Period #9 Notes: PORTLAND CEMENT CONCRETE (I)

A. What is Portland Cement Concrete?

Portland cement concrete is a heterogeneous material. The three main ingredients that go into making the material are the portland cement powder, the aggregate, and the mix water. There can be other ingredients that will be discussed later, but for now, these are the three primary ones.

An exothermic chemical reaction occurs between the portland cement and the water. This chemical reaction is typically called *hydration* and it transforms the cement from a powder into a cohesive matrix of significant strength that binds the aggregate particles together. The hydrated cement is generally called the *hydrated cement paste* or *hydrated cement products*, or just simply *hcp* for brevity.

The word *portland* in portland cement concrete comes from the fact that pcc resembles a naturally occurring stone called “portland stone” near the region of Portland in the U.K. This term was adopted in the nineteenth century when usage of portland cement concrete took off in a big way. Before this, the ancient Romans some two millenia before had discovered and used an earlier form of concrete.

B. The manufacture of portland cement

1. The starting point for the manufacture of portland cement is mixtures of rocks and soils rich in clay minerals (containing aluminum, iron, magnesium, silicon, and potassium) and rich in calcium (such as limestone and chalk). The metallic elements in the rocks and soils generally exist as oxides.

2. The rocks and soils are first ground up into particles finer in size than 75μm.

3. The ground material is then slowly heated in a rotating kiln to T=1500°C. Along the way, a number of important reactions occur:
   - At T=600°C the calcium carbonate ($CaCO_3$) in limestone separates into lime (CaO) and carbon dioxide (CO_2).
   - At T=1200°C the formation of silicates and aluminates begin, and continues up through T=1500°C.
4. The material that emerges from the kiln in roughly millimeter-sized particles is then allowed to cool.
5. 5% gypsum or chalk in the form of calcium sulfate hydrate ($CaSO_4 \cdot 2H_2O$) is then added to the clinker particles.
6. The mixture is then ground down to particles sizes in the range of 2-80μm. The resulting portland cement powder has a specific surface area of roughly 300m^2/kg.

C. Cement Chemistry and the Hydration Reaction

1. Cement Composition

Many different chemical compounds comprise portland cement. To make the description of the chemical composition easier, and to describe the chemical reactions that occur during hydration, a special shorthand notation has been developed for cement chemistry:

Shorthand Notation:

Full notation	**Shorthand notation**	**Common name**
CaO	C	Lime
SiO_2	S	Silica
Al_2O_3	A	Alumina
Fe_2O_3	F	Iron oxide or Ferrite
SO_3	$\hat{S}$	Sulfate
H_2O	H	Water

The five main chemical compounds that comprise ordinary cement particles are:

Formal name	**Common name**	**Full notation**	**Shorthand notation**
Tricalcium silicate	alite	$3CaO \cdot SiO_2$	C_3S
Dicalcium silicate	belite	$2CaO \cdot SiO_2$	C_2S
Tricalcium aluminate	aluminate	$3CaO \cdot Al_2O_3$	C_3A
Tetracalcium aluminoferrite	ferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF
Calcium sulfate hydrate	gypsum or chalk	$CaSO_4 \cdot 2H_2O$	$C\hat{S}H_2$

By manipulating the fineness and the relative proportions of these chemical compounds in portland cement, a cement with different characteristics can be obtained. For example, there exist six relatively standard types of portland cement with the compositions shown in Table 9.1:

Table 9.1 Chemical and compound composition and fineness of some typical portland cements. (adapted from Design and Control of Concrete Mixes, 13th Ed. By S.H. Kosmatka and W.C. Panarese, Portland Cement Association, 1988.)

Type	**Chemical composition (%)**						**Compound composition (%)**				**Fineness (m^2/kg)**
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	C_3S	C_2S	C_3A	C_4AF	
I	20.9	5.2	2.3	64.4	2.8	2.9	55	19	10	7	370
II	21.7	4.7	3.6	63.6	2.9	2.4	51	24	6	11	370
III	21.3	5.1	2.3	64.9	3.0	3.1	56	19	10	7	540
IV	24.3	4.3	4.1	62.3	1.8	1.9	28	49	4	12	380
V	25.0	3.4	2.8	64.4	1.9	1.6	38	43	4	9	380
White	24.5	5.9	0.6	65.0	1.1	1.8	33	46	14	2	490

- Type I portland cement is a general-purpose cement suitable for all uses where the special properties of other types are not required. It is used in concrete that is not subject to aggressive exposures, such as sulfate attack from soil or water, or to an objectionable temperature rise due to heat generated by hydration. Its uses in concrete include pavements, floors, reinforced concrete buildings, bridges, railway structures, tanks and reservoirs, pipe, masonry units, and other precast concrete products.

- Type II portland cement is used where precaution against moderate sulfate attack is important, as in drainage structures where sulfate concentrations in groundwaters are higher than normal but not unusually severe. Type II cement will usually generate less heat at a slower rate than Type I. If heat-of-hydration maximums are specified, this cement can be used in structures of considerable mass, such as large piers, and heavy abutments and retaining walls. Its use will reduce temperature rise, which is especially important when concrete is placed in warm weather.

- Type III portland cement provides high strengths at an early period, usually a week or less. It is chemically and physically similar to Type I cement, except that its particles have been ground finer. It is used when forms need to be removed as soon as possible or when the structure must be put into service quickly. In cold weather its use permits a reduction in the controlled curing period. Although richer mixes of Type I cement can be used to gain high early strength, Type III may provide it more satisfactorily and more economically.

- Type IV portland cement is used where the rate and amount of heat generated from hydration must be minimized. It develops strength at a slower rate than other cement types. Type IV cement is intended for use in massive concrete structures, such as large gravity dams, where the temperature rise resulting from heat generated during hardening must be minimized.

- Type V portland cement is used only in concrete exposed to severe sulfate action-principally where soils or groundwaters have a high sulfate content. It gains strength more slowly than Type I cement. The high sulfate resistance of Type V cement is attributed to a low tricalcium aluminate (C_3A) content as illustrated in Table 9.1. Sulfate resistance also increases with air entrainment and increasing cement contents (low water-cement ratios). Type V cement, like other portland cements, is not resistant to acids and other highly corrosive substance.

- White portland cement is a true portland cement that differs from gray cement chiefly in color. It is made to conform to the specifications of ASTM C 150, usually Type I or Type III, but the manufacturing process is controlled so that the finished product will be white. White portland cement is made of selected raw materials containing negligible amounts of iron and magnesium oxides-the substances that give cement its gray color. White portland cement is used primarily for architectural purposes such as precast curtain walls and facing panels, terrazzo surfaces, stucco, cement paint, tile grout, and decorative concrete. Its use is recommended wherever white or colored concrete or mortar is desired.

2. The Hydration Reaction

In the hydration reaction, water molecules have a very high affinity for the silicate, aluminate, and ferrite cement particles. Due to this high affinity, the water molecules will break the cement particles down into very thin, curly foil-like plates just a few molecules thick. The silicate and aluminate molecules carry a positive charge on their surface. This attracts the negative end of polar water molecules. In this way, the water molecules break down and then become quite strongly attached to the silicate, aluminate, and ferrite particles.

The key chemical reactions that occur during hydration are as follows:

1. Tri-calcium silicate + water produces tricalcium silicate hydrate and calcium hydroxide, liberating 500 J/g.

$$2C_3S + 7H \rightarrow C_3S_2H_8 + 3CH \qquad (\Delta\mathrm{H} = \text{-}500\mathrm{J/g})$$

2. Di-calcium silicate + water produces tricalcium silicate hydrate and calcium hydroxide, liberating 250 J/g.

$$2C_2S + 5H \rightarrow C_3S_2H_8 + CH \qquad (\Delta\mathrm{H} = \text{-}250\mathrm{J/g})$$

3. Tri-calcium aluminate and water produces tricalcium aluminate hydrate

$$C_3A + 6H \rightarrow C_3AH_6$$

4. Tri-calcium aluminate + gypsum + water produces calcium sulfoaluminate hydrate or *ettringite*, liberating 1350 J/g

$$C_3A + 3C\hat{S}H_2 + 26H \rightarrow C_6A\hat{S}_3H_{32} \qquad (\Delta\mathrm{H} = \text{-}1350\mathrm{J/g})$$

5. Ettrringite + tricalcium aluminate + water produces monosulfoaluminate

$$C_6A\hat{S}_3H_{32} + 2C_3A + 4H \rightarrow 3C_4A\hat{S}_3H_{12}$$

6. Tetra-calcium aluminoferrite and calcium-hydroxide and water produce tetracalcium aluminate hydrate and ferric hydroxide or it produces tetracalcium ferrite hydrate and aluminum hydroxide. Since the A and F are interchangeable in this reaction the notation (A,F) is used.

$$C_4AF + 2CH + 14H \rightarrow C_4(A,F)H_{13} + (\mathrm{A,F})\mathrm{H}_3$$

A few comments regarding the hydration chemical reactions.

a. Portland cement usually has 5% gypsum (or calcium sulfate hydrate) added. This gypsum is critical to having the cement hydrate in a timely fashion. If the gypsum were not present, the tricalcium aluminates (C_3A) would hydrate in just a few minutes (chemical reaction #3 on the previous slide) causing the cement to set very quickly. This is not desirable, since the fresh paste needs to remain fluid for at least a few hours. When there is gypsum in the mix, the tricalcium aluminates react with the gypsum and water to form ettringite (reaction #4) which builds up as a layer on the C_3A particles and prevents rapid hydration. Once the gypsum is depleted, then the tricalcium aluminate reacts with *ettringite* and water to form the stable hydration product monosuloaluminate (reaction #5). If one takes the net of these three reactions, the overall reaction is as follows:

$$C_3A + C\hat{S}H_2 + 10H \rightarrow C_4A\hat{S}H_{12} \qquad (\Delta\mathrm{H} = \text{-}350\mathrm{J/g})$$

b. The chemical hydration reactions of the four main cement compounds occur at different rates, and contribute differently to the overall strength of the hcp as shown in Fig. 9.1. Most of the strength comes from the hydration of alite and belite, with most of the early strength coming from the alite, and the later strength development (after 30 days) coming from the belite. Both the tricalcium aluminate and the tetracalcium aluminoferrite contribute relatively small amounts to the final strength of the hcp.

c. As the hydration process progresses, the cement paste properties evolve from those of a viscous fluid to those of a solid material. Fig. 9.2 provides a schematic of the hydration process that helps to explain this transition. The initial setting of the paste occurs when the hydration products first form a continuous matrix rather than isolated islands as shown in Fig. 9.2b.

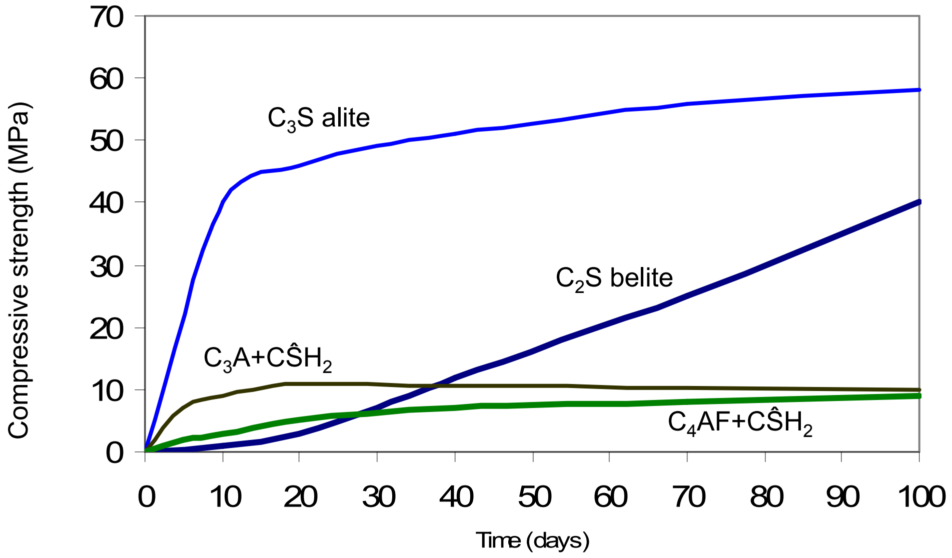


Fig. 9.1. Strength development over time as the four main compounds of portland cement hydrate. (Adapted from S. Mindess and J.F. Young, Concrete, Prentice Hall, 1981, Fig. 3.4, p.29)

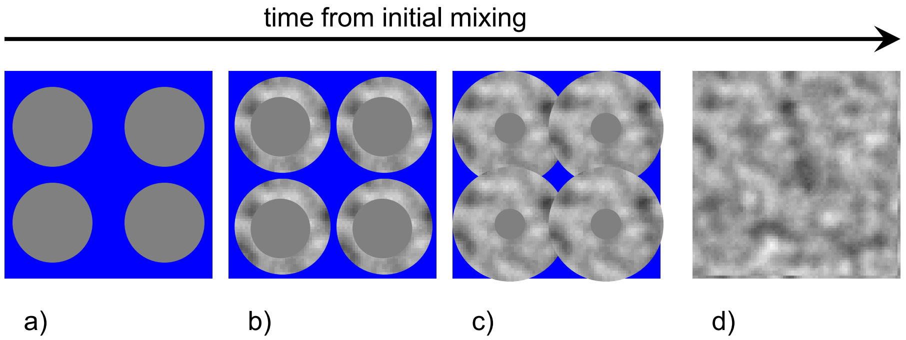


Fig. 9.2. Schematic showing time progression of hydration process. a) grey cement particles suspended in mix-water (blue) before start of hydration; b) hydration products begin to grow outward from the cement particles; c) hydration products form a solid matrix, although hydration is not yet complete; d) hydration products with no residual mix water and no unhydrated cement.

D. PRODUCTS OF HYDRATION

If one looks closely at hydrated cement paste, one will typically see all of the following:

1. *Capillary pores* ranging from microns to millimeters in size containing mix water that did not participate in the hydration reaction;
2. *Gel products* which are the hydrated calcium silicates, the hydrated aluminates, and the hydrated ferrites. Water molecules are bonded to these foil-like particles via hydrogen-bonding. The gel products also have some pores, but these typically are much smaller than the capillary pores, ranging from nanometers to microns in size.
3. *Unhydrated cement* particles may remain in the hcp if not all of the cement in the mix hydrated.
4. *Calcium hydroxide* crystals may also reside in the hcp as an additional hydration product.

A schematic of the microstructure of hcp with these three phases is shown below in Fig. 9.3.

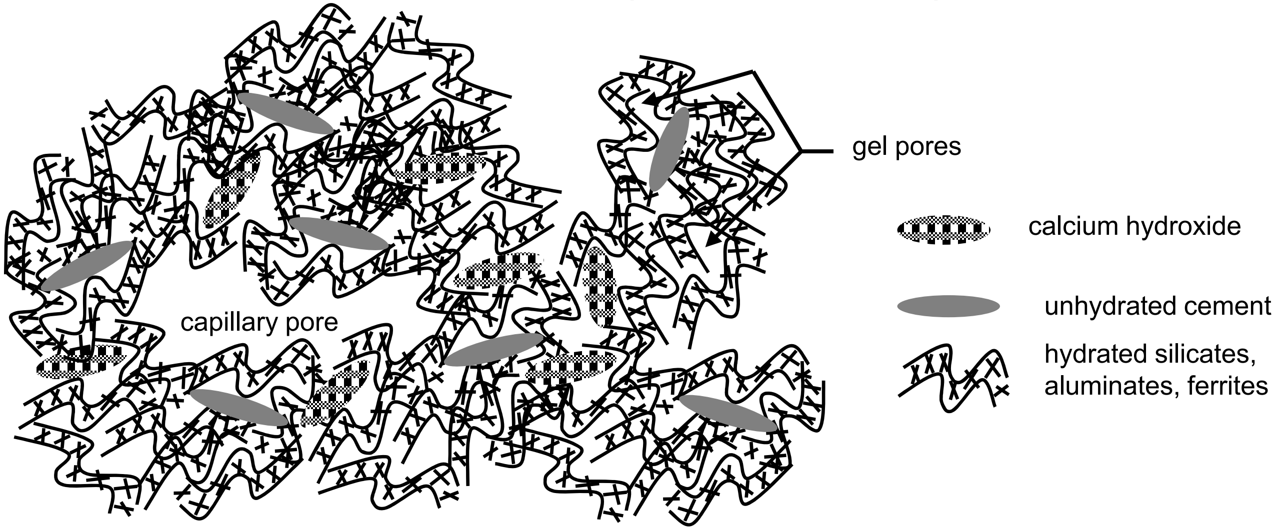


Fig. 9.3. Sketch of hcp microstructure showing the gel and capillary pores, the unhydrated cement, the calcium hydroxide, and the hydrated silicates, aluminates, and ferrites.

E. Quantitative Analysis of Hydration

In the following, we will look at the composition of hcp based on the ratio of water mass to cement mass in the initial mix. While the discussion is strictly valid for Type I portland cement, the same principles also apply to other types as well.

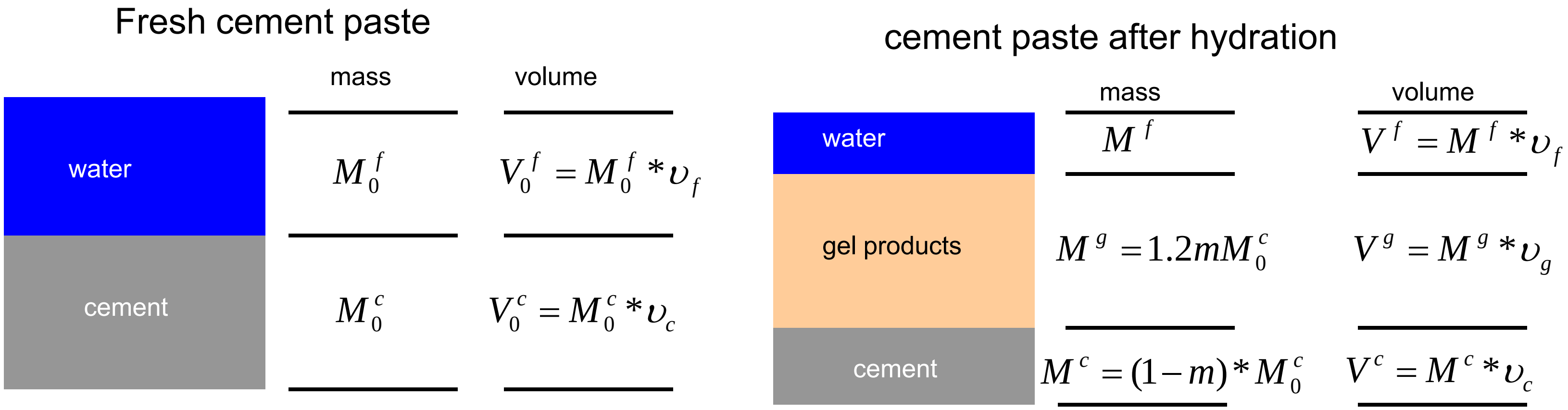
First, some basic facts about portland cement hydration:

1) representative mass densities and specific volumes of water, cement particles, and gel products are provided below in Table 9.2
2) It takes 0.2 grams of water to hydrate 1.0 gram of portland cement.
3) The porosity of the gel products is 0.276 or 27.6%, and these tend to be very small pores.
4) If cement hydrates under "wet conditions" then water enters the mix during the hydration process.
5) If cement hydrates under "sealed conditions" then no water enters or leaves the mix during hydration.
6) For a given mixture of cement and water, it is generally true that only a fraction of the cement will actually hydrate. The fraction that hydrates is here denoted by the term $m \in [0,1]$. The fraction of cement that does not hydrate is obviously 1-m.
7) The hydration process is, to first order, volume preserving. That is, the total volume of the fresh paste before and after hydration are the same.

Table 9.2. Physical properties of cement and hcp constituents.

Phase	Mass density (g/cm^3)	Specific volume (cm^3/g)
Mix water	ρ_f=1.00	υ_f=1.00
Cement particles	ρ_c=3.17	υ_c=.315
Gel products	ρ_g=1.76	υ_g=.568

When considering the composition of fresh cement paste and then hydrated cement paste (hcp), block diagrams such the one in Fig. 9.4 can be helpful.



$$M_0^f \qquad V_0^f = M_0^f * \upsilon_f$$

$$M_0^c \qquad V_0^c = M_0^c * \upsilon_c$$

$$M^f \qquad V^f = M^f * \upsilon_f$$

$$M^g = 1.2mM_0^c \qquad V^g = M^g * \upsilon_g$$

$$M^c = (1-m) * M_0^c \qquad V^c = M^c * \upsilon_c$$

Fig. 9.4. Block diagrams of cement paste before and after hydration.

In the fresh cement paste before any hydration occurs, the total volume can be expressed as follows:

$$\begin{aligned} V &= V^f + V^c \\ &= \mathrm{M}_0^{\mathrm{f}} * \upsilon_f + M_0^c * \upsilon_c \\ &= M_0^c * \left(\frac{\mathrm{M}_0^{\mathrm{f}}}{M_0^c} \upsilon_f + \upsilon_c \right) \end{aligned}$$

In the preceding, the quantity $\left(M_0^f / M_0^c\right)$ is the “water-cement ratio” in the fresh paste. This is a very important parameter in proportioning concrete mixes and in determining the final strength of the hcp.

Example 9.1: Determine the mass and volume composition of 1 cm^3 of fresh cement paste that has a mass water to cement ratio of 0.1.

Solution:
$$1cm^3 = V = M_0^c * \left(\frac{M_0^f}{M_0^c} \upsilon_f + \upsilon_c \right)$$
$$= M_0^c * \left(0.1 * 1.00 cm^3 g^{-1} + .315 cm^3 g^{-1}\right)$$
$$= .415\, cm^3 g^{-1} * M_0^c$$

Solving for M_0^c and then V_0^c yields:

$$M_0^c = \frac{1cm^3}{.415\, cm^3 g^{-1}} = 2.41g \quad \Rightarrow \quad V_0^c = M_0^c * \upsilon_c = 2.41g * .315 cm^3 g^{-1} = .759 cm^3$$

Due to the water-cement ratio of 0.1, the mass and volume of the water in the fresh paste can also be determined:

$$M_0^f = 0.1 * M_0^c = .241g \quad \Rightarrow \quad V_0^f = M_0^f * \upsilon_f = .241g * 1.00 cm^3 g^{-1} = .241 cm^3$$

Summary:
$$\boxed{\begin{array}{l} M_0^f = .241g\,; \quad M_0^c = 2.41g\,; \quad \text{Total mass } \ \mathrm{M} = 2.651\mathrm{g} \\ V_0^f = .241 cm^3; \quad V_0^c = .759 cm^3; \ \text{Total volume } \mathrm{V} = 1.000\, cm^3 \end{array}}$$

There are two factors that limit the hydration process: (1) the amount of water available in the mix; and (2) the amount of cement in the mix. Knowing that these are the limiting factors, we can solve for the volumetric and mass composition of hcp

We begin by assuming that the hydration reaction is limited by the amount of water so that when the paste runs out of water, hydration stops.

The volume of water in the paste, after hydration has begun is: $V_f = V - V_c - V_g$ Since the volume of the paste after hydration is the same as that before, the volume of water in the paste is:

$$\begin{aligned} V_f &= V_0 - V_c - V_g \\ &= \mathrm{M}_0^{\mathrm{c}} \left(\frac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f + \upsilon_c \right) - (1-m)\mathrm{M}_0^{\mathrm{c}} * \upsilon_c - 1.2m\mathrm{M}_0^{\mathrm{c}} * \upsilon_g \end{aligned}$$

The volume of the water can never be less than zero, so:

$$0 \le \mathrm{M}_0^{\mathrm{c}} \left(\frac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f + \upsilon_c \right) - (1-m)\mathrm{M}_0^{\mathrm{c}} * \upsilon_c - 1.2m\mathrm{M}_0^{\mathrm{c}} * \upsilon_g$$

This inequality can be solved for the maximum degree of cement hydration as follows:

$$\begin{aligned} 0 &\le \left(\frac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f + \upsilon_c \right) - (1-m) * \upsilon_c - 1.2m * \upsilon_g \\ &\le \frac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f - m(1.2\upsilon_g - \upsilon_c) \end{aligned}$$

$$\boxed{m \le \frac{\dfrac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f}{(1.2\upsilon_g - \upsilon_c)} = m_{\max} \le 1}$$

For wet curing conditions

Example 9.2: For the 1 cubic centimeter of paste from Example 9.1, determine the composition of the hydrated cement paste:

Solution:

$$\text{Let } m = m_{\max} = \frac{\frac{M_0^f}{M_0^c} * \upsilon_f}{(1.2\upsilon_g - \upsilon_c)} = \frac{0.1}{1.2*.568-.315} = 0.273$$

$$M^c = (1-m)M_0^c = .727*2.41g = 1.753g = \text{mass of unhydrated cement}$$

$$V^c = M^c * \upsilon_c = 1.753g*0.315cm^3g^{-1} = .552cm^3 = \text{volume of unhydrated cement}$$

$$M^g = 1.2mM_0^c = 1.2*.273*2.41g = .789g = \text{mass of gel products}$$

$$V^g = M^g * \upsilon_g = .789g*.568cm^3g^{-1} = .448cm^3 = \text{volume of gel products}$$

$$\text{Mass of water in pores of gel} = 0.275*\mathrm{V}^g*\rho_f = .123g$$

$$\text{Total mass of final product} = 1.753\text{g} + .789\text{g} + .123\text{g} = 2.665\text{g}$$

Observe that in example 9.2 the final mass of the cement paste at 2.665g is slightly larger than the initial mass of the fresh cement paste at 2.651g.

The preceding analysis assumed wet curing conditions, so that a small amount of water could enter the mix to saturate the pores in the gel product.

Under sealed curing conditions, water cannot enter the paste during hydration. Accordingly, water that partially saturates the gel pores comes from the mix water. Typically, the gel pores are about 25% saturated. Accordingly, the volume of water from the mix that partially saturates the gel pores is

$$V_{water}^{gel} = M^g * \upsilon_g * .273 * 0.25 = mM_0^C * \upsilon_g * .0819$$

If this is taken into account, then the volume of mix water in the fresh paste is:

$$V_f = V_0 - V_c - V_g - V_{water}^{gel}$$

$$= \mathrm{M}_0^{\mathrm{c}}\left(\frac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f + \upsilon_c\right) - (1-m)\mathrm{M}_0^{\mathrm{c}} * \upsilon_c - 1.2m\mathrm{M}_0^{\mathrm{c}} * \upsilon_g - mM_0^C * \upsilon_g * .0819$$

As before, the volume of mix-water in the fresh paste cannot be negative. Accordingly:

$$0 \le \mathrm{M}_0^{\mathrm{c}}\left(\frac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f + \upsilon_c\right) - (1-m)\mathrm{M}_0^{\mathrm{c}} * \upsilon_c - 1.2m\mathrm{M}_0^{\mathrm{c}} * \upsilon_g - mM_0^C * \upsilon_g * .0819$$

Solving for the maximum degree of hydration gives:

$$0 \le \frac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f + m * (\upsilon_c - 1.282 * \upsilon_g)$$

$$\boxed{m \le \frac{\frac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f}{1.282\upsilon_g - \upsilon_c} = m_{\max} \le 1 \quad \underline{\textbf{For sealed curing conditions}}}$$

<u>Example 9.3</u>: For the fresh paste of Example 9.1, compute the composition of the hcp if cured under sealed conditions.

$$\text{Let m} = \mathrm{m}_{\max} = \frac{\frac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f}{1.282\upsilon_g - \upsilon_c} = \frac{0.1}{1.282 * .568 - .315} = 0.242$$

$$M^c = (1-m)M_0^c = .758 * 2.41g = 1.827g = \text{mass of unhydrated cement}$$

$$V^c = M^c * \upsilon_c = 1.827g * 0.315cm^3 g^{-1} = .575cm^3 = \text{volume of unhydrated cement}$$

$$M^g = 1.2mM_0^c = 1.2 * .242 * 2.41g = .700g = \text{mass of gel products}$$

$$V^g = M^g * \upsilon_g = .700g * .568cm^3 g^{-1} = .398cm^3 = \text{volume of gel products}$$

$$\text{Mass of water in pores of gel} = 0.275 * .25 * \text{V}^g * \rho_f = .0274g$$

$$\text{Capillary pore volume} = \text{V - V}^c - V^g. = 1.000cm^3 - .575cm^3 \text{ - } .398cm^3 = .027cm^3$$

Summary for sealed curing conditions

Unhydrated cement	V^c=.575cm^3
Gel products	V^g=.398cm^3
Capillary pores	V^{cap}=.027cm^3

End of Example 9.3//

Examples 9.2 and 9.3 indicate that we can compute/estimate the volumetric composition of the hcp based on the water-cement ratio and the curing conditions, either sealed or wet.

The capillary pores in the hcp are fairly large, and thus serve as defects that weaken the hcp. (Recall the Griffith Microcrack model in the Period #3 notes which indicated that the tensile strengths of ceramic materials $\sigma_{ult} \propto a^{-\frac{1}{2}}$. In hcp, the capillary pores are void-like defects that weaken the material. The larger the capillary pores are, the weaker the hcp will be.

Example 9.4: For a cement paste with an initial water-cement ratio of 0.5, calculate the volumetric composition of the hcp under both wet and sealed curing conditions.

Solution: From slide 9.12:

$$1cm^3 = V = M_0^c * \left(\frac{\mathrm{M}_0^{\mathrm{f}}}{M_0^c} \upsilon_f + \upsilon_c \right)$$

$$= M_0^c * \left(0.5 * 1.00 cm^3 g^{-1} + .315 cm^3 g^{-1}\right)$$

$$= .815\, cm^3 g^{-1} * M_0^c$$

$$M_0^c = \frac{1cm^3}{.815\, cm^3 g^{-1}} = 1.227g; \quad \Rightarrow \quad M_0^f = 0.5 * M_0^c = .6135g$$

For wet curing conditions:

$$\text{Let } \mathrm{m} = m_{\max} = \frac{\frac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f}{\left(1.2\upsilon_g - \upsilon_c\right)} = \frac{0.5}{1.2 * .568 - .315} = 1.364 \Rightarrow 1$$

$$M^c = (1-m)M_0^c = 0 = \text{mass of unhydrated cement}$$

$$V^c = M^c * \upsilon_c = 0cm^3 = \text{volume of unhydrated cement}$$

$$M^g = 1.2mM_0^c = 1.2 * 1.227g = 1.472g = \text{mass of gel products}$$

$$V^g = M^g * \upsilon_g = 1.472g * .568cm^3 g^{-1} = .836cm^3 = \text{volume of gel products}$$

$$V^{cap} = V - V^c - V^g = .164cm^3 = \text{volume of capillary pores}$$

For sealed curing conditions:

$$\text{Let }\ \mathrm{m} = m_{\max} = \frac{\dfrac{\mathrm{M}_0^{\mathrm{f}}}{\mathrm{M}_0^{\mathrm{c}}} * \upsilon_f}{\left(1.282\upsilon_g - \upsilon_c\right)} = \frac{0.5}{1.282 * .568 - .315} = 1.21 \Rightarrow 1$$

$$M^c = (1-m)M_0^c = 0 = \text{mass of unhydrated cement}$$

$$V^c = M^c * \upsilon_c = 0cm^3 = \text{volume of unhydrated cement}$$

$$M^g = 1.2mM_0^c = 1.2 * 1.227g = 1.472g = \text{mass of gel products}$$

$$V^g = M^g * \upsilon_g = 1.472g * .568cm^3g^{-1} = .836cm^3 = \text{volume of gel products}$$

$$V^{cap} = V - V^c - V^g = .164cm^3 = \text{volume of capillary pores}$$

So, with a water-cement ratio of 0.5, the predicted composition of the hcp is the same under both wet and sealed curing conditions, with a capillary porosity of 16.4%.

End of Example 9.4//

If the volumetric composition of hcp is computed under wet and sealed curing conditions for all water-cement ratios on the interval [0,1], the plots of Fig. 9.5 are the result.

- Under wet curing conditions capillary porosity begins to develop only for water-cement ratios above about 0.37.
- For sealed curing conditions, capillary porosity develops even at low water-cement ratios.
- For increasing water-cement ratios above about 0.4, the capillary porosity increases, and this generally weakens the hcp.

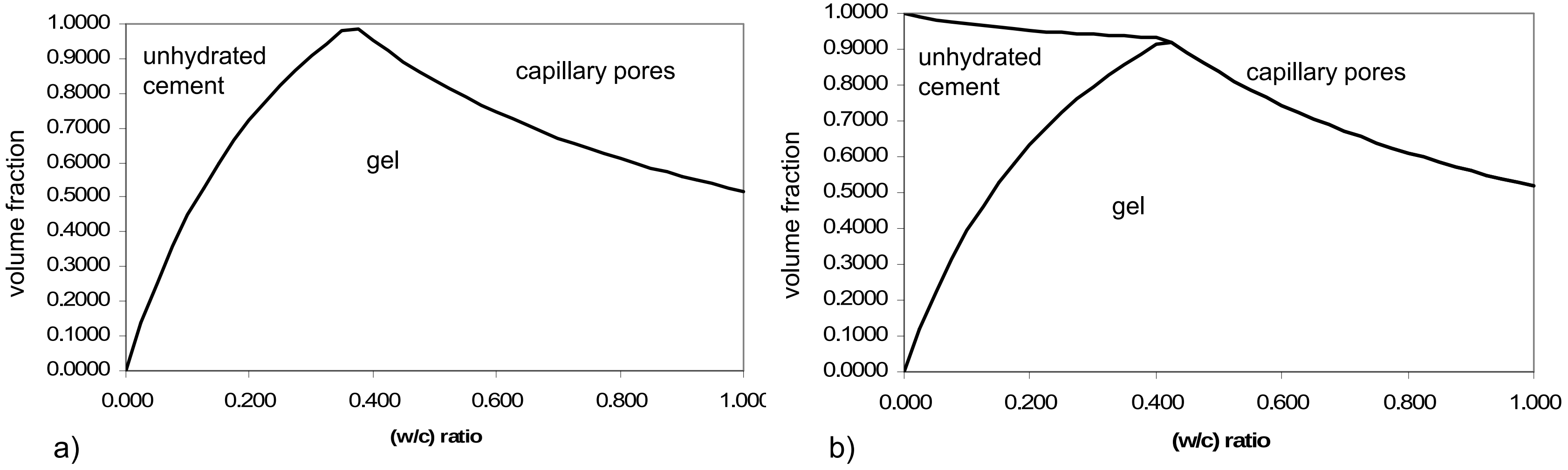


Fig. 9.5. Volumetric composition of hcp under a) wet curing conditions; and b) sealed curing conditions.