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. ACI limits water-soluble ion content based on 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
Seawater	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.

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.

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 chemical and functional physical characteristics (Hewlett 1978). These are:

1. air entrainers
2. water reducers
3. high-range water reducers—superplasticizers
4. retarders
5. accelerators
6. fine minerals
7. specialty admixtures

The Portland Cement Association (PCA) identifies four major reasons for using admixtures (Kasmatka and Panarese 1988). These are

1. to reduce 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, and
4. to overcome certain emergencies during concrete operations.

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, de-icers 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-cement 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.

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. Thus water reducer admixtures were developed to minimize the amount of water required for workability. Water reducers increase the mobility of the cement particles in the plastic mix, allowing workability to be achieved at lower water contents. 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 discussed in Chapter 7.
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 decreasing the amount

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

of water. The amount of cement is then reduced to keep the water-cement 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-cement 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 that was not previously attainable can be produced. Superplasticizers can be used in the following cases:

1. a low water-cement 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. Thus, superplasticizers are usually added at the job site. The setting time varies with the type of agents, the amount used, and the interactions with other admixtures used in the concrete.

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

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

Retarders can reduce the strength of concrete at early ages, 1 to 3 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.

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 is 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, and
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 6.8 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 to plain concrete cured at the same temperature (Hewlett 1978).

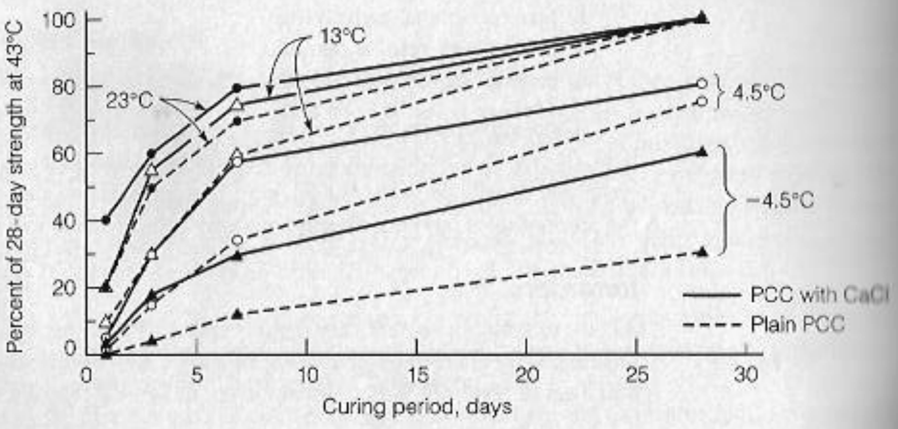

FIGURE 6.8 Effect of $CaCl_2$ on strength development at different curing temperatures.

The PCA recommends against using calcium chloride when

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 of soils containing sulfates;
5. concrete is placed during hot weather; and
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

1. using high early strength (Type III) cement,
2. increasing cement content,
3. curing at higher temperatures, and
4. using non–calcium chloride accelerators such as triethanolamine, sodium thiocyanate, calcium formate, calcium nitrite, or calcium nitrate.

Fine Minerals

Powdered or pulverized mineral admixtures are siliceous materials added to concrete in relatively large amounts (20% to 100% of the cement weight) to improve the characteristics of both plastic and hardened concrete. Mineral admixtures are frequently the waste from a production process. Use of these by-products provides an environmental benefit by reducing waste disposal. The PCA classifies mineral admixtures by chemical and physical characteristics as: (1) cementitious, (2) pozzolanic, (3) pozzolanic-cementitious, and (4) nominally inert materials (Kosmatka and Panarese 1988).

Cementitious minerals, such as blast furnace slag, natural cement, and hydraulic hydrated lime, have hydraulic cementing properties. Iron blast-furnace slag primarily consists of silicates and aluminosilicates of calcium. The molten slag is quenched in water and ground to less than 0.045 mm with a Blaine fineness of 400 m^2/kg to 600 m^2/kg. The rough-angular slag hydrates and sets in the presence of NaOH and CaOH (both produced by hydrating portland cement).

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 the portland cement is hydrated lime. Adding a pozzolan to portland cement generates an opportunity to convert this free lime to a cementitious material.

Fly ash and natural pozzolans are 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.

While natural and other synthetic pozzolans exist, fly ash is the most commonly used pozzolan in civil engineering structures and is, therefore, the focus of this discussion.

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 pass through the combustion chamber. The carbon contents of common coals are the following:

Coal Type	Carbon Content, %
Lignite	70
Subbituminous	75
Bituminous	85
Anthracite	94
Graphite	100

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:

Chemical	Content, %
Silica (SiO_2)	40–90
Alumina (Al_2O_3)	20–60
Iron oxide (Fe_2O_3)	5–25
Lime (CaO)	1–30

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.

Silica fume, or microsilica, is a by-product of silicon or ferrosilicon alloy production and occurs when high-purity quartz and coal are reduced in an electric arc furnace. Silica fume is a silicon dioxide in noncrystalline form with spherical shape. Silica fume has an average diameter of about 0.1 μm and a maximum size of 1.0 μm. The surface area is about 20,000 m^2/kg (about twice the surface area of tobacco smoke).

The spherical shape of fly ash increases the workability of the fresh concrete. In addition, both fly ash and silica fume extend the hydration process, allowing a greater strength development and reduced porosity. Studies have shown that concrete containing more than 20% pozzolan 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.

Nominally inert materials, finely divided quartz, limestone, marble, etc., can be used to improve workability; however, these materials have no cementitious value.

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

TABLE 6.9 Effect of Mineral 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; compensate by using superplasticizer.
Hydration	Fly ash reduces heat of hydration. Silica fume may not affect, but superplasticizer used with silica fume can increase heat.
Set time	Fly ash, natural pozzolans and blast furnace slag increase set time; can compensate by using accelerator.

TABLE 6.10 Effect of Mineral 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 reduced 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.

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.

Silica fume, or microsilica, is a by-product of silicon or ferrosilicon alloy production and occurs when high-purity quartz and coal are reduced in an electric arc furnace. Silica fume is a silicon dioxide in noncrystalline form with spherical shape. Silica fume has an average diameter of about 0.1 μm and a maximum size of 1.0 μm. The surface area is about 20,000 m^2/kg (about twice the surface area of tobacco smoke).

The spherical shape of fly ash increases the workability of the fresh concrete. In addition, both fly ash and silica fume extend the hydration process, allowing a greater strength development and reduced porosity. Studies have shown that concrete containing more than 20% pozzolan 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.

Nominally inert materials, finely divided quartz, limestone, marble, etc., can be used to improve workability; however, these materials have no cementitious value.

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

TABLE 6.9 Effect of Mineral 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; compensate by using superplasticizer.
Hydration	Fly ash reduces heat of hydration. Silica fume may not affect, but superplasticizer used with silica fume can increase heat.
Set time	Fly ash, natural pozzolans and blast furnace slag increase set time; can compensate by using accelerator.

TABLE 6.10 Effect of Mineral 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 reduced 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.

Specialty Admixtures

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

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' discovery of the importance of the water to cement 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