, 7 or 28 days) and tested in compression at a specific rate of loading.

- The compressive strength obtained from the 28-day test is known as the $f'_c$ and is the main property specified for design purposes.

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II. FACTORS INFLUENCING COMpressive STRENGTH OF CONCRETE

- There are a number of factors which can be identified; some of the major ones are:

1) The quality of cement paste

   The quality of cement paste: In well-cured concretes the quality of cement paste depends on the water/cement ratio, (w/c). If one assumes that some cement never hydrates, then, on a weight basis, the water equivalent of approximately 0.25 w/c ratio is required for the hydration of portland cement. Usually more water is used in order to achieve the desired workability characteristics in concrete. The extra water contributes to enhance volume of voids, which act as local stress concentrations that reduce the strength of the cement paste.

2) The characteristics of aggregate

   The characteristics of aggregate: The stiffness, shape, texture, maximum size, and grading of both coarse and fine aggregate are known to exercise significant influence on compressive strength of concrete.

3) The ratio of cement to aggregate.

   The ratio of cement to aggregate: In a concrete mix, as the volume of cement is decreased, and correspondingly as the volume of aggregate is increased, more water is generally needed to attain a fixed workability. According to (1) above, therefore, the decreasing cement/aggregate ratio would cause deterioration in the quality of cement paste and, hence, result in lowered compressive strength. Too much cement can lead to shrinkage problems.

III. MICROSTRUCTURE OF CEMENT PASTE

- “Cementitious” materials are inorganic materials which are mixed with water and used to bind other materials together.

- Hydraulic cements harden by reacting with water to form a water-resistant product.

- The most common hydraulic cement is portland cement and portland cement concrete will be the principal topic of discussion here.

- The hydration of portland cement can be discussed in terms of the chemical reactions and the physical arrangement of the resulting microstructure.
III. MICROSTRUCTURE OF CEMENT PASTE (Continued…)

1. The Chemical Reactions

- In general, the characteristics of the individual compounds (or phases) of portland cement (C₃S, β-C₂S, C₃A, C₄AF, etc.)* are reflected in the behavior of the portland cement. We will focus only on the first two phases. The approximate reactions are:

\[
\begin{align*}
2\text{C}_3\text{S} + 6\text{H} & \rightarrow \text{C} - \text{S} - \text{H} + 3\text{CH} + 120 \text{ Cal/g} \\
2\beta - \text{C}_2\text{S} + 4\text{H} & \rightarrow \text{C} - \text{S} - \text{H} + \text{CH} + 62 \text{ Cal/g}
\end{align*}
\]

\[\text{C}_3\text{A}, \text{C}_4\text{AF}, \text{C}_6\text{S} \rightarrow \text{C} - \text{A} - \text{S} - \text{H} \quad (\text{C}_6\text{A}_3\text{S}_3\text{H}_{32} \text{ Ettringite}, \text{C}_4\text{A}_3\text{S}_1\text{H}_{12-18} \text{ Monosulfate})\]

- The two equations in the Box are the most important, and will be discussed later.

- It is important to note that both calcium silicate phases hydrate to give C-S-H (calcium silicate hydrate) and CH (calcium hydroxide {Ca(OH)₂} which is also known as hydrated lime & portlandite).

- There are some names associated with these phases; some of them are:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>alite, tricalcium silicate</td>
</tr>
<tr>
<td>β-C₂S</td>
<td>blite, β-dicalcium silicate</td>
</tr>
<tr>
<td>C-S-H</td>
<td>calcium silicate hydrate, tobermorite gel (approximately C₅S₂H₃)</td>
</tr>
<tr>
<td>CH</td>
<td>hydrated lime, portlandite, calcium hydroxide {Ca(OH)₂}</td>
</tr>
<tr>
<td>C₃A</td>
<td>tricalcium aluminate</td>
</tr>
<tr>
<td>C₄A₃H₁₃</td>
<td>tetracalcium aluminate hydrate</td>
</tr>
<tr>
<td>C₄A₃S₁₈H₁₈</td>
<td>calcium monosulfoaluminate hydrate, the &quot;low-sulfate&quot; form of aluminosulfate hydrate</td>
</tr>
<tr>
<td>C₆A₃S₃H₃₂</td>
<td>ettringite, the &quot;high-sulfate&quot; form of alumino-sulfate hydrate</td>
</tr>
<tr>
<td>C₆A₆FH₁₂</td>
<td>calcium aluminoferrite hydrate</td>
</tr>
</tbody>
</table>

* There is convention followed by cement chemists in which:  C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, H = H₂O, and S = SO₃.
III. MICROSTRUCTURE OF CEMENT PASTE (Continued…)

- All of these compounds have been produced separately, and they have been studied extensively.

- The compounds in the box are the most important for the development of strong, durable concrete, and compounds containing Al₂O₃ and Fe₂O₃ are present in the final product, but they are not as important as the calcium silicate products.

- C₄AF and C₃A react much faster with water than C₃S or β-C₂S and it is believed that the stiffening (loss of consistency) and the setting (solidification) characteristics of portland cement paste are largely determined by the hydration reactions involving aluminates.

- The hydration of C₃A is controlled by the addition of gypsum to portland cement.

2. Space Filling in Portland Cement Pastes

- It is to be expected that as the hydration reactions occur the space between the originally discrete cement grains is filled with the hydration products, and the paste will transform from a material with the consistency of wet mud to the hard phase that is strong and impermeable.

- There are a number of levels to consider the way in which the originally water-filled space is filled by hydration products. Let us first consider the hydration products from one grain of cement. The spatial relationship of the hydration products with respect to the original cement grain can be determined by microscopic investigation.

- The partial hydration of one grain of cement is schematically represented in Fig. 2. There are many details in this process that are not yet understood, but there is sufficient information available to allow a consistent mental picture to be considered.
III. MICROSTRUCTURE OF CEMENT PASTE (Continued...)

2. Space Filling in Portland Cement Pastes (Continued...)

Fig. 2 The hydration products formed inside and outside the cement grain are schematically represented. The multiple nature of the cement grain is neglected and assumed to be a single phase that shows two types of products. P1 refers to the "primary" portlandite which appears early in the originally water-filled space.

- The hydration of a number of cement grains is schematically represented on the next page in Fig. 3 at different degrees of hydration. The fresh paste (i.e., the initial combination of water and cement grains) is drawn to approximately represent the 0.4 water/cement ratio, and thus there are not enough hydration products to fill the originally-water-filled space and a capillary porosity remains in the final microstructure.

- A large amount of this capillary porosity leads to a more permeable solid. By choosing a lower w/c ratio, the permeability may be decreased to very small values. After the concrete has been allowed to dry, the water in the capillary pores evaporates and the hydration stops.
III. MICROSTRUCTURE OF CEMENT PASTE (Continued...)

2. Space Filling in Portland Cement Pastes (Continued...)

Fig. 3 A schematic representation of the hydration of a number of cement grains. The multiphase nature of the cement grains has been neglected as this is like the hydration of tricalcium silicate alone. (a) Fresh paste of water-to-cement ratio of 0.4 is shown with unhydrated cement represented by /// and the originally water-filled space clear. (b) After 33% hydration, the inner hydration are represented by □ and the outer products by □. The primary portlandite is labeled “P1” and the columnar zone is shown around each grain. (c) After 67% hydration, the unhydrated cores are clearly surrounded by thick "rims" of inner hydration products and the columnar zone of outer products is growing on the outer surface of each grain. The primary portlandite, P1, is shown with the dendrite morphology. (d) At 100% hydration, the unhydrated cement has been consumed but the shape of the original cement grains can be distinguished if the inner product differs from the columnar zone of outer products. The intergrowth of the columnar zones from two different grains is shown at several points, but this would be larger at low water/cement ratios.

- The originally-water-filled space within the cement paste becomes the capillary pores in which act as stress concentrations and reduce the strength significantly.
III. MICROSTRUCTURE OF CEMENT PASTE (Continued…)

2. Space Filling in Portland Cement Pastes (Continued…)

- The strength of most engineering materials is increased with a decrease in porosity, and by controlling the water/cement ratio the engineer is assured that the basic porosity of the paste is also controlled. That is not to say the other sources of porosity will not occur, but at least the cement paste will have a given porosity.

- If cement paste specimens are prepared with a range of w/c ratios it is apparent that the density of high w/c samples is much lower than low w/c samples.

- Thus if we consider the hydration of portland cement paste on a Macroscopic Level we find that the hydration of one cm$^3$ of cement yields approximately 2 cm$^3$ of solid hydration product. This is illustrated in Fig. 4 in a presentation originally given by T.C. Powers†

![Diagram of cement paste hydration](image)

**Fig. 4** Composition of Cement Paste at Different Stages of Hydration. The percentage indicated applied only to paste with enough water-filled space to accommodate the products at the degree of hydration indicated.

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III. MICROSTRUCTURE OF CEMENT PASTE (Continued...)

3. The Curing Process

- Another influence on the quality of cement paste is the curing process.

- Concrete increases in strength with age as long as drying of the concrete is prevented. When the concrete is permitted to dry, the chemical reactions slow down or stop. It is, therefore, desirable to keep the concrete moist as long as possible.

- The importance of the curing process is illustrated in Fig. 5. When moist curing is discontinued, the strength increases for a short period and then does not increase further to any great extent. However, if moist curing is resumed after a period of drying, the strength will again increase. Although this can be done in a laboratory, it is difficult on most jobs to supply sufficient water over a long period to resaturate concrete. It is best to moist cure the concrete continuously from the time it is placed until it has attained the desired quality.

![Fig. 5 Influence of curing conditions on Strength.](image-url)
III. MICROSTRUCTURE OF CEMENT PASTE (Continued…)

4. Effects of Chemical Composition of Portland Cements on Strength

- In classic research from over sixty years ago Bougue and Lerch* found that of the four portland cement phases only C₃S and C₂S developed appreciable compressive strength when pure samples of each were hydrated.

- The compressive strengths found by Bougue and Lerch* are plotted in Fig. 6 as a function of age. Compressive strengths of C₃A and C₄AF, hydrated alone and with gypsum, fall within the cross-hatched region labeled "A" and have not been plotted explicitly.

![Fig. 6](image)

Fig. 6 The compressive strength found by Bougue and Lerch* for hydrated samples of the pure cement phases C₃S and C₂S are plotted as a function of age. The compressive strengths of C₃A and C₄AF, hydrated alone and with gypsum, fall within the cross-hatched region labeled “A” and have not been plotted explicitly. (a) The time scale is linear. (b) The time scale is logarithmic, which has the effect of expanding the early ages, and this shows the differences between strength gain of C₃S and C₂S pastes.

- The same trend identified by Bogue and Lerch is evident in Fig. 7 for two cements with different ratios of the calcium silicates. It is evident that the C₂S hydrates much more slowly than the C₃S, but they gain comparable strengths at later ages.

III. MICROSTRUCTURE OF CEMENT PASTE (Continued...)

4. Effects of Chemical Composition of Portland Cements on Strength (Continued...)

![Graph showing compressive strength development with curing for two mortars made from portland cements containing different amounts of two calcium silicates. A = 70% C₃S and 10% C₂S; B = 30% C₃S and 50% C₂S.]

- Mehta and Williamson* investigated the possible role of C₄AF and C₃A on the strength development of cement pastes containing 75% C₃S (alite).

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IV. INFLUENCE OF AGGREGATE ON CONCRETE STRENGTH

- It is obvious that the nature of the aggregate will strongly influence the strength of concrete if the cement paste has sufficient quality.

- The interface between the paste and aggregate is, perhaps, the most important area to consider first. The "bond" between aggregate and paste is influenced by the texture of the aggregate (roughness vs. smoothness) and on the grading of the aggregate.

- The rougher the surface of the aggregate and the greater the area in contact with the cement paste, the stronger a concrete will be.

- There is an extensive discussion of the "transition zone" between cement paste and the aggregate in the textbook*, between pages 37 and 41, and this is an area of active research interest currently.

- The influence of the maximum aggregate size can be considered from several points of view.

  1. The use of large aggregate size is sometimes considered advantageous since, holding everything else constant, there is less water required with larger aggregate sizes to achieve a given workability. This leads to a lower water/cement ratio and, thus, improved strength.

  2. On the other hand, at a fixed water/cement ratio the presence of large-size aggregate leads to a reduction of strength. One can consider the possibility that the total interfacial area between the aggregate and the paste is decreased and that the stresses between the aggregate and the paste are high. There are larger stress concentrations present in any event, and there are greater chances for shrinkage, segregation, and bleeding effects near the larger aggregate particles.

- In discussing these effects, Neville* summarized them as follows:

  "It seems therefore that there are two opposing effects on strength when large aggregate is used, and in practice the net result depends on the mix proportions. Generally, high strength of rich mixes is adversely affected by the use of large-size aggregate but in lean mixes, say with less cement than 470 lb. per cu. yd. of concrete and a strength lower than 4000 psi, the detrimental effects of large aggregate are small" (See Fig. 8.)

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IV. INFLUENCE OF AGGREGATE ON CONCRETE STRENGTH (Continued...)

Fig. 8 Influence of Maximum Size of Aggregate on Compressive Strength of Concrete (slump between 3.8 and 5.8 in.)

- Aggregates of different sizes but of a given type can be evaluated also on the basis of strength of concrete per lb. of cement per cu. yd. of concrete: this is a reasonable approach as the cost of cement largely influences the price of concrete. It appears that in lean mixes, large aggregate give the best value but in rich mixes it is the smaller aggregate that results in highest strength per pound of cement per cubic yard of concrete. A typical relationship between aggregate size and compressive strength is shown in Fig. 9.

- A further limitation on the general influence of aggregate size on a strength of concrete lies in the role of shape and texture of the particles actually used. Generally, rounded particles result in a lower strength than crushed aggregate; the effect is greater with respect to tensile than compressive strength and is greater in high-strength concrete than at high water/cement ratios.
IV. INFLUENCE OF AGGREGATE ON CONCRETE STRENGTH (Continued...)

Fig. 9  Strength of Concretes made with Aggregates of Different Maximum Size---Actual and Expected from the Water-Cement Ratio.

V. INFLUENCE OF CEMENT CONTENT ON CONCRETE STRENGTH

- Historically, the cement content was the first factor to be emphasized in considering concrete strength. Gilkey* explained it in this way:

"Initially the concept of concrete was that of an active constituent (the cement) diluted for the sake of economy, with an inert, inexpensive filler-type material (aggregate). Water was an incidental constituent to be added in whatever amount produced the desired fluidity or workability. Eventually it was recognized that as the aggregate was increased the water necessary to produce suitable workability had to be increased and that a designated ratio of water to cement (with aggregate being added by trial to produce the desired workability) gave a more sensitive and uniform basis for estimating and controlling strengths than did a specified ratio of aggregate to cement.

- It is obvious, therefore, that what was hailed as a revolutionary change in basic concrete technology was actually (in retrospect) nothing more than an operational improvement in concrete mix design, which constituted a marked advance in the interest of simplification and control of concrete mixes."

- There are some situations where the amount of cement in the mix will influence the strength independent of the other factors. Rich mixes, particularly with large size aggregates, often exhibit shrinkage cracks at the aggregate/paste interface and thus lower strengths. Excessively lean mixes show poor workability with a resultant loss of strength.
Transition Zone

Diagrammatic representation of the transition zone and bulk cement paste in concrete
(Mehta and Monteiro 1993)