6

PORTLAND CEMENT

Portland cement concrete is the most widely used manufactured construction material in the world. The importance of concrete in our daily lives cannot be overstated. It is used in structures such as buildings, bridges, tunnels, dams, factories, pavements, and playgrounds. Portland cement concrete consists of portland cement, aggregates, water, air voids, and, in many cases, admixtures. This chapter covers the topics of portland cement, mixing water, and admixtures; Chapter 7 will describe portland cement concrete.

There are many types of concrete, based on different cements. However, portland cement concrete is so prevalent that, unless otherwise identified, the term concrete is always assumed to mean portland cement concrete. Portland cement was patented by Joseph Aspdin in 1824 and was named after the limestone cliffs on the Isle of Portland in England (Kosmatka et al. 2002).

Portland cement is an instant glue (just add water) that bonds aggregates together to make portland cement concrete. Materials specialists concerned with the selection, specification, and quality control of civil engineering projects should understand the production, chemical composition, hydration rates, and physical properties of portland cement.

6.1 Portland Cement Production

Production of portland cement starts with two basic raw ingredients: a calcareous material and an argillaceous material. The calcareous material is a calcium oxide, such as limestone, chalk, or oyster shells. The argillaceous material is a combination of silica and alumina that can be obtained from clay, shale, and blast furnace slag. As shown in Figure 6.1, these materials are crushed and then stored in silos. The raw materials, in the desired proportions, are passed through a grinding mill, using either a wet or dry process. The ground material is stored until it can be sent to the kiln. Modern dry process cement plants use a heat recovery cycle to preheat the ground material, or feed

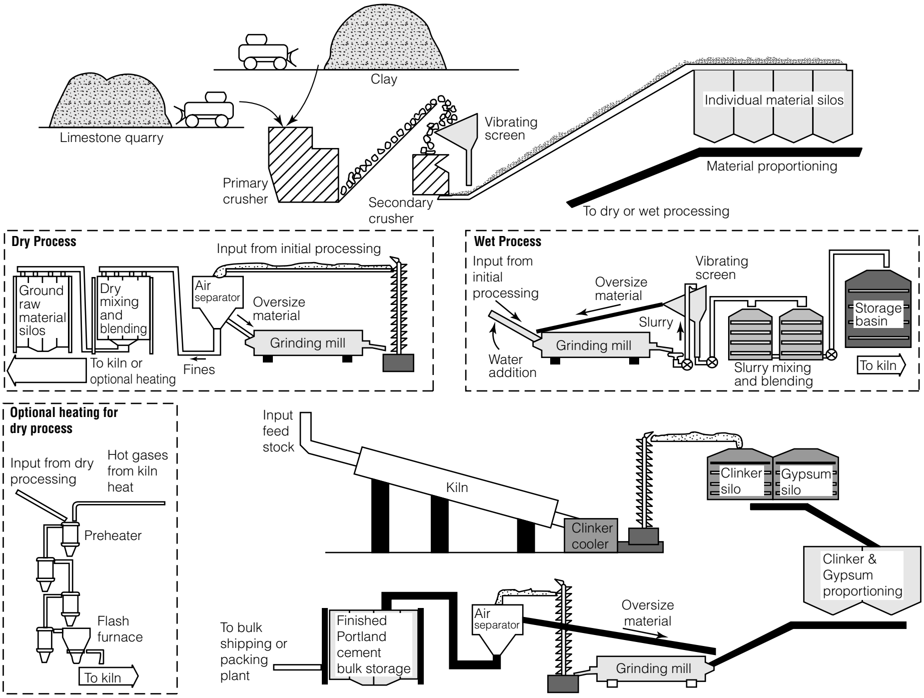


FIGURE 6.1 Steps in the manufacture of portland cement.

stock, with the exhaust gas from the kiln. In addition, some plants use a flash furnace to further heat the feed stock. Both the preheater and flash furnace improve the energy efficiency of cement production. In the kiln, the raw materials are melted at temperatures of 1400°C to 1650°C (2500°F to 3000°F), changing the raw materials into cement *clinker.* The clinker is cooled and stored. The final process involves grinding the clinker into a fine powder. During grinding, a small amount of gypsum is added to regulate the setting time of the cement in the concrete.

The finished product may be stored and transported in either bulk or sacks. In the United States, a standard *sack* of cement is 94 lb, which is approximately equal to 1 ft^3 of loose cement when freshly packed. The cement can be stored for long periods of time, provided it is kept dry.

6.2 Chemical Composition of Portland Cement

The raw materials used to manufacture portland cement are lime, silica, alumina, and iron oxide. These raw materials interact in the kiln, forming

TABLE 6.1 Main Compounds of Portland Cement.

Compound	Chemical Formula	Common Formula*	Usual Range by Weight (%)
Tricalcium Silicate	$3\ CaO \cdot SiO_2$	C_3S	45–60
Dicalcium Silicate	$2\ CaO \cdot SiO_2$	C_2S	15–30
Tricalcium Aluminate	$3\ CaO \cdot Al_2O_3$	C_3A	6–12
Tetracalcium Aluminoferrite	$4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	6–8

* The cement industry commonly uses shorthand notation for chemical formulas: C = Calcium oxide, S = silicon dioxide, A = Aluminum oxide, and F = Iron oxide.

complex chemical compounds. *Calcination* in the kiln restructures the molecular composition, producing four main compounds, as shown in Table 6.1.

C_3S and C_2S, when hydrated, provide the desired characteristics of the concrete. Alumina and iron, which produce C_3A and C_4AF, are included with the other raw materials to reduce the temperature required to produce C_3S from 2000°C to 1350°C (3500°F to 2500°F). This saves energy and reduces the cost of producing the portland cement.

In addition to these main compounds, there are minor compounds, such as magnesium oxide, titanium oxide, manganese oxide, sodium oxide, and potassium oxide. These minor compounds represent a few percent by weight of cement. The term minor compounds refers to their quantity and not to their importance. In fact, two of the minor compounds, sodium oxide (Na_2O) and potassium oxide (K_2O), are known as alkalis. These alkalis react with some aggregates causing the disintegration of concrete and affecting the rate of strength development, as discussed in Chapter 5.

6.3 Fineness of Portland Cement

Fineness of cement particles is an important property that must be carefully controlled. Since hydration starts at the surface of cement particles, the finer the cement particles, the larger the surface area and the faster the hydration. Therefore, finer material results in faster strength development and a greater initial heat of hydration. Increasing fineness beyond the requirements for a type of cement increases production costs and can be detrimental to the quality of the concrete.

The maximum size of the cement particles is 0.09 mm (0.0035 in.); 85% to 95% of the particles are smaller than 0.045 mm (0.0018 in.), and the average diameter is 0.01 mm (0.0004 in.). (For reference, a number 200 sieve

FIGURE 6.2 Blaine air permeability apparatus.

passes material smaller than 0.075 mm.) A kilogram of portland cement has approximately 7 trillion particles with a total surface area of about 300 m^2 to 400 m^2 (1500 ft^2 to 2000 ft^2 per pound). The total surface area per unit weight is a function of the size of the particles and is more readily measured. Thus, particle size specifications are defined in terms of the surface area per unit weight.

Fineness of cement is usually measured indirectly by measuring the surface area with the Blaine air permeability apparatus (ASTM C204) or the Wagner turbidimeter apparatus (ASTM C115). In the Blaine test (Figure 6.2), the surface area of the cement particles in cm^2/g is determined by measuring the air permeability of a cement sample and relating it to the air permeability of a standard material. The Wagner turbidimeter determines the surface area by measuring the rate of sedimentation of cement suspended in kerosene. The finer the cement particles, the slower the sedimentation. Both the Blaine and Wagner tests are indirect measurements of surface area and use somewhat different measurement principles. Therefore, tests on a single sample of cement will produce different results. Fineness can also be measured by determining the percent passing the 0.045 mm sieve (No. 325) (ASTM C430).

6.4 Specific Gravity of Portland Cement

The specific gravity of cement is needed for mixture proportioning calculations. The specific gravity of portland cement (without voids between particles) is about 3.15 and can be determined according to ASTM C188. The density of the bulk cement (including voids between particles) varies considerably, depending on how it is handled and stored. For example, vibration during transportation of bulk cement consolidates the cement and increases its bulk density. Thus, cement quantities are specified and measured by weight rather than volume.

6.5 Hydration of Portland Cement

Hydration is the chemical reaction between the cement particles and water. The features of this reaction are the change in matter, the change in energy level, and the rate of reaction. The primary chemical reactions are shown in Table 6.2. Since portland cement is composed of several compounds, many reactions are occurring concurrently.

The hydration process occurs through two mechanisms: through-solution and topochemical. The through-solution process involves the following steps (Mehta and Monteiro 1993):

1. dissolution of anhydrous compounds into constituents
2. formation of hydrates in solution
3. precipitation of hydrates from the supersaturated solution

The through-solution mechanism dominates the early stages of hydration. Topochemical hydration is a solid-state chemical reaction occurring at the surface of the cement particles.

The aluminates hydrate much faster than the silicates. The reaction of tricalcium aluminate with water is immediate and liberates large amounts of heat. Gypsum is used to slow down the rate of aluminate hydration. The gypsum goes into the solution quickly, producing sulfate ions that suppress the solubility of the aluminates. The balance of aluminate to sulfate determines the rate of *setting* (solidification). Cement paste that sets at a normal rate requires low concentrations of both aluminate and sulfate ions. The cement paste will remain workable for about 45 minutes; thereafter, the paste starts to stiffen as crystals displace the water in the pores. The paste begins to solidify within 2 to 4 hours after the water is added to the cement. If there is an excess of both aluminate and sulfate ions, the workability stage may only last for 10 minutes and setting may occur in 1 to 2 hours. If the availability of aluminate ions is high, and sulfates are low, either a *quick set* (10 to 45 minutes) or *flash set* (less than 10 minutes) can occur. Finally, if the aluminate ions availability is low and the sulfate ions availability is high, the gypsum can recrystalize in the pores within 10 minutes, producing a flash set. Flash set is associated with large heat evolution and poor ultimate strength (Mehta and Monteiro 1993).

Calcium silicates combine with water to form calcium-silicate-hydrate, C-S-H. The crystals begin to form a few hours after the water and cement are mixed and can be developed continuously as long as there are unreacted cement particles and free water. C-S-H is not a well-defined compound. The calcium-to-silicate ratio varies between 1.5 and 2.0, and the structurally combined water content is more variable.

As shown in Table 6.2, the silicate hydration produces both C-S-H and calcium hydroxide. Complete hydration of C_3S produces 61% C-S-H and 39% calcium hydroxide; hydration of C_2S results in 82% C-S-H and 18% calcium hydroxide. Since C-S-H is what makes the hydrated cement paste strong, the

TABLE 6.2 Primary Chemical Reactions During Cement Hydration

$2(3\ CaO \cdot SiO_2)$	+	$6\ H_2O$			=	$3\ CaO \cdot 2\ SiO_2 \cdot 3\ H_2O$	+	$3\ Ca(OH)_2$
Tricalcium silicate		Water				Calcium silicate hydrates		Calcium hydroxide
$2(2\ CaO \cdot SiO_2)$	+	$4\ H_2O$			=	$3\ CaO \cdot 2\ SiO_2 \cdot 3\ H_2O$	+	$Ca(OH)_2$
Dicalcium silicate		Water				Calcium silicate hydrates		Calcium hydroxide
$3\ CaO \cdot Al_2O_3$	+	$12\ H_2O$	+	$Ca(OH)_2$	=	$3\ CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12\ H_2O$		
Tricalcium aluminate		Water		Calcium hydroxide		Calcium aluminate hydrate		
$4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$	+	$10\ H_2O$	+	$2\ Ca(OH)_2$	=	$6\ CaO \cdot Al_2O_3 \cdot Fe_2O_3 \cdot 12\ H_2O$		
Tetracalcium aluminoferrite		Water		Calcium Hydroxide		Calcium aluminoferrite hydrate		
$3\ CaO \cdot Al_2O_3$	+	$10\ H_2O$	+	$CaSO_4 \cdot 2\ H_2O$	=	$3\ CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\ H_2O$		
Tricalcium aluminate		Water		Gypsum		Calcium monosulfoaluminate hydrate		

ultimate strength of the concrete is enhanced by increasing the content of C_2S relative to the amount of C_3S. Furthermore, calcium hydroxide is susceptible to attack by sulfate and acidic waters. Increasing the proportion of C_2S relative to C_3S reduces the quantity of calcium hydroxide and, therefore, improves the durability of the concrete.

C_3S hydrates more rapidly than C_2S, contributing to the final set time and early strength gain of the cement paste. The rate of hydration is accelerated by sulfate ions in solution. Thus, a secondary effect of the addition of gypsum to cement is to increase the rate of development of the C-S-H.

6.5.1 Structure Development in Cement Paste

The sequential development of the structure in a cement paste is summarized in Figure 6.3. The process begins immediately after water is added to the cement [Figure 6.3(a)]. In less than 10 minutes, the water becomes highly alkaline. As the cement particles hydrate, the volume of the cement particle reduces, increasing the space between the particles. During the early stages of hydration, weak bonds can form, particularly from the hydrated C_3A [Figure 6.3(b)]. Further hydration stiffens the mix and begins locking the structure of the material in place [Figure 6.3(c)]. Final set occurs when the C-S-H phase has developed a rigid structure, all components of the paste lock into place and the spacing between grains increases as the grains are consumed by hydration [Figure 6.3(d)]. The cement paste continues hardening and gains strength as hydration continues [Figure 6.3(e)]. Hardening develops rapidly at early ages and continues, as long as unhydrated cement particles and free water exist. However, the rate of hardening decreases with time.

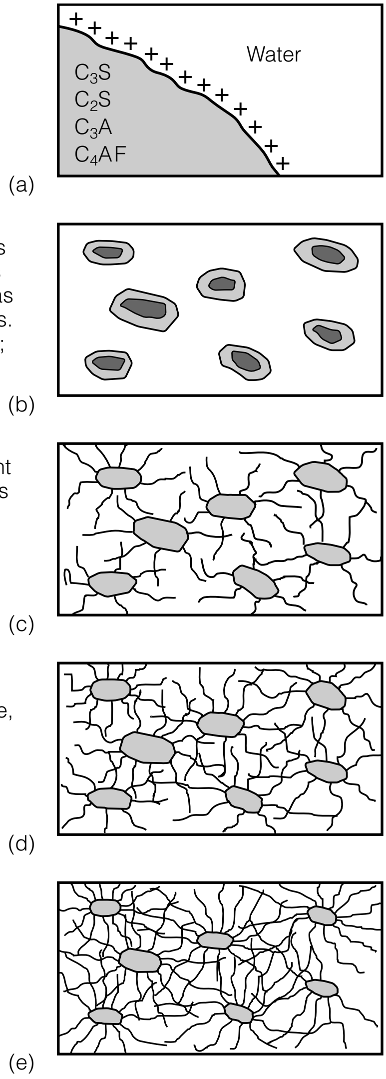
6.5.2 Evaluation of Hydration Progress

Several methods are available to evaluate the progress of cement hydration in hardened concrete. These include measuring the following properties (Neville 1981):

1. the heat of hydration
2. the amount of calcium hydroxide in the paste developed due to hydration
3. the specific gravity of the paste
4. the amount of chemically combined water
5. the amount of unhydrated cement paste using X-ray quantitative analysis
6. the strength of the hydrated paste, an indirect measurement

6.6 Voids in Hydrated Cement

Due to the random growth of the crystals and the different types of crystals, voids are left in the paste structure as the cement hydrates. Concrete strength, durability, and volume stability are greatly influenced by voids.



The C-S-H phase is initially formed. C_3A forms a gel fastest.

The volume of cement grain decreases as a gel forms at the surface. Cement grains are still able to move independently, but as hydration grows, weak interlocking begins. Part of the cement is in a thixotropic state; vibration can break the weak bonds.

The initial set occurs with the development of a weak skeleton in which cement grains are held in place.

Final set occurs as the skeleton becomes rigid, cement particles are locked in place, and spacing between cement grains increases due to the volume reduction of the grains.

Spaces between the cement grains are filled with hydration products as cement paste develops strength and durability.

FIGURE 6.3 Development of structure in the cement paste: (a) initial C-S-H phase, (b) forming of gels, (c) initial set--development of weak skeleton, (d) final set--development of rigid skeleton, (e) hardening (Hover and Phillco 1990).

Two types of voids are formed during hydration: the interlayer hydration space and capillary voids.

Interlayer hydration space occurs between the layers in the C-S-H. The space thickness is between 0.5 nm and 2.5 nm, which is too small to affect the strength. It can, however, contribute 28% to the porosity of the paste. Water in the interparticle space is strongly held by hydrogen bonds, but can be removed when humidity is less than 11%, resulting in considerable shrinkage.

Capillary voids are the result of the hydrated cement paste having a lower bulk specific gravity than the cement particles. The amount and size of capillary voids depends on the initial separation of the cement particles, which is largely controlled by the ratio of water to cement paste. For a highly hydrated cement paste in which a minimum amount of water was used, the capillary voids will be on the order of 10 nm to 50 nm. A poorly hydrated cement produced with excess water can have capillary voids on the order of 3 mm to 5 mm. Capillary voids greater than 50 nm decrease strength and increase permeability. Removal of water from capillary voids greater than 50 nm does not cause shrinkage, whereas removal of water from the smaller voids causes shrinkage.

In addition to the interlayer space and capillary voids, air can be trapped in the cement paste during mixing. The *trapped air* reduces strength and increases permeability. However, well-distributed, minute air bubbles can greatly increase the durability of the cement paste. Hence, as described later in this chapter, admixtures are widely used to *entrain air* into the cement paste.

6.7 Properties of Hydrated Cement

The proper hydration of portland cement is a fundamental quality control issue for cement producers. While specifications control the quality of the portland cement, they do not guarantee the quality of the concrete made with the cement. Mix design, quality control, and the characteristics of the mixing water and aggregates also influence the quality of the concrete. Properties of the hydrated cement are evaluated with either *cement paste* (water and cement) or *mortar* (paste and sand).

6.7.1 Setting

Setting refers to the stiffening of the cement paste or the change from a plastic state to a solid state. Although with setting comes some strength, it should be distinguished from *hardening,* which refers to the strength gain in a set cement paste. Setting is usually described by two levels: initial set and final set. The definitions of the initial and final sets are arbitrary, based on measurements by either the Vicat apparatus (ASTM C191) or the Gillmore needles (ASTM C266).

The Vicat test (Figure 6.4) requires that a sample of cement paste be prepared, using the amount of water required for normal consistency according to a specified procedure. The 1 mm (0.04 in.) diameter needle is allowed to penetrate the paste for 30 seconds and the amount of penetration is measured. The penetration process is repeated every 15 minutes (every 10 minutes for Type III cement) until a penetration of 25 mm (1 in.) or less is obtained. By interpolation, the time when a penetration of 25 mm occurs is

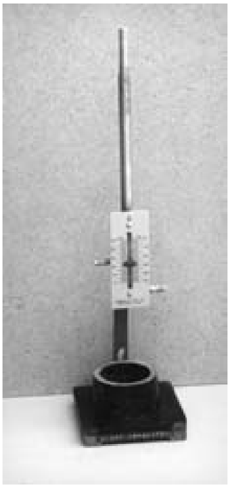


FIGURE 6.4 Vicat set time apparatus.

determined and recorded as the initial set time. The final set time is when the needle does not penetrate visibly into the paste.

Similar to the Vicat test, the Gillmore test (Figure 6.5) requires that a sample of cement paste of normal consistency be prepared. A pat with a flat top is molded and the initial Gillmore needle is applied lightly to its surface. The application process is repeated until the pat bears the force of the needle without appreciable indentation, and the elapsed time is recorded as the initial set time. This process is then repeated with the final Gillmore needle and the final set time is recorded. Due to the differences in the test apparatuses and procedures, the Vicat and Gillmore tests produce different results for a single sample of material.

The initial set time must allow for handling and placing the concrete before stiffening. The maximum final set time is specified and measured to ensure normal hydration. During cement manufacturing, gypsum is added to

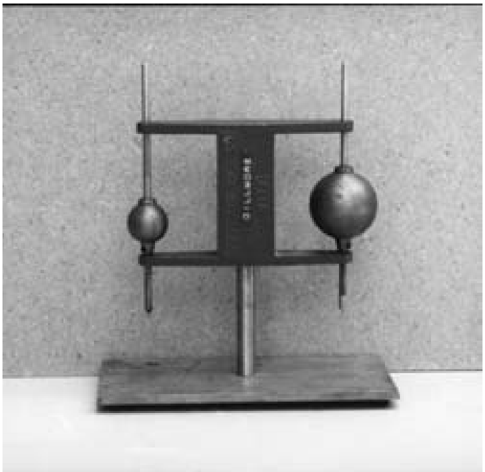


FIGURE 6.5 Gillmore set time apparatus.

regulate the setting time. Other factors that affect the set time include the fineness of the cement, the water–cement ratio, and the use of admixtures.

If the cement is exposed to humidity during storage, a *false set* might occur in which the cement stiffens within a few minutes of being mixed, without the evolution of much heat. To resolve this problem, the cement paste can be vigorously remixed, without adding water, in order to restore plasticity of the paste and to allow it to set in a normal manner without losing strength. A false set is different than a quick set and a flash set mentioned earlier; a false set can be remedied by remixing, whereas a quick set and a flash set cannot be remedied.

6.7.2 Soundness

Soundness of the cement paste refers to its ability to retain its volume after setting. Expansion after setting, caused by delayed or slow hydration or other reactions, could result if the cement is unsound. The autoclave expansion test (Figure 6.6) (ASTM C151) is used to check the soundness of the cement paste. In this test, cement paste bars are subjected to heat and high pressure, and the amount of expansion is measured. ASTM C150 limits autoclave expansion to 0.8%.

FIGURE 6.6 Cement autoclave expansion apparatus.

6.7.3 Compressive Strength

Compressive strength of mortar is measured by preparing 50-mm (2 in.) cubes and subjecting them to compression according to ASTM C109. The mortar is prepared with cement, water, and standard sand (ASTM C778). Minimum compressive strength values are specified by ASTM C150 for different cement types at different ages. The compressive strength of mortar cubes is proportional to the compressive strength of concrete cylinders. However, the compressive strength of the concrete cannot be predicted accurately from mortar cube strength, since the concrete strength is also affected by the aggregate characteristics, the concrete mixing, and the construction procedures.

6.8 Water–Cementitious Materials Ratio

In 1918, Abrams found that the ratio of the weight of water to the weight of cement, *water–cement ratio,* influences all the desirable qualities of concrete. For fully compacted concrete made with sound and clean aggregates, strength and other desirable properties are improved by reducing the weight of water used per unit weight of cement. This concept is frequently identified as Abrams's law.

Supplementary cementitious materials, such as fly ash, slag, silica fume, and natural pozzolans, have been used as admixtures in recent years to alter some of the properties of portland cement concrete. Therefore, the term water–cement ratio has been expanded to *water–cementitious materials ratio* to include these cementitious materials.

Hydration requires approximately 0.22 kg to 0.25 kg of water per 1 kg of cement. Concrete mixes generally require excess moisture, beyond the hydration needs, for workability. Excess water causes the development of capillary voids in the concrete. These voids increase the porosity and permeability of the concrete and reduce strength. Figure 6.7 shows a typical relationship between the water–cementitious materials ratio and compressive strength. It is easy to see that increasing the water–cementitious materials ratio decreases the compressive strength of the concrete for various curing times. A low water–cementitious materials ratio also increases resistance to weathering, provides a good bond between successive concrete layers, provides a good bond between concrete and steel reinforcement, and limits volume change due to wetting and drying. Air-entrained concrete includes an air entraining agent, an admixture, which is used to increase the concrete's resistance to freezing and thawing, as will be discussed later in this chapter. Curing maintains satisfactory moisture content and temperature in the hardened concrete for a definite period of time to allow for hydration (see Chapter 7).

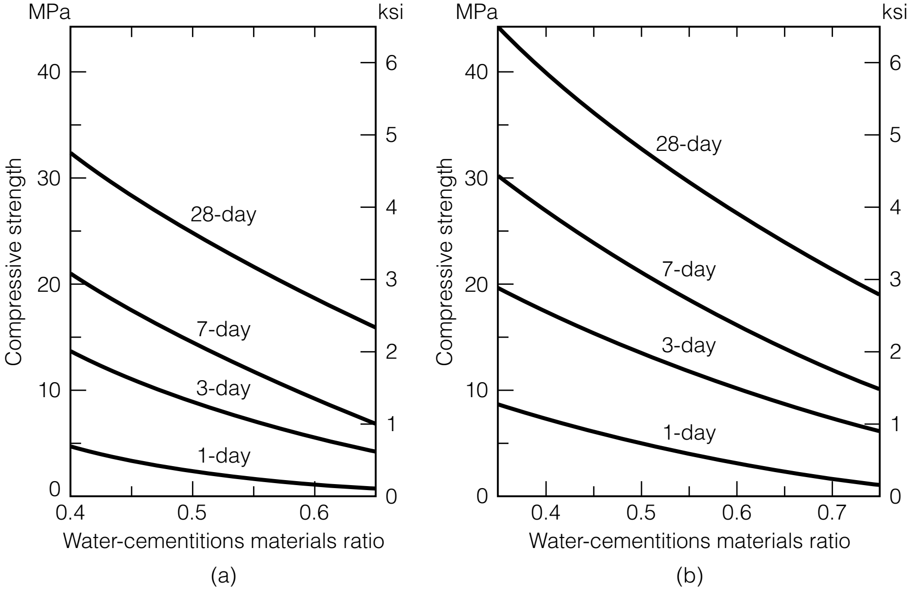


FIGURE 6.7 Typical age-strength relationships of concrete based on compression tests of 0.15 x 0.30 m (6 x 12 in.) cylinders, using Type I portland cement and moist-curing at 21C (70F): (a) air entrained concrete, (b) non-air entrained concrete (Kosmatka et al. 1988).

6.9 Types of Portland Cement

Different concrete applications require cements with different properties. Some applications require rapid strength gain to expedite the construction process. Other applications require a low heat of hydration to control volume change and associated shrinkage cracking. In some cases, the concrete is exposed to sulfates (SO_4), which can deteriorate normal portland cement concrete. Fortunately, these situations can be accommodated by varying the raw materials used to produce the cement, thereby altering the ratios of the four main compounds of portland cement listed in Table 6.1. The rate of hydration can also be altered by varying the fineness of the cement produced in the final grinding mill. Cement is classified to five standard types, as well as other special types.

6.9.1 Standard Portland Cement Types

Table 6.3 describes the five standard types of portland cement (Types I through V) specified by ASTM C150. In addition to these five types, air entrainers can be added to Type I, II, and III cements during manufacturing,

TABLE 6.3 Types and Applications of Standard Portland Cement

Type	Name	Application
I	Normal	General concrete work when the special properties of other types are not needed. Suitable for floors, reinforced concrete structures, pavements, etc.
II	Moderate Sulfate Resistance	Protection against moderate sulfate exposure, 0.1–0.2% weight water soluble sulfate in soil or 150–1500 ppm sulfate in water (sea water). Can be specified with a moderate heat of hydration, making it suitable for large piers, heavy abutments, and retaining walls. The moderate heat of hydration is also beneficial when placing concrete in warm weather.
III	High Early Strength	Used for fast-track construction when forms need to be removed as soon as possible or structure needs to be put in service as soon as possible. In cold weather, reduces time required for controlled curing.
IV	Low Heat of Hydration	Used when mass of structure, such as large dams, requires careful control of the heat of hydration.
V	High Sulfate Resistance	Protection from severe sulfate exposure, 0.2–2.0% weight water soluble sulfate in soils or 1500–10,800 ppm sulfate in water.

producing Types IA, IIA, and IIIA, which provide better resistance to freeze and thaw than do non–air-entrained cements. The use of air-entrained cements (Types IA, IIA, and IIIA) has diminished, due to improved availability and reliability of the air entrainer admixtures that can be added during concrete mixing. The uses and effects of air entrainers will be described in the section on admixtures. The ASTM specifications of the standard cement types are shown in Table 6.4.

The allowable maximum compound compositions are given in Table 6.5, along with the required Blaine fineness (controls particle size). Note that the chemical compositions of Type I and III cements are almost identical; the primary difference is the much greater surface area of the Type III cement. The C_3A contents of Type II and V cements are lower than that of Type I to improve sulfate resistance. C_3S and C_3A are limited in Type IV cement to limit the rate of hydration.

The existence of an ASTM specification for a type of cement does not guarantee that cement's availability. Type I cement is widely available and represents most of the United States' cement production. Type II is the second most available type. Cements can be manufactured that meet all the requirements of both Types I and II; these are labeled Type I/II. Type III cement represents about 4% of U.S. production. Due to the stricter grinding requirements for Type III, it is more expensive than Type I. The strength

TABLE 6.4 Standard Properties of Portland Cement (ASTM C150) (Copyright ASTM, reprinted with permission)

Cement Type	I	IA	II	IIA	III	IIIA	IV	V
Air content of mortar[A], volume %								
max.	12	22	12	22	12	22	12	12
min.	—	16	—	16	—	16	—	—
Fineness[B], specific surface, m^2/kg (alternative methods)								
Turbidimeter test, min.	160	160	160	160	—	—	160	160
Air permeability test, min.	280	280	280	280	—	—	280	280
Autoclave expansion, max., %	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Minimum compressive strength, psi (MPa)[C]								
1 day	—	—	—	—	1800	1450	—	—
	—	—	—	—	(12.4)	(10.0)	—	—
3 days	1800	1450	1500	1200	3500	2800	—	1200
	(12.4)	(15.5)	(10.3)	(8.3)	(24.1)	(19.3)	—	(8.3)
			1000[D]	800[D]				
			(6.9)[D]	(5.5)[D]				
7 days	2800	2250	2500	2000	—	—	1000	2200
	(19.3)	(15.5)	(17.2)	(13.8)	—	—	(6.9)	(15.2)
			1700[D]	1350[D]				
			(11.7)[D]	(9.3)[D]				
28 days	—	—	—	—	—	—	2500	3000
	—	—	—	—	—	—	(17.2)	(20.7)
Time of setting (alternative methods):[E]								
Gillmore test:								
Initial set, minutes, not less than	60	60	60	60	60	60	60	60
Final set, minutes, not more than	600	600	600	600	600	600	600	600
Vicat test:								
Initial set, minutes, not less than	45	45	45	45	45	45	45	45
Initial set, minutes, not more than	375	375	375	375	375	375	375	375

[A] Compliance with the requirements of this specification does not necessarily ensure that the desired air content will be obtained in concrete.

[B] Either of the two alternative fineness methods may be used at the option of the testing laboratory. However, when the sample fails to meet the requirements of the air-permeability test, the turbidimeter test shall be used and the requirements in this table for the turbidimetric method shall govern.

[C] The strength at any specified test age shall be not less than that attained at any previous specified test age.

[D] When the optional heat of hydration or the chemical limit on the sum of the tricalcium silicate and tricalcium aluminate is specified.

[E] The purchaser should specify the type of setting-time test required. In case he does not so specify, the requirements of the Vicat test only shall govern.

TABLE 6.5 ASTM Chemical and Fineness Requirements for Portland Cement (ASTM C150)

Portland Cement Type	Maximum Compound Composition (%) C_3S	C_2S	C_3A	C_4AF	Blaine Fineness (m^2/kg)
I	55	19	10	7	370
II	51	24	6	11	370
III	56	19	10	7	540
IV	28	49	4	12	380
V	38	43	4	9	380

gain of Type I cement can be accelerated by increasing the cement content per unit volume of concrete, so the selection of Type III becomes a question of economics and availability. Type IV can be manufactured on demand. As discussed later, adding fly ash to Type I or II portland cement reduces the heat of hydration, producing the benefits of Type IV, but at a lower cost. Type V cement is produced only in locations with a severe sulfate problem.

6.9.2 Other Cement Types

Other than the five standard types of portland cement, several hydraulic cements are manufactured in the United States, including

white portland cement
blended hydraulic cements
  portland blast furnace slag cement (Type IS)
  portland-pozzolan cement (Type IP and Type P)
  slag cement (Type S)
  pozzolan-modified portland cement (Type I(PM))
  slag-modified portland cement (Type I(SM))
masonry cements
expansive cements (Type K)
specialty cements

In general, these cements have limited applications. Civil and construction engineers should be aware of their existence, but should study them further before using them.

6.10 Mixing Water

Any potable water is suitable for making concrete. However, some nonpotable water may also be suitable. Frequently, material suppliers will use unprocessed surface or well water if it can be obtained at a lower cost than processed water. However, impurities in the mixing water can affect concrete set time, strength, and long-term durability. In addition, chloride ions in the mixing water can accelerate corrosion of reinforcing steel.

6.10.1 Acceptable Criteria

The acceptance criteria for questionable water are specified in ASTM C94. After 7 days, the compressive strength of mortar cubes made with the questionable water should not be less than 90% of the strength of cubes made with potable or distilled water (ASTM C109). Also, the set time of cement paste made with the questionable water should, as measured using the Vicat apparatus (ASTM C191), not be 1 hour less than or 1-1/2 hours more than the set time of paste made with potable or distilled water.

Other adverse effects caused by excessive impurities in mixing water include efflorescence (white stains forming on the concrete surface due to the formation of calcium carbonate), staining, corrosion of reinforcing steel, volume instability, and reduced durability. Therefore, in addition to the compressive strength and set time, there are maximum chemical limits that should not be exceeded in the mixing water, as shown in Table 6.6. Several tests are available to evaluate the chemical impurities of questionable water. Over 100 different compounds and ions can exist in the mixing water and can affect concrete quality; the more important effects are described in the Table 6.7.

6.10.2 Disposal and Reuse of Concrete Wash Water

Disposal of waste water from ready-mixed concrete operations is a great concern of the ready-mixed concrete producers (Chini and Mbwambo 1996).

TABLE 6.6 Chemical Limits for Wash Water Used as Mixing Water (ASTM C94) (Copyright ASTM, reprinted with permission)

Chemical	Maximum Concentration (ppm)	Test Method
Chloride, as Cl		ASTM D512
Prestressed concrete or concrete in bridge decks	500	
Other reinforced concrete in moist environments or containing aluminum embedments or dissimilar metals or with stay-in-place galvanized metal forms	1000	
Sulfate, as SO_4	3000	ASTM D516
Alkalis, as (Na_2O + 0.658 K_2O)	600	
Total Solids	50,000	AASHTO T26

TABLE 6.7 Summary of Effects of Water Impurities on Concrete Quality

Impurity	Effect
Alkali Carbonate and Bicarbonate	Can retard or accelerate strength test setting and 28-day strength when total dissolved salts exceed 1000 ppm. Can also aggravate alkali–aggregate reaction.
Chloride	Corrosion of reinforcing steel is primary concern. Chloride can enter the mix through admixtures, aggregates, cement, and mixing water, so limits are expressed in terms of total free chloride ions. ACl limits water-soluble ion content based on the type of reinforcement: Prestressed concrete 0.06% Reinforced concrete exposed to chloride in service 0.15% Reinforced concrete protected from moisture 1.00% Other reinforced concrete 0.30%
Sulfate	Can cause expansive reaction and deterioration
Other Salts	Not harmful when concentrations limited to Calcium Bicarbonate 400 ppm Magnesium Bicarbonate 400 ppm Magnesium Sulfate 25,000 ppm Magnesium Chloride 40,000 ppm Iron Salts 40,000 ppm Sodium Sulfide 100 ppm
Sea Water	Do not use for reinforced concrete. Can accelerate strength gain but reduces ultimate strength. Can aggravate alkali reactions.
Acid Water	Limit concentrations of hydrochloric, sulfuric, and other inorganic acids to less than 10,000 ppm.
Alkaline Water	Possible increase in alkali–aggregate reactivity. Sodium hydroxide may introduce quick set at concentrations higher than 0.5%. Strength may be lowered. Potassium hydroxide in concentrations over 1.2% may reduce 28-day strength of some cements.
Sanitary Sewage Water	Dilute to reduce organic matter to less than 20 ppm.
Sugar	Concentrations over 500 ppm can retard setting time and alter strength development. Sucrose in the range of 0.03 to approximately 0.15% usually retards setting. Concentrations over 0.25% by weight of cement can accelerate strength gain, but substantially reduce 28-day strength.
Oils	Mineral oil (petroleum) in excess of 2.5% by weight of mix may reduce strength by 20%.
Algae	Can reduce hydration and entrain air. Do not use water containing algae.

This waste water is usually generated from truck wash systems, washing of central mixing plant, storm water runoff from the ready-mix plant yard, waste water generated from water sprayed dust control, and conveyor wash down. According to the Water Quality Act (part 116), waste water from ready-mixed concrete operations is a hazardous substance (it contains caustic soda and potash) and its disposal is regulated by the Environmental Protection Agency (EPA). In addition, the high pH makes concrete wash water hazardous under the EPA definition of corrosivity.

The conventional practices for disposing of concrete wash water include dumping at the job site, dumping at a landfill, or dumping into a concrete wash water pit at the ready-mix plant. The availability of landfill sites for the disposal of concrete wash water has been drastically reduced in the past few decades. In addition, the current environmental restrictions either prevent or limit these conventional disposal practices. As a result, most ready-mix batch plants have developed a variety of operational configurations to manage their own wash water. The alternatives include settling ponds, storm water detention/retention facilities, and water reuse systems. Chemical stabilizing admixture systems have been used to circumvent the necessity to remove any wash water from concrete truck drums, and allow wash water to be reused for mixing more concrete. Studies have concluded that concrete properties are not significantly affected by the use of stabilized wash water (Borger et al. 1994).

Currently, concrete wash water is being used as mixing water for concrete in many places throughout the U.S. Some agencies, however, do not allow its use due to the existence of other impurities derived from concrete admixtures.

6.11 Admixtures for Concrete

Admixtures are ingredients other than portland cement, water, and aggregates that may be added to concrete to impart a specific quality to either the plastic (fresh) mix or the hardened concrete (ASTM C494). Some admixtures are charged into the mix as solutions. In such cases the liquid should be considered part of the mixing water. If admixtures cannot be added in solution, they are either weighed or measured by volume as recommended by the manufacturer. Admixtures are classified by the following chemical and functional physical characteristics (Hewlett 1978):

1. air entrainers
2. water reducers
3. retarders
4. hydration controller admixtures
5. accelerators
6. supplementary cementitious admixtures
7. specialty admixtures

The Portland Cement Association (PCA) identifies four major reasons for using admixtures (Kosmatka et al. 2002):

1. to reduce the cost of concrete construction
2. to achieve certain properties in concrete more effectively than by other means

3. to ensure quality of concrete during the stages of mixing, transporting, placing, and curing in adverse weather conditions
4. to overcome certain emergencies during concrete operations

6.11.1 Air Entrainers

Air entrainers produce tiny air bubbles in the hardened concrete to provide space for water to expand upon freezing. As moisture within the concrete pore structure freezes, three mechanisms contribute to the development of internal stresses in the concrete:

1. Critical saturation—Upon freezing, water expands in volume by 9%. If the percent saturation exceeds 91.7%, the volume increase generates stress in the concrete.
2. Hydraulic pressure—Freezing water draws unfrozen water to it. The unfrozen water moving throughout the concrete pores generates stress, depending on length of flow path, rate of freezing, permeability, and concentration of salt in pores.
3. Osmotic pressure—Water moves from the gel to capillaries to satisfy thermodynamic equilibrium and to equalize alkali concentrations. Voids permit water to flow from the interlayer hydration space and capillaries into the air voids, where it has room to freeze without damaging the parts.

Internal stresses reduce the durability of hardened concrete, especially when cycles of freeze and thaw are repeated many times. The impact of each of these mechanisms is mitigated by providing a network of tiny air voids in the hardened concrete using air entrainers. In the late 1930s, the introduction of air entrainment in concrete represented a major advance in concrete technology. Air entrainment is recommended for all concrete exposed to freezing.

All concrete contains entrapped air voids, which have diameters of 1 mm or larger and which represent approximately 0.2% to 3% of the concrete volume. Entrained air voids have diameters that range from 0.01 mm to 1 mm, with the majority being less than 0.1 mm. The entrained air voids are not connected and have a total volume between 1% and 7.5% of the concrete volume. Concrete mixed for severe frost conditions should contain approximately 14 billion bubbles per cubic meter. Frost resistance improves with decreasing void size, and small voids reduce strength less than large ones. The fineness of air voids is measured by the specific surface index, equal to the total surface area of voids in a unit volume of paste. The specific surface index should exceed 23,600 m^2/m^3 (600 $in.^2/in.^3$) for frost resistance.

In addition to improving durability, air entrainment provides other important benefits to both freshly mixed and hardened concrete. Air entrainment improves concrete's resistance to several destructive factors, including freeze–thaw cycles, deicers and salts, sulfates, and alkali–silica reactivity. Air entrainment also increases the workability of fresh concrete. Air entrainment decreases the strength of concrete, as shown in Figure 6.7; however, this effect can be reduced for moderate-strength concrete by lowering the water–cementitious materials ratio and increasing the cement factor. High strength is difficult to attain with air-entrained concrete.

Air-entraining admixtures are available from several manufacturers and can be composed of a variety of materials, such as

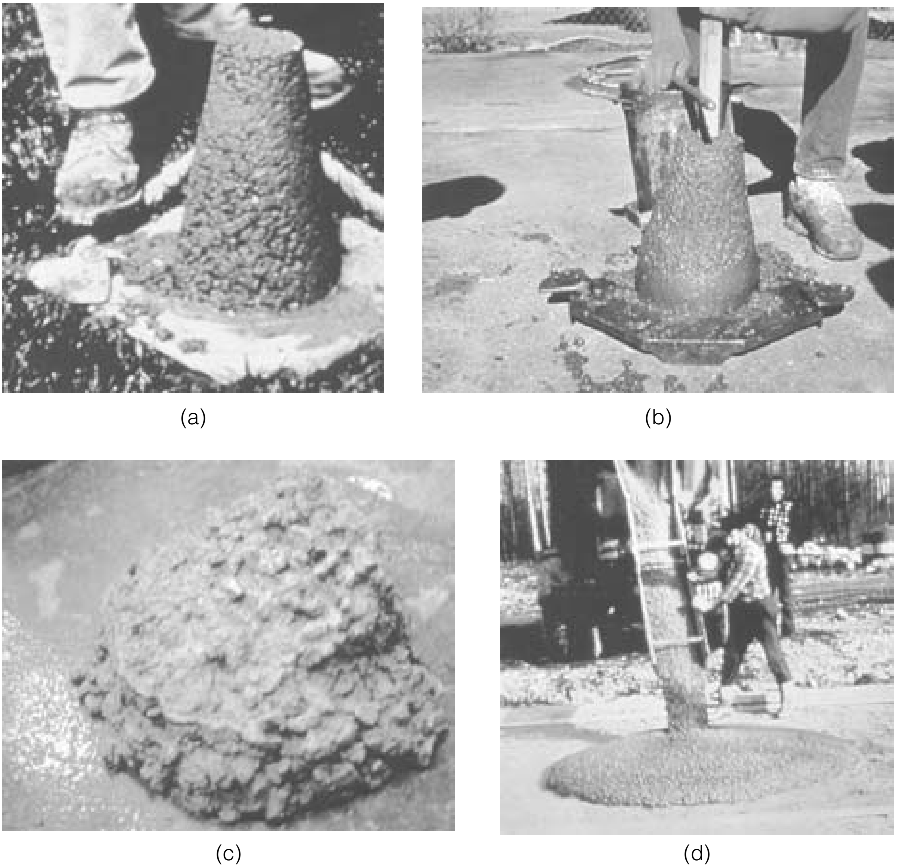
salts of wood resins (Vinsol resin)
synthetic detergents
salts of sulfonated lignin (by-product of paper production)
salts of petroleum acids
salts of proteinaceous material
fatty and resinous acids
alkylbenzene sulfonates
salts of sulfonated hydrocarbons

Air entrainers are usually liquid and should meet the specifications of ASTM C260. The agents enhance air entrainment by lowering the surface tension of the mixing water. Anionic air entrainers are hydrophobic (water hating). The negative charge of the agent is attracted to the positive charge of the cement particle. The hydrophobic agent forms tough, elastic, air-filled bubbles. Mixing disperses the air bubbles throughout the paste, and the sand particles form a grid that holds the air bubbles in place. Other types of air entrainers have different mechanisms but produce similar results.

6.11.2 Water Reducers

Workability of fresh or plastic concrete requires more water than is needed for hydration. The excess water, beyond the hydration requirements, is detrimental to all desirable properties of hardened concrete. Therefore, water-reducing admixtures have been developed to gain workability and, at the same time, maintain quality. Water reducers increase the mobility of the cement particles in the plastic mix, allowing workability to be achieved at lower water contents. Water reducers are produced with different levels of effectiveness: conventional, mid-range, and high-range. Figure 6.8 shows concrete without the addition of admixture and with the addition of conventional, mid-range, and high-range water reducers. As shown in the figure, the slump of the concrete increases, indicating an increase in workability. The high-range water reducer is typically called superplasticizer.

Water Reducers Mechanism Cement grains develop static electric charge on their surface as a result of the cement-grinding process. Unlike charges attract, causing the cement grains to cluster or "flocculate" [Figure 6.9(a)], which in turn limits the workability. The chemicals in the water-reducing admixtures reduce the static attraction among cement particles. The molecules of water-reducing admixtures have both positive and negative charges at one end, and a single charge (usually negative) on the other end, as illustrated in Figure 6.9(b). These molecules are attracted by the charged surface of the cement grains. The water reducers neutralize the static attraction on



(a) (b)

(c) (d)

FIGURE 6.8 Slumps of concretes with the same water-cement ratio: (a) no water reducer, (b) conventional water reducer, (c) mid-range water reducer, (d) high-range water reducer (Superplasticizer).

the cement surfaces. As a result, the clusters of cement grains are broken apart. Mutual repulsion of like charges pushes the cement grains apart, achieving a better distribution of particles [see Figure 6.9(c)], more uniform hydration, and a less-viscous paste.

Water reducing admixtures can be used indirectly to gain strength. Since the water-reducing admixture increases workability, we can take advantage of this phenomenon to decrease the mixing water, which in turn reduces the water–cementitious materials ratio and increases strength. Hewlett (1978) demonstrated that water reducers can actually be used to accomplish three different objectives, as shown in Table 6.8.

1. Adding a water reducer without altering the other quantities in the mix increases the slump, which is a measure of concrete consistency and an indicator of workability, as will be discussed in Chapter 7.

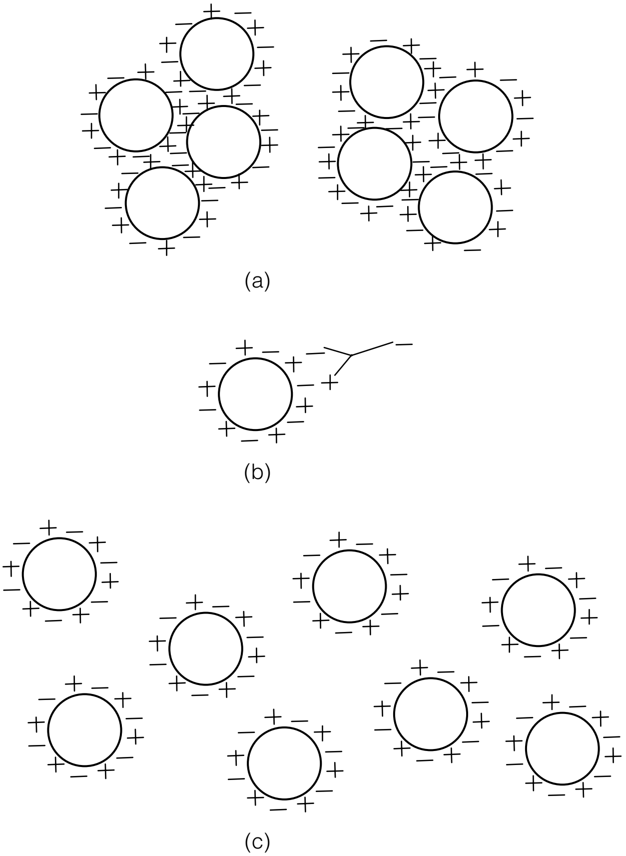


FIGURE 6.9 Water reducer mechanism: (a) clustering of cement grains without water reducer, (b) molecule of water reducer, and (c) better distribution of cement grains due to the use of water reducer.

TABLE 6.8 Effects of Water Reducer

	Cement Content kg/m^3	Water–Cement Ratio	Slump (mm)	Compressive Strength (MPa)	
				7 day	28 day
Base Mix	300	0.62	50	25	37
Improve Consistency	300	0.62	100	26	38
Increase Strength	300	0.56	50	34	46
Reduce Cost	270	0.62	50	25.5	37.5

2. The strength of the mix can be increased by using the water reducer by lowering the quantity of water and keeping the cement content constant.
3. The cost of the mix, which is primarily determined by the amount of cement, can be reduced. In this case, the water reducer allows a decrease in the amount of water. The amount of cement is then reduced to keep the water–cementitious materials ratio equal to the original mix. Thus, the quality of the mix, as measured by compressive strength, is kept constant, although the amount of cement is decreased.

Superplasticizers Superplasticizers, or high-range water reducers, can either greatly increase the flow of the fresh concrete or reduce the amount of water required for a given consistency. For example, adding a superplasticizer to a concrete with a 75-mm (3 in.) slump can increase the slump to 230 mm (9 in.), or the original slump can be maintained by reducing the water content 12% to 30%. Reducing the amount of mixing water reduces the water–cementitious materials ratio, which in turn, increases the strength of hardened concrete. In fact, the use of superplasticizers has resulted in a major breakthrough in the concrete industry. Now, high-strength concrete in the order of 70–80 MPa (10,000-12,000 psi) compressive strength or more can be produced when superplasticizers are used. Superplasticizers can be used in the following cases:

1. a low water–cementitious materials ratio is beneficial (e.g., high-strength concrete, early strength gain, and reduced porosity)
2. placing thin sections
3. placing concrete around tightly spaced reinforcing steel
4. placing cement underwater
5. placing concrete by pumping
6. consolidating the concrete is difficult

When superplasticizers are used, the fresh concrete stays workable for a short time, 30 min to 60 min, and is followed by rapid loss in workability. Superplasticizers are usually added at the plant to ensure consistency of the concrete. In critical situations, they can be added at the jobsite, but the concrete should be thoroughly mixed following the addition of the admixture. The setting time varies with the type of agents, the amount used, and the interactions with other admixtures used in the concrete.

6.11.3 Retarders

Some construction conditions require that the time between mixing and placing or finishing the concrete be increased. In such cases, retarders can be used to delay the initial set of concrete. Retarders are used for several reasons, such as the following:

1. offsetting the effect of hot weather
2. allowing for unusual placement or long haul distances
3. providing time for special finishes (e.g., exposed aggregate)

Retarders can reduce the strength of concrete at early ages (e.g., one to three days). In addition, some retarders entrain air and improve workability. Other retarders increase the time required for the initial set but reduce the time between the initial and final set. The properties of retarders vary with the materials used in the mix and with job conditions. Thus, the use and effect of retarders must be evaluated experimentally during the mix design process.

6.11.4 Hydration-Control Admixtures

These admixtures have the ability to stop and reactivate the hydration process of concrete. They consist of two parts: a stabilizer and an activator. Adding the stabilizer completely stops the hydration of the cementing materials for up to 72 hours, while adding the activator to the stabilized concrete reestablishes normal hydration and setting. These admixtures are very useful in extending the use of ready-mixed concrete when the work at the jobsite is stopped for various reasons. They are also useful when concrete is being hauled for a long time.

6.11.5 Accelerators

Accelerators are used to develop early strength of concrete at a faster rate than that developed in normal concrete. The ultimate strength, however, of high early strength concrete is about the same as that of normal concrete. Accelerators are used to

1. reduce the amount of time before finishing operations begin
2. reduce curing time
3. increase rate of strength gain
4. plug leaks under hydraulic pressure efficiently

The first three reasons are particularly applicable to concrete work placed during cold temperatures. The increased strength gained helps to protect the concrete from freezing and the rapid rate of hydration generates heat that can reduce the risk of freezing.

Calcium chloride, $CaCl_2$, is the most widely used accelerator (ASTM D98). Both initial and final set times are reduced with calcium chloride. The initial set time of 3 hours for a typical concrete can be reduced to 1.5 hours by adding an amount of calcium chloride equal to 1% of the cement weight; 2% reduces the initial set time to 1 hour. Typical final set times are 6 hours, 3 hours, and 2 hours for 0%, 1%, and 2% calcium chloride. Figure 6.10 shows that strength development is also affected by $CaCl_2$ for plain portland cement concrete (PCC) and portland cement concrete with 2% calcium chloride. Concrete with $CaCl_2$ develops higher early strength compared with plain concrete cured at the same temperature (Hewlett 1978).

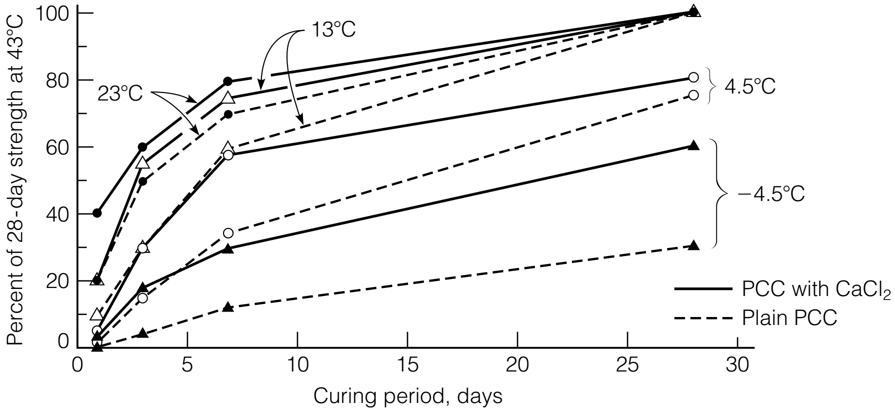


FIGURE 6.10 Effect of $CaCl_2$ on strength development at different curing temperatures.

The PCA recommends against using calcium chloride under the following conditions:

1. concrete is prestressed
2. concrete contains embedded aluminum such as conduits, especially if the aluminum is in contact with steel
3. concrete is subjected to alkali–aggregate reaction
4. concrete is in contact with water or soils containing sulfates
5. concrete is placed during hot weather
6. mass applications of concrete

The American Concrete Institute (ACI) recommends the following limits to water-soluble chloride ion content based on percent weight of cement (American Concrete Institute 1986):

Member Type	Chloride Ion Limit, %
Prestressed concrete	0.06
Reinforced concrete subjected to chloride in service	0.15
Reinforced concrete protected from moisture	1.00
Other reinforced concrete	0.30

Several alternatives to the use of calcium chloride are available. These include the following:

1. using high early strength (Type III) cement
2. increasing cement content

3. curing at higher temperatures
4. using non–calcium chloride accelerators such as triethanolamine, sodium thiocyanate, calcium formate, calcium nitrite, or calcium nitrate

6.11.6 Supplementary Cementitious Admixtures

Several byproducts of other industries have been used in concrete as supplementary cementitious admixtures since the 1970s, especially in North America. These materials have been used to improve some properties of concrete and to reduce the problem of discarding them. Since these materials are cementitious, they can be used in addition to or as a partial replacement for portland cement. In fact, two or more of these supplementary cementitious additives have been used together to enhance concrete properties. These supplementary cementitious materials include fly ash, ground granulated blast furnace slag, silica fume, and natural pozzolans.

Fly Ash Fly ash is the most commonly used pozzolan in civil engineering structures. Fly ash is a by-product of the coal industry. Combusting pulverized coal in an electric power plant burns off the carbon and most volatile materials. However, depending on the source and type of coal, a significant amount of impurities passes through the combustion chamber. The carbon contents of common coals ranges from 70 to 100 percent. The noncarbon percentages are impurities (e.g., clay, feldspar, quartz, and shale), which fuse as they pass through the combustion chamber. Exhaust gas carries the fused material, fly ash, out of the combustion chamber. The fly ash cools into spheres, which may be solid, hollow (cenospheres), or hollow and filled with other spheres (plerospheres). Particle diameters range from 1 μm to more than 0.1 mm, with an average of 0.015 mm to 0.020 mm, and are 70% to 90% smaller than 0.045 mm. Fly ash is primarily a silica glass composed of silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3), and lime (CaO). Fly ash is classified (ASTM C618) as follows:

Class N—Raw or calcined natural pozzolans, including diatomaceous earths, opaline cherts and shales, ruffs and volcanic ashes or pumicites, and some calcined clays and shales
Class F—Fly ash with pozzolan properties
Class C—Fly ash with pozzolan and cementitious properties

Class F fly ash usually has less than 5% CaO but may contain up to 10%. Class C fly ash has 15% to 30% CaO.

The spherical shape of fly ash increases the workability of the fresh concrete. In addition, fly ash extends the hydration process, allowing a greater strength development and reduced porosity. Studies have shown that concrete containing more than 20% fly ash by weight of cement has a much smaller pore size distribution than portland cement concrete without fly ash. The lower heat of hydration reduces the early strength of the concrete. The extended reaction permits a continuous gaining of strength beyond what can be accomplished with plain portland cement.

Ground Granulated Blast Furnace Slag Ground granulated blast furnace slag (GGBF slag) is made from iron blast furnace slag. It is a nonmetallic hydraulic cement consisting basically of silicates and aluminosilicates of calcium, which is developed in a molten condition simultaneously with iron in a blast furnace. The molten slag is rapidly chilled by quenching in water to form a glassy sandlike granulated material. The material is then ground to less than 45 microns. The specific gravity of GGBF slag is in the range of 2.85 to 2.95.

The rough and angular-shaped ground slag in the presence of water and an activator, NaOH or CaOH, both supplied by portland cement, hydrates and sets in a manner similar to portland cement.

Ground slag has been used as a cementitious material in concrete since the beginning of the 1900s. Ground granulated blast furnace slag commonly constitutes between 30% and 45% of the cementing material in the mix. Some slag concretes have a slag component of 70% or more of the cementitious material. ASTM C 989 (AASHTO M 302) classifies slag by its increasing level of reactivity as Grade 80, 100, or 120.

Silica Fume Silica fume is a byproduct of the production of silicon metal or ferrosilicon alloys. One of the most beneficial uses for silica fume is as a mineral admixture in concrete. Because of its chemical and physical properties, it is a very reactive pozzolan. Concrete containing silica fume can have very high strength and can be very durable. Silica fume is available from suppliers of concrete admixtures and, when specified, is simply added during concrete production either in wet or dry forms. Placing, finishing, and curing silica fume concrete require special attention on the part of the concrete contractor.

Silicon metal and alloys are produced in electric furnaces. The raw materials are quartz, coal, and woodchips. The smoke that results from furnace operation is collected and sold as silica fume.

Silica fume consists primarily of amorphous (noncrystalline) silicon dioxide (SiO_2). The individual particles are extremely small, approximately 1/100th the size of an average cement particle. Because of its fine particles, large surface area, and the high SiO_2 content, silica fume is a very reactive pozzolan when used in concrete. The quality of silica fume is specified by ASTM C 1240 and AASHTO M 307.

In addition to producing high-strength concrete, silica fume can reduce concrete corrosion induced by deicing or marine salts. Silica fume concrete with a low water content is highly resistant to penetration by chloride ions. More information is available at the www.silicafume.org website.

Natural Pozzolans A pozzolan is a siliceous and aluminous material which, in itself, possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, react chemically with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (ASTM C595). Naturally occurring pozzolans, such as fine volcanic ash, combined with burned lime, were used about 2000 years ago for building construction, and pozzolan continues to be used today. As shown in Table 6.2, calcium hydroxide is one of the products generated by the hydration of C_3S and C_2S. In fact, up to 15% of the weight of portland cement is hydrated lime. Adding a pozzolan to portland cement generates an opportunity to convert this free lime to a cementitious material.

Tables 6.9 and 6.10 summarize the effects of supplementary cementitious admixtures on fresh and hardened concrete. These summaries are based on general trends and should be verified experimentally for specific materials and construction conditions.

6.11.7 Specialty Admixtures

In addition to the admixtures previously mentioned, several admixtures are available to improve concrete quality in particular ways. The civil engineer

TABLE 6.9 Effect of Supplementary Cementitious Admixtures on Freshly Mixed Concrete

Quality Measure	Effect
Water Requirements	Fly ash reduces water requirements. Silica fume increases water requirements.
Air Content	Fly ash and silica fume reduce air content, compensate by increasing air entrainer.
Workability	Fly ash, ground slag, and inert minerals generally increase workability. Silica fume reduces workability; use superplasticizer to compensate.
Hydration	Fly ash reduces heat of hydration. Silica fume may not affect heat, but superplasticizer used with silica fume can increase heat.
Set Time	Fly ash, natural pozzolans and blast furnace slag increase set time. Can use accelerator to compensate.

TABLE 6.10 Effect of Supplementary Cementitious Admixtures on Hardened Concrete

Quality Measure	Effect
Strength	Fly ash increases ultimate strength, but reduces rate of strength gain. Silica fume has less effect on rate of strength gain than pozzolans.
Drying shrinkage and creep	Low concentrations usually have little effect. High concentrations of ground slag or fly ash may increase shrinkage. Silica fume may reduce shrinkage.
Permeability and absorption	Generally reduce permeability and absorption. Silica fume is especially effective.
Alkali–aggregate reactivity	Generally reduced reactivity. Extent of improvement depends on type of admixture.
Sulfate resistance	Improved due to reduced permeability.

should be aware of these admixtures, but will need to study their application in detail, as well as their cost, before using them. Examples of specialty admixtures include

workability agents
corrosion inhibitors
damp-proofing agents
permeability-reducing agents
fungicidal, germicidal, and insecticidal admixtures
pumping aids
bonding agents
grouting agents
gas-forming agents
coloring agents
shrinkage reducing

SUMMARY

The development of portland cement as the binder material for concrete is one of the most important innovations of civil engineering. It is extremely difficult to find civil engineering projects that do not include some component constructed with portland cement concrete. The properties of portland cement are governed by the chemical composition and the fineness of the particles. These control the rate of hydration and the ultimate strength of the concrete. Abrams's discovery of the importance of the water-to–cementitious materials ratio as the factor that controls the quality of concrete is perhaps the single most important advance in concrete technology. Second to this development was the introduction of air entrainment. The subsequent development of additional admixtures for concrete has improved the workability, set time, strength, and economy of concrete construction.

QUESTIONS AND PROBLEMS

6.1 What ingredients are used for the production of portland cement?

6.2 What is the role of gypsum in the production of portland cement?

6.3 What is a typical value for the fineness of portland cement?

6.4 What are the primary chemical reactions during the hydration of portland cement?

6.5 Define the C-S-H phase of cement paste.

6.6 What are the four main chemical compounds in portland cement?

6.7 What chemical compounds contribute to early strength gain?

6.8 Define
   a. interlayer hydration space
   b. capillary voids
   c. entrained air
   d. entrapped air

6.9 Define *initial set* and *final set*. Briefly discuss one method used to determine them.

6.10 The following laboratory tests are performed:
   a. Setting time test of cement paste samples
   b. Compressive strength of mortar cubes

   What are the significance and use of each of these tests?

6.11 What is a false set of portland cement? State one reason for false set. If false set is encountered at the job site, what would you do?

6.12 You are an engineer in charge of mixing concrete in an undeveloped area where no potable water is available for mixing concrete. A source of water is available that has some impurities. What tests would you run to evaluate the suitability of this water for concrete mixing? What criteria would you use?

6.13 The water–cementitious materials ratio is important because it influences all of the desirable qualities of concrete.
   a. What is a typical water–cementitious materials ratio for normal strength concrete?
   b. What is the minimum water–cementitious materials ratio for hydration only?
   c. Why is the extra water necessary?
   d. Briefly describe how super high strength concrete (f'_c = 15,000 psi) can be made.

6.14 Discuss the effect of water-to–cementitious materials ratio on the quality of hardened concrete. Explain why this effect happens.

6.15 Draw a graph to show the general relationship between the compressive strength of the concrete and the water-to–cementitious materials ratio for different curing times. Label all axes and curves.

6.16 What are the five primary types and functions of portland cement? Describe an application for each type.

6.17 Why isn’t pozzolan used with Type III cement?

6.18 What type of cement would you use in each of the following cases? Why?
   a. Construction of a large pier
   b. Construction in cold weather

c. Construction in a warm climate region such as the Phoenix area
d. Concrete structure without any specific exposure condition
e. Building foundation in a soil with severe sulfate exposure

6.19 In order to evaluate the suitability of nonpotable water available at the job site for mixing concrete, six standard mortar cubes were made using that water and six others using potable water. The cubes were tested for compressive strength after 7 days of curing and produced the following loads to failure (in pounds).

Cubes Made with Nonpotable Water	Cubes Made with Potable Water
17,810	16,730
15,110	18,870
14,200	15,230
18,290	17,470
14,650	16,990
16,430	17,850

a. Based on these results only, would you accept that water for mixing concrete according to ASTM C94?
b. According to ASTM C94, are there other tests to be performed to evaluate the suitability of that water? Discuss briefly.

6.20 Three standard mortar cubes were made using nonpotable water available at the job site, and three others were made using potable water. The cubes were tested for compressive strength after 7 days of curing and produced the following failure loads in kips:

Nonpotable water	Potable water
15.2	17.1
14.5	18.6
15.9	16.2

Based on these results only, would you accept that water for mixing concrete according to ASTM standards? Explain why.

6.21 Discuss the problem of disposal of waste water from ready-mixed concrete operations. State three alternate methods that can be used to alleviate this problem.

6.22 State five types of admixtures and discuss their applications.

6.23 If you were a materials engineer in Minnesota (cold climate) and could use only one type of admixture, which would you select? Explain.

6.24 Under what condition is an air-entraining agent is needed? Why? Discuss how the air-entraining agent performs its function.

6.25 If a water reducer is added to the concrete mix without changing other ingredients, what will happen to the properties of the concrete? If the intention of adding the water reducer is to increase the compressive strength of hardened concrete, how can this be achieved?

6.26 Why is a superplasticizer used? How does it perform its function?

6.27 A concrete mix includes the following ingredients per cubic foot:

Cement = 25 lb
Water = 11 lb
No admixture

Table P6.27 shows possible changes that can be made to the mix ingredients. Indicate in the appropriate boxes in the table what will happen in each case for the workability and the ultimate compressive strength as *increase*, *decrease*, or *approximately the same*.

Table P6.27

			What will happen?	
Cement (lb)	**Water (lb)**	**Admixture**	**Workability**	**Ultimate Compressive Strength**
25	15	None		
28	11	None		
25	11	Water reducer		
25	8	Water reducer		
25	11	Superplasticizer		
25	11	Air entrainer		
25	11	Accelerator		

6.28 A materials engineer is working in a research project to evaluate the effect of one type of admixture on the compressive strength of concrete. She tested 10 mortar cubes made without admixture and 10 others with admixture after 28 days of curing. The compressive strengths of cubes without admixture were 25.1, 24.4, 25.8, 25.2, 23.9, 24.7, 24.3, 26.0, 23.8, and 24.6 MPa. The compressive strengths of cubes with admixture were 25.3, 26.8, 26.5, 24.5, 27.2, 24.8, 24.1, 25.9, 25.3, and 25.0 MPa. Using the statistical *t*-test, does this admixture show an increase of the compressive strength of the cement mortar at a level of significance of 0.05?

6.29 A materials engineer is working in a research project to evaluate the effect of one type of admixture on the compressive strength of concrete. He tested 8 mortar cubes made with admixture and 8 others without admixture after 28 days of curing. The compressive strengths of cubes in psi with and without admixture are shown in Table P6.29.

Table P6.29

	Compressive strength, psi	
Cube No.	With admixture	Without admixture
1	3520	3550
2	3645	3785
3	3715	3720
4	3500	3645
5	3414	3560
6	3685	3645
7	3545	3400
8	3515	3555

Using the statistical *t*-test, is there a significant difference between the means of the compressive strengths of the two cement mortars at a level of significance of 0.10?

6.12 References

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