



CHAPTER 2

CONCRETE CONSTRUCTION MATERIALS

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2 CONCRETE CONSTRUCTION MATERIALS

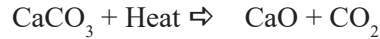
What are the components of concrete? The standard answer, “cement, aggregate, water and possibly admixtures” is the same as it was 100 years ago. However, with today’s 21st century concrete, the standard answer is an oversimplification. Portland cement is only one of many cementitious materials. Aggregates are more than inert fillers. Recycled water may contain excessive amounts of alkali chemicals. The various materials that may be encountered in the construction and repair of concrete structural elements are described in this chapter.

Cementitious Materials

Cements are substances that bind fragments of solid matter into a compact whole. For building materials this is taken to mean a fluid or semi-fluid (plastic) material that eventually hardens within an aggregate matrix (stones, pebbles, sands, bricks, and the like) to form structural elements of predetermined shape. Historically, adhesives were derived from a number of naturally available materials. Asphaltic materials were used as glue and sealants in areas where asphalt naturally seeped to the earth’s surface and either accumulated in pools or combined with local aggregates and hardened into rock asphalt. Adhesives are still made from boiled animal and fish parts, tree sap, milk protein (casein), and polymers like natural rubber. Early mortars were based on mud and clay.

Calcium-based cements were first used in the mortar that united the stone blocks used for the massive masonry projects built in ancient Egypt. Early calcium-based mortar was made with calcium sulfate (gypsum) and sand. Gypsum is water soluble, but was a suitable masonry binder for construction in the dry Mediterranean climate. Although the technology has been traced to ruins of ancient Mesopotamian and Greek structures, the use of lime cement became widely used when it was later adopted for Roman construction. Lime was produced by heating limestone to high temperatures. The lime powder was subsequently mixed with water to form a mortar that hardened over time. The ancient engineers knew lime-based mortar gained strength over time; but the reason behind the strength was unknown. As civilization developed, cement derived from heating calcareous (calcium containing) rocks became the preferred material for binding an aggregate matrix. Over 3,000 years would pass before scientists determined that lime mortar gained strength as carbon dioxide permeated through the mortar and combined with the mortar to form calcium carbonate in the process known as carbonation.

Limestone, chalk and seashells are composed of calcium carbonate, CaCO_3 . Historically, materials containing calcium carbonate were heated (calcined) to produce quicklime (calcium oxide, CaO). Carbon dioxide (CO_2) was driven off by the heating process to become atmospheric gas.



Adding water to calcium oxide creates slaked lime, or calcium hydroxide.



As CO_2 gradually permeates through the hardened mortar, carbonation occurs, where carbon dioxide and calcium hydroxide combine into calcium carbonate (limestone).



Roman buildings constructed with lime sand mortars owed their durability to thorough mixing and compacting. Romans later discovered that the fine grinding of volcanic sands or tuff from Pozzuoli, a seaport near Naples and Mt. Vesuvius, resulted in a material that was stronger than the lime sand mortar. The Pozzuolian sands contained silica and alumina which reacted with calcium hydroxide from slaked lime to become hydraulic cement that activated and hardened in the presence of water and was insoluble under water. Pozzolan materials are named after the volcanic ash from the Pozzuoli area. The ancient Roman writer Vitruvius wrote: “there is a species of sand which possesses extraordinary qualities. It is found...in the neighborhood of Mount Vesuvius...mixed with lime and rubble, it hardens as well under water as in ordinary buildings.” Roman also know that finely crushing clay bricks and mixing it with lime produced a similar product. Roman pozzolan concrete was used by Roman architects for structures such as the Pantheon (Figure 2-1). The Pantheon’s dome (diameter: 142 feet) is the largest unreinforced concrete dome in the world. Greece produced the same kind of hydraulic cements well into the 20th century by mixing lime with the volcanic tuff from the island of Thera, now called Santorini.

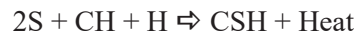


Figure 2-1. Roman Pantheon, 120 AD.

The use of pozzolanic materials and lime is the foundation of modern concrete, because the volcanic ash and clay brick consists of silica and alumina that combine with lime after the addition of water. Two precursors of Portland cement, Hydraulic Lime Cement and Natural Cement, were developed in the late 18th and early 19th century. Like Greek and Roman hydraulic cements, the new cements developed strength due to the mixing of lime with silica or alumina compounds. For Natural Cement, septaria nodules, consisting of limestone and clay, were mined in Rosenberg, New York and subsequently calcined. Hydraulic Lime Cements were produced by mixing limestone with clay in a kiln.

Modern Portland cements contain compounds of calcium, silica and alumina that can be precisely blended during the manufacturing process. Supplementary cementitious materials (SCMs), like fly ash or silica fume, that harden through the pozzolanic reaction with free lime produced as a byproduct of Portland cement hydration are also standard components of 21st century concrete. Ground volcanic sand, fly ash, silica fume, slag, and rice hull ash provide reactive silica (SiO_2), for the pozzolanic reaction.

As cement chemistry knowledge grew, the chemical equations became familiar and abbreviations were used to represent complex chemical formulas. Silicates (SiO_2 , SiO_4 , SiO_5 , etc.) were collected with the term “S.” Hydrates, or chemical multiples of water (H_2O) were referred to as “H,” calcium hydroxide was abbreviated “CH,” and calcium-silica-hydrate (e.g., $3\text{CaO}\cdot 2\text{SiO}_2\cdot 8\text{H}_2\text{O}$) was abbreviated CSH. The abbreviated reaction for pozzolanic composed of silica became:



Clay based pozzolans such as metakaolin provide silicates as well as alumina (Al_2O_3) based materials. Alumina is symbolized in the following chemical equations as “A.” Metakaolin (Al_2O_3 (SiO_2)), a calcined clay material, would be symbolized as “ AS_2 .” The resulting aluminous cement product calcium aluminate was termed “ C_3A .”



Ground granulated blast furnace slag (GGBFS), a byproduct of iron smelting, contains silicates, alumina and quicklime (CaO). Like lime, GGBFS reacts directly with water to produce $\text{CA}(\text{OH})_2$.



Portland Cement

Portland cement is hydraulic cement produced by pulverizing clinker, which consists of calcium silicates formed from limestone (CaCO_3), silica (SiO_2), alumina (Al_2O_3), and ferrous oxide (Fe_2O_3). ASTM C150 is the standard specification for Portland cement. Portland cement also may include water, 5% limestone, and processing additives like oxides of magnesium or iron.

The four major calcium-based compounds present in Portland cement and significant characteristics are listed in Table 2-1.

Table 2-1. Portland Cement Calcium Compounds.

Compound and Abbreviation	Chemical Formula	Typical Percent	Characteristics
Dicalcium silicate (C ₂ S)	2CaO•SiO ₂	10-40%	Low early strength, lower hydration heat (60 cal/g), excellent ultimate strength.
Tricalcium silicate (C ₃ S)	3CaO•SiO ₂	35-65%	Good early strength, medium hydration heat (120 cal/g), good ultimate strength.
Tricalcium aluminate (C ₃ A)	3CaO•Al ₂ O ₃	0-15%	Good early strength, high hydration heat (320 cal/g), good ultimate strength.
Tetracalcium aluminoferrite (C ₄ AF)	4CaO•Al ₂ O ₃ •Fe ₂ O ₃	5-15%	Good early strength, medium hydration heat (100 cal/g), good ultimate strength.
Note: 100 cal/g = 418.5 joule/g			

Depending on proportions of starting compounds (shown in chemical notation), the resulting clinker (shown in cement chemistry notation) would be:



The proportions of the basic compounds control the ratios of the various types of Portland cement in the final product. Heat of hydration is a function of reaction to water; a faster reaction generates more heat. Cement with a high early strength requirement would have larger percentages of C₃S and C₃A. Cement with a requirement for low heat production would have more C₂S. As cement becomes finer, the relative surface area increases; this increases water demand, reaction to water, heat of hydration and early strength. Substituting equal amounts of SCMs like fly ash for Portland cement generally reduces hydration heat 15–30%, however ultrafine SCMs do not significantly reduce the heat of hydration.

Portland Cement Types

Portland cements used on Caltrans projects must comply with ASTM C 150, which identifies five cement types. The type and major characteristics of each type are listed in Table 2-2.

Table 2-2. Portland Cements.

Cement Type	Common Name	Cement Characteristics
I	Ordinary Portland cement	General purpose cement, suitable for all uses when the special properties of the other types are not required.
II	Modified or Moderate sulfate resistance	Greater resistance to sulfate attack, $C_3A < 8\%$. Slower strength development. To moderate hydration heat, $C_3S + C_3A < 58\%$.
III	High early strength	Similar to Type I, but more finely ground, hydrates faster, hardens faster. $C_3A < 15\%$. Strength gains compared to Type I: 180% at 3 days, 120% at 90 days, 100% at 360 days.
IV	Low heat of hydration	Formulated for use in mass concrete where the heat generated must be minimized. Hydration and hardening are at a slower rate than Type I cement. $C_2S > 40\%$, $C_3S < 35\%$, $C_3A < 7\%$.
V	Sulfate resistant	Formulated for use when severe sulfate attack from groundwater or soil is anticipated. $C_3A < 5\%$ for higher sulfate resistance. Hydration and hardening are at a slower rate than Type I cement.
Note: ASTM C150 also recognizes entrained air as a specifiable concrete; this is noted by the addition of the suffix "A" to Types I, II, and III cements.		

Blended Portland Cements

Within the five general type classifications, there are a number of blending options; these options are summarized in Table 2-3. Selected materials are added during the manufacturing process to obtain desired properties or characteristics. Blended cements are designated by a code that includes the primary cement type followed by a descriptive term or letter. Binary blended hydraulic cement is a combination of Portland cement and a supplementary cementitious material that is either slag (S) or a pozzolan (P). The labeling convention for blended cements is in the form Type I (P%) or Type I (S%), where the cement type is listed first, the SCM (P for pozzolanic and S for slag) second with the percentage of the SCM, and then special properties are listed. For example, "Type I (P15)-A" designates a cement containing a blend of Type I cement, with 15% pozzolanic material and air-entrainment admixture added. Type I (S50) MH designates a Type I cement with 50% slag that produces a moderate heat of hydration level. Type IIT (S15) (P20) is Type II cement ternary mix with 15% slag and 20% pozzolan.



Table 2-3. Secondary Designations for Blended Cements.

Label	Description
X (%)	Cementitious Materials where X = P, S, or T. (P for pozzolanic, S for Slag, T for Ternary, is a mix with two SCMs, and (%) = percentage of SCM use).
A	Air-entraining admixture added to improve workability and durability. Batch plants typically prefer to maintain control over air entrainment by adding admixtures as part of the batch process rather than using premixed cements.
S	Sulfate Resistance (where MS = moderate sulfate resistance, HS = high sulfate resistance).
H	Heat of hydration (where MH = moderate heat, LH = low heat).
M	Modified with expansive admixture that causes a volume increase in concrete after initial set; this compensates for volume reduction associated with shrinkage.

Portland Cement Manufacturing Process

The cement manufacturing process consists of three following basic steps:

1. Initial crushing and proportion of raw materials.
2. Slow burning the raw materials into clinker.
3. Final mixing and fine grinding clinker into Portland cement powder.

Initial crushing sequentially reduces limestone and other materials from 3 inches to ¾-inch diameter particles. After initial crushing, materials are proportioned, mixed and coarse ground in a rotating mill containing thousands of steel balls that pulverize the materials. Grinding may be performed with dry materials, or water may be added during the process.

The homogeneous fine amalgam is then conveyed into a sloped rotating cylindrical kiln (oven), typically 10-12 feet in diameter and 500 feet long, for calcination. Cement kilns are steel plated, lined with fire brick and rotate at approximately one revolution per minute. Oil, gas or powdered coal is burned at the lower end of the kiln, heating the materials to about 2,700°F. Carbon dioxide is driven off as the materials pass through the kiln. Calcium silicates, aluminates and aluminoferrites are amalgamated into clinkers about ¾-inch diameter during the 4-hour calcination process. After the clinker has cooled, calcium sulfate (gypsum) may be added and the mixture is ground into a fine powder: Portland cement.



Particle Size and Appearance

Finished Portland cement is a white or grayish-white substance resembling flour in texture and appearance. Most cement will pass a sieve with 40,000 openings per inch. Blaine Fineness is a measure of surface area per unit weight; for ordinary Portland cement, the Blaine fineness is typically 300 to 500 square meters per kilogram. Smaller-size particles hydrate faster than larger-sized particles, but require more water to maintain workability.

Specific Gravity

The specific gravity of Portland cement varies depending on the source of the raw materials and the manufacturing processes. Typically the specific gravity will vary from 3.05 to 3.20 with an average of 3.15. Specific gravity does not influence concrete quality and is used to determine concrete unit weights.

Hot Cement

Final grinding is a heat intensive process, cement temperatures can approach 200°F. The normal time interval (usually several weeks) between manufacture and work site delivery allows cement to cool to ambient temperature. However, if cement is shipped too soon after manufacture, it may arrive at the job site hotter than ambient temperature; thus the term “hot cement.” Hot cement can cause problems in fresh concrete. The increased temperatures can reduce set time and workability, particularly on warmer days.

Supplementary Cementitious Materials

Supplementary Cementitious Materials (SCMs) are natural or man-made pozzolanic materials that are added to concrete to reduce the demand for Portland cement, improve workability and durability. ASTM C125 defines a pozzolan as either a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value. SCMs will react with calcium hydroxide (CH) in the presence of water to form calcium silica hydrates (CSH). The resulting concrete is stronger, less permeable, and more durable but will require more time for strength gain.

Natural pozzolans include some clays and shales, opaline cherts, diatomites, and glassy materials of volcanic origin like tuffs and pumices. Clays, shales and cherts require calcination to become pozzolanic. Metakaolin, one of the only natural pozzolans approved for Caltrans use, is calcined kaolin clay. Diatomites are natural depositing of pozzolanic material; however they are almost always mixed with clay and would need calcination to utilize the pozzolanic effect. Volcanic glasses are inherently pozzolanic, calcination rarely improves their pozzolanic activity.



Man-made pozzolans include fly ash, ultra-fine fly ash, silica fume, and rice hull ash, are byproducts of combustion required for power production. Ground granulated blast furnace slag (GGBFS) is the byproduct of iron smelting. Because of the very small particle size, ultra fine fly ash, rice hull ash, and silica fume are high reactivity pozzolans

SCMs that are approved for use on Caltrans projects are listed on the Caltrans METS Authorized Materials List (AML) (http://www.dot.ca.gov/hq/esc/approved_products_list/) under “Cementitious Materials for Use in Concrete”. The AML varies over time because products are added and deleted as warranted. A good practice is checking the AML for a material’s current status prior to approving the material for use. SCM technical and specifications references are summarized in Table 2-4. The effects of SCM usage on quality characteristics are summarized in Table 2-5.

Table 2-4. Supplementary Cementitious Materials.

	Color	Specific Gravity	Usage	Specifications
Fly Ash Ultra fine Fly Ash	Grey or Tan	1.90 - 2.80	8 - 25%	ASTM C618 AASHTO M 295
Metakaolin	Off-white - Grey	2.50 - 2.60	5 - 10%	ASTM C618 AASHTO M 295
Ground Granulated Blast Furnace Slag	Off-white	2.85 - 2.95	25 - 60%	ASTM C989 AASHTO M 302
Silica Fume	Light or Dark Grey	2.20 - 2.60	3 - 10%	ASTM C1240 AASHTO M 307
Rice Hull Ash	Grey-Black	2.05 - 2.20	5 - 15%	AASHTO M 321
*Note: 50% where maximum strength is required. Higher percentages (>60%) may be used in mass concrete or for ASR mitigation.				

Table 2-5. Summary of SCM Characteristics.

Characteristic	GGBFS	Fly Ash	Metakaolin	Silica Fume	Rice Hull Ash
Water Demand	▼	▼▼	▲	▲▲	▼
Workability	▲	▲	▼	▼▼	▼
Initial Set	▼	▼▲	◄►	◄►	▼
Final Set	◄►	◄►	◄►	◄►	▼
Heat of Hydration	▼	▼	◄►	◄►	◄►
Dry Shrinkage	Unknown	◄►	◄►	▲▲	Unknown
Plastic Shrinkage	◄►	◄►	◄►	▲	◄►
Early Strength	▼	▼	▲▲	▲▲	▲
Long Term Strength	▲	▲	▲▲	▲▲	▲
Permeability	▼	▼	▼▼	▼▼	▼
Sulfate Resistance	▲▲	▲▲	▲	▲	▲
Chloride Resistance	▲	▲	▲▲	▲▲	▲
ASR Mitigation	▲▲	▲▲	▲	▲	▲
<p>Legend</p> <ul style="list-style-type: none"> ▲ - Increased / Improved ▲▲ - Significantly Increased / Improved ▼ - Reduced / Decreased ▼▼ - Significantly Reduced / Decreased ▼▲ - Effect Varies ◄► - No Change 					

Fly Ash

Fly ash and ultra fine fly ash are pozzolanic materials and are normally less expensive than Portland cement as they are byproducts of coal combustion for power generation. Ultra fine fly ash is chemically identical to fly ash. The physical difference is in size, ultra fine fly ash median size is about 6 μm , and fly ash is about three times larger at 19 μm .

Fly ash must comply with AASHTO M 295. Class F fly ash, produced from anthracite (bituminous coal) contains a minimum of 70% combined silica and alumina. Class C fly ash contains a minimum of 50% combined silica and alumina. Class F fly ash may have up to 12% CaO. Because Class C fly ash could have up to 30% CaO, it acts as a lime cement, combining with H_2O and CO_2 to form CaCO_3 (limestone).

Freshly mixed concretes that use Class F fly ash exhibit the following:

- Longer set time
- Improved workability
- Lower heat of hydration
- Lower water demand
- Reduced bleed water
- Reduced segregation

Hardened concretes using Class F fly ash have:

- Reduced permeability (improving chloride and sulfate corrosion resistance)
- Improved abrasion resistance
- Lower early strengths (< 28 days) with higher long term strength (> 28 days)
- Increased ASR resistance
- No change in early age shrinkage cracking of concrete

Typical chemical composition of fly ash

- Silica: 52%
- Alumina: 23%
- Iron Oxide: 11%
- Calcium Oxide: 5%
- Sulfate: 0.8%
- Sodium Oxide: 1%
- Potassium Oxide: 2%

Fly ash is beneficial in:

- Freeze-thaw areas because of its low permeability (resistance to chloride penetration) and abrasion resistance
- High temperature zones because of its longer setting time
- Marine or sulfate rich soil environments because of its sulfate resistance
- Long life structures (pavements, bridges and buildings)
- Mass concrete pours because of lower heat of hydration
- Concrete where potential for ASR is high

Metakaolin

Metakaolin, a natural pozzolan, is derived from the calcination of high-purity kaolin clay. The product is then ground to between 1 - 2 μm (about 10 times finer than cement), but since it is manufactured and not waste from another process, it is significantly more expensive than other pozzolans. Metakaolin particles fill voids between other concrete materials and result in a denser mix. Metakaolin must comply with AASHTO M 295 as a Class N (natural) pozzolan. Metakaolin contains a minimum of 70% combined silica and alumina.

Freshly mixed concretes using metakaolin have:

- Increased water demand
- Significantly reduced workability
- Decreased heat of hydration
- No change in set time

Hardened concretes using metakaolin have:

- Significantly increased early and long-term strength
- Increased flexural strength
- Reduced permeability (improving chloride and sulfate corrosion resistance)
- Increased abrasion resistance
- Increased ASR resistance
- No change in plastic shrinking cracking

Typical chemical composition of metakaolin:

- Silica: 53%
- Alumina: 43%
- Iron Oxide: 0.5%
- Calcium Oxide: 0.1%



- Sulfate: 0.1%
- Sodium Oxide: 0.05%
- Potassium Oxide: 0.4%

Metakaolin is beneficial in:

- Freeze-thaw areas because of its low permeability (resistance to chloride penetration) and abrasion resistance
- Low temperature zones because of its shorter setting time
- Chemically aggressive environments because of lower permeability
- Marine or sulfate rich soil environments because of its sulfate resistance
- Situation where early strength gain and high strength are required
- Situations where visual appeal because of lighter color is important

Ground Granulated Blast Furnace Slag

Ground Granulated Blast Furnace Slag (GGBFS) or slag cement, is a glassy, granular material, created as a byproduct of iron smelting, that has been ground to suitable fineness to have cementitious properties. GGBFS must comply with AASHTO M 302 grade 100 or 120. The grade is the slag activity index. Concrete mixes that include grade 120 GGBFS usually exceed comparable amounts of Portland cement concrete strength after 7 days. Concrete mixes that include grade 100 GGBFS usually exceed comparable amounts of Portland cement concrete strength after 28 days. Portland cement usually exceeds Grade 80 GGBFS in strength, regardless of age. Grade 80 produces less heat during hydration and may be specified in situations where strength is less important than hydration heat, as in mass concrete. Concrete with GGBFS has an initial green hue that fades to grey after a few days exposure to air.

Freshly mixed concrete using GGBFS may have:

- Longer initial set time
- Lower water demand
- Improved workability
- Lower heat of hydration
- No change in plastic shrinkage cracking

Hardened concretes using GGBFS have:

- Reduced permeability (improving chloride and sulfate corrosion resistance)
- Lower early strengths (1-7 days) with higher long-term strength (7+ days)
- Increased ASR resistance

Typical chemical composition of GGBFS:

- Silica: 35%
- Alumina: 12%
- Iron Oxide: 1%
- Calcium Oxide: 40%
- Sulfate: 9%
- Sodium Oxide: 0.3%
- Potassium Oxide: 0.4%

GGBFS should be used in:

- Freeze-thaw areas because of low permeability
- High ambient temperature zones because of longer setting time
- Marine or sulfate rich soil environments because of sulfate resistance
- Long life structures (pavements, bridges, and buildings) since higher long term strength
- Mass concrete pours because of lower heat of hydration
- With fly ash and silica fume in ternary concrete blends

Silica Fume

Silica Fume, also known as fume silica or micro silica, is an extremely fine pozzolanic material, typically 100 times finer than Portland cement, but is more expensive than Portland cement. Silica fume is a byproduct of the silicon and ferrosilicon industries and produced through the electric arc furnaces. Silica fume must comply with AASHTO M 307.

Freshly mixed concretes using silica fume have:

- Significantly increased water demand
- Significantly decreased workability
- Less bleed water

Hardened concretes using silica fume have:

- Significantly increased early and long-term strengths
- Reduced permeability (improving chloride and sulfate corrosion resistance)
- Significantly increased chloride resistance
- Better sulfate resistance
- Increased ASR resistance

Typical chemical composition of silica fume:

- Silica: 90%
- Alumina: 0.4%
- Iron Oxide: 0.4%
- Calcium Oxide: 1.6%
- Sulfate: 0.4%
- Sodium Oxide: 0.5%
- Potassium Oxide: 2.2%

Silica Fume should be used in:

- Freeze-thaw areas because of its low permeability (resistance to chloride penetration) and abrasion resistance
- Chloride or sulfate rich environments because concrete permeability is reduced
- Long life structures (pavements, bridges and buildings) because of increased strength and durability
- With fly ash or GGBFS in ternary mixes to improve durability

Rice Hull Ash

Rice Hull Ash (RHA) is a pozzolanic material formed as a byproduct of the rice milling process. RHA exhibits several similar properties to that of silica fume as it is comparable in chemical composition. Although RHA is an economical substitute for Portland cement, it is only approved for minor concrete uses.

Freshly mixed concrete using RHA have:

- Longer initial set time
- Comparable final set time
- Lower water requirement
- Decreased workability
- No change in heat of hydration

Hardened concretes using RHA have:

- Increased early and long-term strengths
- Reduced permeability (increased chloride and sulfate resistance)
- Increased abrasion resistance
- Increased ASR resistance

Typical chemical composition of RHA:

- Silica 90%
- Alumina -
- Iron Oxide 0.21%
- Calcium Oxide 0.22%
- Sodium Oxide 0.01%
- Potassium Oxide 0.04%

Specialty Cementitious Materials

Unique application requirements such as architecturally specified color and concrete repairs can be met with specialty cements. White cement can be blended with standard Portland cement for a variety of colors between white and grey. Fast-setting concretes which gain acceptable strength in a matter of hours can be used for structure concrete repair.

Type I, Type II or Type III (White) Portland Cement

White Portland cement is used to produce a white finished concrete primarily used for architectural concrete. Small amounts of white cement may be added to adjust the color of a mortar patch used to repair a section of concrete. The white color is obtained by keeping iron and magnesium oxides to less than 0.5% of the raw materials, and by modifying the manufacturing process. The primary use of iron oxide in regular cement function is as flux in the calcining process. When iron oxide is eliminated, a higher calcination temperature (about 500°F higher) is required. White cement is also ground more finely than Portland cement.

Magnesium Phosphate Cements

Magnesium phosphate cement (MPC) is produced by calcining mined magnesia, forming a substance consisting of magnesium and calcium oxides. Hardening is initiated by adding phosphoric acid, which yields magnesium phosphate and calcium phosphate.

All MPCs are prepackaged products. Two generic types are available commercially:

- Two-component products, which consist of a dry granular material and a liquid solution of phosphoric acid
- Single-component products, which contain phosphoric acid in dry powder form and are activated by adding water



For both types, the recommended mix proportions must be followed carefully to ensure satisfactory results. MPCs may be extended up to 60% with pea gravel aggregate filler.

Surface preparation should receive careful attention. Most manufacturers recommend sandblasting to obtain the clean, sound surface that is necessary for adequate bond. MPC bonds well to dry Portland cement concrete. Epoxy has been used to enhance the bond, but its use is not considered necessary. Provided the hardened surface is dry, MPC will bond to previously placed MPC and thus is well suited to stage construction. MPC will not bond to damp or wet concrete. The moisture intolerance may continue for as long as a week after placement, and has resulted in bond failures where the patch material was placed on a force dried (by heating or other means) surface. Debonding occurred because moisture equilibrium in the substrate, when restored, contaminated the magnesium phosphate material at the bond line interface.

NOTE
Magnesium phosphate will react with aluminum, so aluminum tools or mixing bowls should not be used.

MPCs are self-leveling; consequently, they are not suitable for use on steep slopes or vertical surfaces. Water cannot be added to improve the workability of the two-component products, which may be a disadvantage under some circumstances. For the single-component products, following manufacturer's instructions and use only enough water to make the material workable. Water should not be added to aid surface finishing as this will result in high water content at the surface, reducing strength and lowering abrasion resistance.

Set times are typically 15 to 30 minutes, and full strength is achieved within 45 minutes to 1 hour. The normal set time may be retarded by the addition of borax or other buffers used in accordance with the manufacturer's recommendations. (Tests indicate that 1 ounce of borax per 50-pound bag of prepackaged mix will retard the set time 5 minutes at 72°F.) Curing is not required; curing compound prevents the escape of gases generated by the chemical reaction, which inhibits the hardening process. Lab tests indicate that reinforcing steel does not corrode as fast in magnesium phosphate concrete as in normal Portland cement concrete. Accordingly, MPCs are suitable for bonding dowels as well as patching bridge decks.

Calcium Aluminate Cements

High aluminate cements (HAC) are produced by fusing limestone and bauxite in an electric or blast furnace to produce a clinker, which is then cooled and ground. Like Portland cement, the high alumina cements gain strength by hydration; however, the water-cement ratio is critical, so it is essential to use the mix proportions recommended by the manufacturer.

As the name implies, HACs have a high concentration of aluminates. The calcium to aluminate ratio is typically 40:60 as compared to the approximately 50:50 ratio for normal Portland cements.

Unmodified HAC has a significant strength loss at high temperatures (over about 135°F when moisture is present). Under these conditions, the hardened concrete will undergo a crystalline conversion that changes the internal structure of the concrete and results in a strength loss of up to 70%; calcium sulfate is added to counteract this.

HACs are usually single-component, and water-activated packages; the strength gain occurs rapidly after the initial set period of 15 to 30 minutes, depending on the temperature. Typical compressive strengths exceed 3,000 psi in 3 hours and 5,000 psi in 24 hours. Lab tests indicate that the set time will be retarded by the addition of borax, and accelerated by the addition of lithium carbonate. They may be extended up to 100% with pea gravel filler.

Placing and finishing characteristics are similar to normal Portland cement concrete. HACs are generally self-leveling, but can be modified for low-flow application. Although lab tests indicate that high alumina cements will bond to a damp substrate, bond failures have been observed in the field when placed under wet weather conditions. Accordingly, a dry substrate is recommended.

Initial shrinkage is low. Curing is unnecessary for most applications; however, a curing seal may prevent surface cracking when ambient conditions are hot, dry or windy. After a surface skin has formed, concrete made with modified high alumina cement will not bond to itself. To prevent delamination between lifts, patches must be placed in a single lift. If multiple lifts are unavoidable, abrasive blast cleaning of the surface between lifts will be necessary.

Aggregate

Aggregates typically comprise 60 to 75% of concrete volume. Once thought of as inert filler materials, aggregate affects water-cement ratio and contributes to concrete strength. Porous, fractured, and chemically active aggregates negatively affect concrete durability. Suitable aggregate requires several quality control checks prior to use.



Typical aggregate sources are:

- Natural gravels and sands: excavated, washed, and screened for gradation requirements
- Natural rock: excavated, crushed, washed, and screened to meet aggregate gradation requirements

Other aggregates such as marine dredged aggregate or recycled concrete aggregate are not typically used for structural concrete. Marine aggregates may contain shells and deleterious seawater salts. Recycled concrete aggregate is used primarily for pavement. Good quality aggregate will consist of clean, hard particles having sufficient strength and durability to resist deterioration under normal conditions of exposure and wear. Coarse aggregate must be able to withstand abrasion and surface wear caused by vehicular traffic and environmental factors such as flowing water and freezing weather.

Contamination

Aggregate must be free from contamination, because clay and organic matter reduce the bond between aggregate and paste. As contaminated aggregates have a greater surface area, the ratio of cement paste to aggregate surface area is reduced, resulting in a leaner mix and weaker concrete than anticipated. Contaminants such as clay and organic matter are lighter than aggregates and tend to rise as concrete consolidates, weakening the surface strength and reducing durability.

Moisture

The four moisture conditions are:

- Oven dry
- Air dry
- Saturated Surface Dry (SSD)
- Wet

Of the four moisture conditions, saturated surface dry (SSD) is the standard for mix design moisture assumptions. Oven dry aggregate, has been baked dry; there is no water on particle surfaces or within pore spaces. Air dry aggregate is surface dry, but carries some pore water. The pores of SSD aggregates are filled with water, but no water is adsorbed to the exterior surface. SSD is the condition where aggregate has the least effect on the water-cement ratio. Wet aggregate pores are filled with water, and water is adsorbed on the exterior surface.

Porous aggregate maintains a water balance with the local environment. If surface moisture is present or humidity is high, moisture will be absorbed. When humidity is decreasing, moisture is released to the atmosphere. During severe weather conditions, absorbed moisture may freeze and expand, causing aggregate deterioration and defective concrete.

Shape and Texture

Aggregate shape and texture affect durability, strength, and water demand. Shape is categorized by sphericity and roundness. Sphericity measures compactness of shape (surface area divided by volume), where a sphere or a cube would be more compact than a plate. Roundness refers to angularity at the particle edges, rounded edges signify better workability. The surface texture can range from glassy to rough. Smooth aggregate requires less mixing water, is more workable but has less area for bonding with cement paste.

Gradation

Over the years a great deal of study and research has been devoted to grading theory and much has been learned about the influence of aggregate gradation on the properties of a concrete mixture. Thus far, however, no one has discovered a simple, reliable method of determining the “ideal” grading for a given aggregate; consequently, most grading curves have been developed empirically and are based on experience rather than theory.¹ The blend of aggregate particles in each specified sieve size must meet the specified particle size distribution. When the gradation falls out of tolerance, the variation from specification will have negative effects on workability, ultimate strength, density, and shrinkage characteristics.

Alkali-Silica Reactivity

Alkali-silica reactivity (ASR) is a two-step process with three required ingredients.

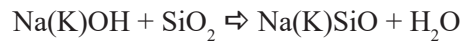
- Reactive aggregate is the first required ingredient. Reactive aggregates are typically cherts, like opal or obsidian, made of hydrous or amorphous silica (SiO_2), siliceous limestones and dolomites, intensely strained quartzes and quartzite. The key characteristic is the availability of silica. Aggregate taken from granite, gneiss, schist, sandstone and basalt are more commonly tested and found to be innocuous as the silica is locked into larger crystal formations.
- Alkali-metal ions, Sodium (Na) and Potassium (K), are limited by Caltrans specifications to a maximum of 0.6% of the weight of Portland cement. Other sources of alkali-metal ions can be admixtures or salt contamination (seawater, deicing or wind-blown materials).

¹The term “ideal” grading means the particle size distribution that will produce maximum workability for the specified cementitious content, provided the particular distribution can be obtained economically and will not produce a concrete mixture that is incompatible with the purpose intended.

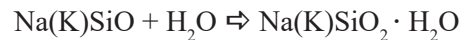


- Moisture is the expansive component. If moisture could be excluded, ASR would stop before the expansive phase starts.

In the first part of the reaction, one or more alkali atoms, Sodium (Na) and Potassium (K), in combination with a hydroxide (OH) molecule react with silica (SiO_2) to create alkali-silica gel.



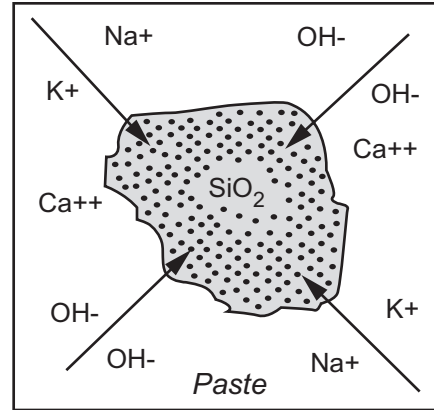
In the second part of the reaction, moisture is absorbed, making an alkali-silica hydrate, which is an expansive gel. (See Figure 2-2).



As the alkali-silica gel absorbs water and expands, pop-outs may occur at the surface and in severe cases, extensive map cracking can occur.

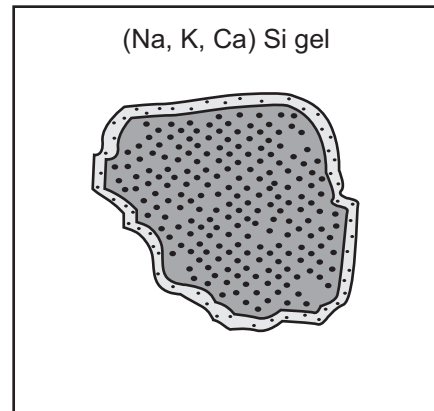
(a)
Concrete pore solutions is dominated by Na, K & OH (with minor amounts of Ca).

If the silica in the aggregate is reactive - the OH and then the Na & K will react with the SiO_2 .



(b)
The product of the reaction is an alkali-silica gel composed of Na, K, Ca & Si.

The gel forms around and within the aggregate.



(c)
The gel imbibes water from the surrounding cement paste.

The gel expands.

Eventually the swelling pressures may exceed the tensile strength of the surrounding paste allowing expansion and cracking of the concrete.

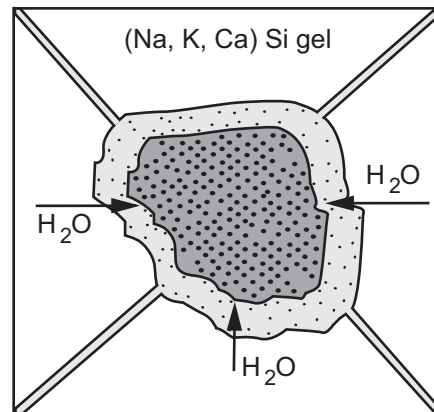


Figure 2-2. Alkali-Silica Reaction².

² The Use of Lithium to Prevent or Mitigate Alkali-Silica Reaction in Concrete Pavements and Structures, FHWA-HRT-06-133, March 2007

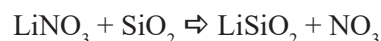
ASR is controlled by:

- Use of innocuous aggregate, removing free silica stops the reaction before it occurs.
- Limiting alkali metal content in cement, similar to aggregate, removing reactants limits the reaction. However, sodium from road de-icers or seawater may still find its way into the aggregate.
- Adding SCMs to the concrete mix reduces the alkali-metal ion content. If say 30% fly ash were used as cementitious, there would then be a 30% reduction in alkali-metal content. Instead of 0.6% maximum limit, the content would be $0.6 - (0.3 \times 0.6)$ or a maximum of 0.42%.
- Adding lithium nitrate as an admixture provides a new alkali-metal to the mix. Lithium is lighter than the other alkali-metals and responds quicker to forces attracting alkali-metals and silica. When lithium reacts with silica the gel forms, but since the gel does not absorb water, it is not expansive; which defeats the ASR reaction.

Aggregate testing to verify non-reactive materials is performed under ASTM C1260 or ASTM C1293. Aggregate that passes the ASTM testing is certified as innocuous. All aggregates currently accepted by Caltrans as innocuous are on the Caltrans Authorized Materials List under Aggregates for Concrete http://www.dot.ca.gov/hq/esc/approved_products_list.

Low-alkali cements are specified under Standard Specifications Section 90. SCMs control ASR by combining with alkali before it combines with aggregates. The SCMs need be in sufficient amounts to remove available alkali from the mix. The amount needed depends on the SCM. Although research has shown silica fume and Metakaolin may be effective at 10%, current specifications set the minimum amount at 12%. Class F fly ash with less than 10% CaO is effective at 25%. Class F fly ash with more than 10% CaO require more than 25% fly ash. An SCM like ground granulated blast furnace slag may require up to 50% slag in the mix. The equations listed in Standard Specifications Section 90 must be met to ensure adequate use of SCMs.

Lithium nitrate may also be combined with 15% Class F fly ash. Lithium is chemically more reactive than Sodium or Potassium in single replacement reactions, so lithium will combine more readily with silica. Individual molecular components vary with availability, the reactants are lithium nitrate and silicon dioxide and the products are lithium silicate and a nitrate. The assumption is that other alkali will combine with the nitrate (sodium nitrate or potassium nitrate).





Water

As a general rule, any water suitable for drinking may be used for concrete production and curing. In the future, if wastewater treatment continues to advance, recycled water may become a common part of a concrete mix. Currently, water added to concrete may come from:

- Batch plants adding water from municipal or private supplies
- Batch plants adding reclaimed water (from municipal and batch plant operations)
- Ice added for additional cooling on hot days
- Transport trucks added on the job site
- Moisture adsorbed by aggregates

The water quality requirements for washing aggregate, mixing, and curing concrete are found in Section 90-1.02D of the Standard Specifications. Although non-potable water may be used, there are limitations on impurities:

- No oil
- No substances that significantly change set time, reduce compressive strength, or cause discoloration
- Restricted presence of alkali ($\text{Na}_2\text{O} + 0.658 \text{K}_2\text{O}$) to < 300 parts per million (ppm)
- Restricted presence of chloride (650 ppm) and sulfate (<1,300 ppm) ions for prestressed concrete. Note that the specification limit applies to the chlorine and sulfate ions, not to compounds containing these elements in combined form

The adverse effects of materials dissolved in water are listed in Table 2-6. If there is any doubt regarding water quality, the best course is to test the water.

Table 2-6. Adverse Effect of Dissolved Chemicals on Concrete.

Chemical	Altered Set	Strength Reduction	Other
Alkali Carbonates/Bicarbonates (NaCO ₃ , NaHCO ₃ , KCO ₃ , KHCO ₃)	Yes	Lower 28 day strength	Alkali-silica reaction, may affect air entrainment
Chloride	Yes	No	Increased drying shrinkage, steel corrosion, efflorescence
Sulfate	No	No	Expansive sulfate reaction
Seawater	No	Lower 28 day strength	Potential for steel corrosion, alkali-silica reaction, higher potential for efflorescence, may affect air entrainment
Alkali (Sodium (Na) Potassium (K))	No	Lower 28 day strength	Alkali-silica reaction, may affect air entrainment
Sugar	Yes	Lower 28 day strength	N/A
Silts and clays	No	No	Changes in workability
Oil	No	Lower 28 day strength	N/A
Alkali (Sodium (Na) Potassium (K))	No	Lower 28 day strength	Alkali-silica reaction, changes in workability
Acids	No	Tannic acid reduces strength	High strength acids may alter workability
Inorganic Salts (manganese, zinc, copper, sodium, and lead)	Retarded set	Lower 28 day strength	Changes in workability

Concrete Admixtures

Admixtures are added to the basic concrete mix of cementitious materials, aggregate and water to modify workability and durability characteristics of concrete. Some admixtures affect fresh concrete by increasing fluidity and workability, reducing the water demand, or retarding or accelerating the setting time. Other admixtures affect the properties of hardened concrete by increasing its strength and durability. Table 2-7 lists the various admixture types that are accepted on Caltrans projects. When used properly, admixtures will produce the intended results, such as entrained air or set acceleration, in a manner that could not be achieved economically by any other means. While admixtures are widely used to enhance the desirable characteristics of concrete, no admixture is 100% beneficial, as all admixtures can produce undesirable results under certain circumstances. To ensure that the desired results are obtained, it is essential to anticipate the effect of a given admixture on the characteristics of the plastic concrete mixture as well as on the hardened concrete, before that admixture is used in the work. Admixtures should not be used indiscriminately, and they should not be viewed as substitutes for the best general recommended concrete construction practice and procedure.

Table 2-7. Concrete Admixtures.

Type	Admixture Description
AE	Air Entrainment
A	Water Reducer
B	Set retarder
C	Set accelerator
D	Water reducer and set retarder
E	Water reducer and set accelerator
F	High range water reducer (superplasticizer)
G	High range water reducer and set retarder
S	Specific Performance, such as corrosion inhibition, shrinkage reduction, hydration stabilization, and alkali-silica reaction reduction. Note: New Type S admixtures that have not been placed on the AML would require a contract change order prior to approval of their use in a mix design.

Table 2-8 summarizes the advantages and disadvantages of admixture types commonly used for structure concrete work.

Table 2-8. Admixture Characteristics.

Admixture Type	Advantages	Disadvantages
Water-reducing	Water reduction. At constant water content, increases workability and facilitates consolidation. At constant penetration, reduces water content, which increases strength and reduces permeability. At constant water content, lignosulphonic types reduce bleeding.	At constant water content, the hydroxyated types increase bleeding. (May be an advantage under some conditions.) Mixtures with low to moderate slump may be more difficult to finish due to surface stickiness. With high range water reducers, an accelerated rate of slump loss may occur, causing a sudden loss of workability.
Set-retarding	Delays initial set time, thereby extending the time available for concrete placing and finishing.	Increases bleeding. Unless dosage is controlled, the delayed set time may result in an unwanted and excessive delay in hardening.
Accelerating	Decreases time to initial set. Increases initial rate of strength gain.	Excessive dosage may severely reduce time to initial set, or may produce flash set. Increases drying shrinkage. Accelerators with high chloride content may aggravate corrosion of embedded reinforcing steel.
High Range Water Reducer (HRWR)	Water reduction. Reduced cementitious content. Increases workability. Higher early strength and long-term strength. Reduced permeability.	Additional admixture cost. Higher slump. Must coordinate with air entrainment. Varied response to different cements. Mild discoloration or blemishing and presence of air voids on exposed surfaces.

Section 90 of the Standard Specifications covers the use of admixtures on State highway projects. The specifications list three admixture classifications: chemical, air-entraining, and lithium nitrate. Only admixtures that have been previously tested and approved may be used in the work. Admixtures that have been approved for use on State highway projects are shown on a list of approved chemical admixtures for use in concrete issued by Caltrans METS.

When more than one admixture is used, the admixtures must be compatible. That is, the admixtures must not react with each other, and the admixture combination must not produce any detrimental effect on the concrete. Compatibility should not be a concern if the admixtures are products of the same manufacturer. However, if admixtures from different manufacturers are proposed for use, the combination should be discussed with the Caltrans METS organization and approval obtained before use. If there is any uncertainty, the combination should be tested to verify compatibility.



When an air-entraining admixture is used with any other liquid admixture, the air-entraining admixture must be the first admixture dispensed into the concrete mixture. It is essential that this batching sequence be followed; otherwise the effectiveness of the air-entraining admixture may be severely impaired.

Liquid admixtures are furnished in 55-gallon drums. The drums should remain sealed until used to prevent contamination, and stored in accordance with manufacturer's recommendations, which should be shown on the label affixed to the container. For most liquid admixtures, protection from freezing will be the only special precaution indicated.

Some liquid admixtures have a limited shelf life. This should not present a problem at commercial plants where large quantities of concrete are produced and admixtures are used routinely. It may present a problem when admixtures are used infrequently and only in small amounts.

Type AE, Air-Entraining Admixtures

Air-entrained concrete contains literally billions of closely spaced, microscopic-sized air bubbles uniformly distributed throughout the cement paste. Production and distribution of the air bubbles occurs during the mixing cycle by using air-entraining cement (Type IA, IIA or IIIA) or by adding an air-entraining admixture to an otherwise normal concrete mixture. Unlike entrapped air voids, which are about the size of the smaller sand particles, the air bubbles produced by air-entrainment are extremely small, ranging in size from about 1 to 3 thousandths of an inch in diameter. Because they are so small, as many as 500 billion bubbles may be present in a cubic yard of air-entrained concrete.

Entrained air improves workability by increasing the volume of the cement-water paste, helping the plasticity of the mix. The micro-bubbles of air act as ball bearings to reduce internal friction. Entrained air cushions aggregate particles, allowing them to slide past each other more easily. The improvement in workability will be particularly noticeable in lean mixes and in mixes made with angular and/or poorly graded aggregates. Without air-entrainment, the concrete mix relies on the fluidity of paste for workability; in those mixes about twice as much water would be required for a workable mix as would be needed merely for chemical reaction with the cementitious materials. The water-cement ratio is limited because of the adverse effect excessive water has on the cohesiveness of the fluid mixture and on the strength and durability of hardened concrete.



Air-Entrainment Advantages

On State projects, an air-entraining admixture will be specified wherever the estimated annual number of freeze-thaw cycles exceeds 15 and the concrete will attain high moisture content during the winter months. This includes most of Northern and Central California above the 1,000-1,500 foot elevation mark, and the mountainous regions of Southern California as well. Freeze-thaw resistance is a particularly desirable physical property in concrete that may become saturated with water. As water freezes, it expands, producing pressure within the concrete mass. This internal pressure causes stresses that exceed the tensile strength of concrete, and this in turn leads to the surface scaling and delamination, which is characteristic of freeze-thaw damage.

The ability of concrete to resist deterioration that occurs as a consequence of exposure to repeated cycles of freezing and thawing is significantly improved by the use of entrained air. In air-entrained concrete, the air bubbles produce a system of spherical air voids that serve as reservoirs to accommodate the expansion of free water within the concrete mass. As the water freezes, the expansive pressure is relieved as the excess water volume is taken up by the air voids, thus preventing damage to the concrete. The phenomenon is similar to leaving a gap of air at the top of a water bottle when you freeze it, so that the bottle will not burst.

There are additional benefits, which include improved workability, reduced bleeding and segregation of fresh concrete, and lower permeability of the hardened concrete which leads to improved resistance to damage from deicing salt and sulfates.

Air-Entrainment Disadvantages

Adding entrained air without adjusting mix proportions, will result in a slight strength reduction in most cases. The actual strength loss varies with the air content, and depends on cementitious content as well. Minor concrete, may lose a moderate amount of strength. Richer mixes will show a strength loss, acting inversely to increases in cement and air content. For strength mixes, air-entrainment will reduce the 28-day compressive strength (as compared to a similar mix without entrained air) about 5% for each 1% of air added.

If the mix proportions of a normal concrete mixture are adjusted with proper reduction in the amounts of mixing water and fine aggregate, or if the mix is properly designed for air-entrainment, the resulting strength reduction will be small and more than offset by improved workability and increased durability.

When high strength is required, as will be the case for some prestressed concrete construction, the use of air-entrained concrete may make it more difficult to attain the specified strength. Even though air-entrainment will permit a reduction in the amount of mixing water, obtaining

the specified strength will generally require an increase in the cement content, and this in turn will increase the water demand. This increased water demand will offset, to some extent at least, the initial water reduction made possible by air-entrainment. When the specified strength of air-entrained concrete exceeds about 4,000 psi, a water-reducing admixture will usually be required as well.

Both the rate at which bleeding occurs and the amount of bleed water reaching the surface are reduced by air-entrainment. The air bubbles in the paste buoy up the aggregate and cement particles; this action reduces their rate of settlement toward the bottom of the concrete mass after placement. Bleeding is retarded because water in the mixture moves less easily through the barrier created by the billions of microscopic-sized air bubbles. When entrained air is present in a concrete mixture, the rate of settlement is reduced; if reduced enough, the bleed water formed will evaporate as soon as it reaches the surface, and eliminate the appearance of bleeding. Because of reduced bleeding, and with other factors remaining the same, air-entrained concrete can be finished sooner than ordinary concrete. Reduced bleeding might be an adverse finishing factor during periods of hot weather.

The Air-Entrainment Process

All concrete contains voids that are the result of air bubbles produced by mechanical agitation of the concrete as it is mixed. Most of these bubbles, which are about the same size as the smaller grains of sand, either dissipate or escape from the mix before the concrete hardens. Some, however, become trapped between the smaller sand particles and cannot escape or dissipate; hence the term “entrapped” air. In most ordinary concrete, the entrapped air voids constitute about 1 to 1.5% of the total volume of the hardened concrete.

The voids in air-entrained concrete are also the result of air bubbles formed during the mixing process. Mixers of the rotating drum type, such as those used on transit mixers, are particularly effective in their ability to produce the myriad of bubbles that is characteristic of air-entrained concrete. Air-entraining admixtures function in two ways to produce air-entrained concrete. First, the surface tension of water is reduced, which enables the shearing action developed as the mixer drum rotates to create smaller bubbles. Second, the hydrophilic (charged) end of the admixture molecule is attracted to the cement grains while the hydrophobic (water repelling) end forms a coating on the air bubbles, encasing the bubbles in a film of air-entraining agent and cement. The film is cohesive and imparts a high degree of stability to the normally fragile air bubbles, which prevents them from coalescing or dissipating.



Most air-entraining admixtures are organic materials which are classified chemically as surfactants³ or surface-active agents. The most widely used and the oldest, air-entraining substance is neutralized vinsol resin. Vinsol resin is a by-product of the process that removes various solvents and resins from pine wood pulp. In its natural state, vinsol resin is insoluble in water and must be neutralized with sodium hydroxide to form a soluble soap which is the basis of the commercial formulations. Besides vinsol, other commercial air-entraining agents are made from petroleum distillates, animal and vegetable fats and oils, and synthetic materials.

There are a number of air-entraining admixtures on the market today, and several brands are approved for use on State highway projects. All function in the same way, and based on lab tests, no particular brand is clearly superior to the others. However, under field conditions one admixture may produce more consistent results than another, for reasons that may not be evident at the time. Because of this, changing admixture brands may be helpful in any case where results are erratic for no apparent reason.

Dosage

The obvious factor affecting the air content of a given batch of air-entrained concrete is the amount or dosage of air-entraining admixture used in the batch. All admixture manufacturers furnish recommended dosage rates to achieve specified air content, but these rates should be viewed as no more than starting estimates since the actual dosage for a given set of conditions will depend on a number of other factors. The cementitious content, water-cement ratio, fine-coarse aggregate ratio, use of other admixtures, concrete temperature, transit batching, delivery, and construction methods employed will all affect air content to some degree. The effect of each admixture must be considered to obtain the maximum effectiveness of the air-entraining admixture.

As the cement content of a concrete mixture is increased, the proportional amount of air-entraining agent needed per unit of cement increases as well. To maintain a given air content in a concrete mix of normal consistency (ball penetration of about 1 to 2 inches), the required dosage will increase as cementitious materials are added.

Cement particle size is a factor for consideration, with finer grinds requiring a higher dosage than coarser grinds to obtain the same air content. Type III cement may require as much as twice the amount of the same air-entraining admixture as a Type I or Type II cement to maintain the same air content. The use of fly ash will increase the amount of air-entraining

³ The term "surface-active" designates a substance that is capable of reducing the surface tension of the liquid in which it is dissolved. Such substances have a linear molecular structure in which one end of the molecule is hydrophobic (repels water) and the other end is hydrophilic (has an affinity for water) and is electrically charged.

agent needed when compared to a similar concrete with no fly ash. Ultra-fine SCMs like silica fume require increased dosages for comparable air-entrainment levels. This is due primarily to the greater fineness of the pozzolanic particles.

The amount of alkali present in cement will affect air content to some degree. Low-alkali cements, such as those specified for State highway work, require a 20 to 40% higher dosage than regular cements.

Water Content

The amount of water in the mix has a significant effect on air content. As water is added to a mix, there is more free water available for the generation of air bubbles; consequently, the addition of water in even small amounts will usually result in an increase in the air content of a given concrete mixture with no increase in admixture dosage. Other factors being equal, mixes with lower water-cement ratios will require larger dosages of air-entraining agent than mixes with higher water-cement ratios. When air-entrained concrete is used for cast-in-place prestressed construction, specified concrete high-strength requirements will dictate a low water-cement ratio mix design, and this may make it difficult to obtain the specified air content at normal admixture dosage rates. In such cases, the use of a water reducing admixture will produce a more fluid mixture and make it easier to obtain the specified air content.

Mixes with very low water-cement ratios, such as those used for bridge deck overlays where the w/c ratio may be as low as 0.32 or less, will require a substantial increase in the amount of air-entraining agent, possibly as much as 10 times the normal dosage, to obtain the specified air content. If a high range water reducer is also used, additional air entrainment may be needed.

Aggregate

Fine aggregate contributes to total air content by retention of air bubbles in the sand grain interstices, so that an increase or decrease in fine aggregate will increase or decrease the air content as well. For example, a 1% increase in the fine aggregate (with a corresponding decrease in coarse aggregate) will cause the total air content to increase about 0.1%. Thus a more heavily sanded mix will require a lower air-entrainment dosage to obtain the same air content. An excessive amount of very fine material (material passing the No. 200 sieve) will reduce the total air content. Therefore, when the fine aggregate has a relatively low sand equivalent value, a larger dosage of admixture will be required to produce a given air content. Coarse aggregate with a low cleanness value will have the same effect.

Other Admixtures

In general, less air-entraining agent will be needed to produce a given air content when a water reducing admixture is also used. For lignosulfonate-based materials, the required dosage of the air-entraining admixture may be reduced by as much as 80% of the amount that would be needed if no water reducer were used. For organic-acid types, the expected reduction will be lower, ranging from about 20 to 40%.

The effect of high-range water reducers on air content is not always predictable. Reductions of up to 50% in the amount of air-entraining agent needed have been achieved in some cases; in other cases the dosage requirement was actually increased. Highly fluid mixtures occasionally experience a loss of air content with time, and it has not been possible in all cases to achieve the specified air content even though additional air-entraining agent is added. Other factors that influence air content, such as cement and aggregate, and the concrete temperature, may have a more pronounced effect when high-range water reducing admixtures are used. Because of the uncertainties associated with the use of high-range water reducers, trial batches are recommended to ensure an adequate concrete mix.

Mixing

Mixing action is the most important factor in the production of air-entrained concrete. Because of differences in mixing time and mixing action and with other factors being equal, the amount of air entrained for a given dosage will vary with the type and condition of the mixer, the amount of concrete being mixed, and the mixing rate.

As a general rule, more air will be entrained as the mixing speed is increased, within the range of mixing speeds recommended by the manufacturer. Also, increased air content may occur if the mixer is loaded to less than its rated capacity; however, decreased air content may result from overloading.

Prolonged mixing will cause a significant reduction in the air content of a given mixture. Loss of air is the result of reduced fluidity that occurs over time. Loss of fluidity decreases the ratio of air formation to air escape, resulting in a net air loss. Furthermore, since air-entrainment improves initial workability, a reduction in the air content decreases fluidity independent of any other cause, and this has a compounding effect that accelerates the air loss. (As fluidity is decreased, air formation decreases as well. The net air loss further decreases fluidity, which increases the rate at which air loss occurs. The effect is exacerbated as fluidity is reduced significantly during the latter part of the mixing period.)

In most cases air content can be restored by adding water to increase the fluidity of the mix. However, additional water increases the water-cement ratio and reduces ultimate strength.

Concrete Temperature

The temperature of the concrete affects the air content, with less air being entrained as concrete temperatures increase. The relationship between temperature and air content is roughly linear, but inversely acting; that is, an increase in concrete temperature will produce a commensurate decrease in air content, while a decrease in concrete temperature will increase the amount of air in the mix, other factors remaining equal.

For a typical strength concrete mix, experience has shown that an internal temperature variation of about 20°F will result in a corresponding change in the air content of about 30% for the same admixture dosage. This means that a 20°F rise in temperature will require a 30% increase in the admixture dosage to maintain the same air content. A falling temperature will require a similar decrease in dosage.

With other factors remaining unchanged, the normal air temperature variation expected during the course of a typical concrete pour can produce a wide fluctuation in the air content. In view of this, the effect of temperature variation should be anticipated and admixture dosages adjusted accordingly.

Vibration

Tests have shown that the amount of vibration needed to adequately consolidate a properly proportioned concrete mixture does not result in any significant loss of entrained air. There is some air loss, but this is primarily in the form of large bubbles of entrapped air; there is little loss of intentionally entrained air during normal vibration, which should not exceed about 15 seconds.

Excessive vibration can have a negative effect on air content. Air loss during vibration is also a function of the consistency of the concrete as measured by the ball penetration test. That is, for a given amount (time) of vibration, the air loss will increase as the penetration increases.

Type A--Water Reducing Admixtures

Water reducing admixtures decrease the amount of mixing water needed to produce concrete of a given consistency by at least 5% and more typically 6-10%, thus allowing the use of a lower water-cement ratio for a given workability or increased workability for a given water-cement ratio and fixed cement content. Water reducers cannot advance set time by more than 1 hour or retard set time by more than 1.5 hours. Water-reducing admixtures increase the fluidity of the cement paste by lubricating and disbursing the cement particles and decreasing the surface tension of the water. Generally, water reducers do not act on supplementary cementitious materials.



Based on their chemical composition, most commonly used water reducing admixtures fall into one of three groups:

- The HC group, which contain salts and various modifications of hydroxylated carboxylic acids.
- The LS group, commonly called “lignins”, which contain salts and various modifications of ligno-sulfonic acids.
- The PS group, which are composed of polymer compounds.

For most admixture brands, some set retardation will occur at normal dosages, even with those admixtures (ASTM Type A) that are not marketed as retarders. Typically, set retardation will not exceed 1 hour for Type A admixtures. Overdoses, caused by considering SCM as Portland cement can cause the set time to exceed 1 hour.

When used at the manufacturer’s recommended dosages, a water reduction of 6 to 10% is typical for all normal range admixtures. Increased water reduction can be achieved with higher dosages, but this may result in excessive retardation.

Typically, the HC and PS water reducers increase the rate at which bleeding occurs, but because the total water content is reduced, the actual amount of bleed water reaching the surface is about the same as would be the case for a similar concrete without the water-reducing admixture. The lignin-based water reducers reduce the bleed rate, and this may cause problems in hot, dry or windy conditions. At maximum dosages, slump and workability loss will occur at a faster rate than similar concrete without an admixture.

The HC and PS admixtures do not entrain air, but since they produce a more workable concrete, less air-entraining agent is required to produce a given air content when these admixtures are used. The lignin based admixtures (LS) normally add about 1 to 2% mixed air to the mix.

Type B – Retarding and Type D – Water Reducing and Retarding Admixtures

The principal use of set retarders is to delay the initial set for a predetermined period of time to compensate for the effect of accelerated setting that normally occurs during hot weather. Retarders may be used in concrete intended for large volume footings, piers and similar locations where a delay in setting is advisable to eliminate cold joints and facilitate bonding of successive lifts. Many set retarding admixtures also function as water reducers, and these are called water-reducing retarders. Mixing water reductions of 5 to 10% are typical for these retarders.

Commercially available retarders and water-reducing retarders are formulated to delay setting from 1 to 3 hours, and the admixture manufacturers will provide dosage recommendations to achieve the delay desired. However, the actual delay for a given dosage is difficult to predict, because the concrete temperature, cementitious properties, and the water-cement ratio will affect the performance of the admixture. The use of trial batches is recommended in any situation where it is necessary to ascertain the delay time in advance with a reasonable degree of precision.

Once the initial set has occurred, retardation has little effect on early strength development, with normal strength being reached within 1 to 2 days following placement. When a retarder having water reducing properties is used, the 28-day strength is often 10 to 20% higher than comparable non-retarded concrete.

Type C – Accelerating and Type E – Water Reducing and Accelerating Admixtures

An accelerating admixture is a substance which, when added to a concrete mixture, will shorten the time to initial set, or increase the rate of hardening and strength development, or both. Until the concrete sets, accelerators have no direct effect on the properties of plastic concrete. Bleeding is usually reduced, but this is attributed to rapid hardening rather than any change in the plastic concrete itself. The most important consideration is the shorter time available to place, consolidate, and finish the concrete when an accelerator is used. Concrete temperature affects the setting time to some degree, and most accelerators are more effective, i.e., the rate of acceleration is increased, at the lower end of the allowable concrete temperature range.

The most widely used accelerating admixture is calcium chloride, which is a soluble inorganic salt. Calcium chloride shortens the setting time by accelerating the hydration of the tricalcium and dicalcium silicate compounds in the cement. Calcium chloride increases the early strength of concrete as well; typically, about 75% of the expected 28-day strength is reached within 3 to 5 days.

Calcium chloride is available commercially as a liquid solution or in the form of dry flakes. Under the current specifications, neither form may be used as the chloride ion induces reinforcement corrosion. However, from a quality control standpoint, the use of liquid-calcium chloride is preferred since it is added with the mixing water and uniformly dispersed throughout the mix. When added in dry form, there is less assurance that all particles are dissolved prior to discharge, particularly when the mixing period is relatively short. If flakes must be used, consideration may be given to dissolving the flakes in a measured amount of water and adding the resulting solution to the mixing water prior to batching. Because of its



tendency to promote corrosion of embedded steel, most authorities no longer recommend the use of calcium chloride for prestressed construction or in any reinforced concrete structure in a moist environment. Note that under current policy, the use of calcium chloride, or any other accelerator containing chlorides, is not permitted in structures on State highway construction projects under any circumstances.

Moderate acceleration of early strength gain may be achieved by using a calcium-nitrite corrosion inhibitor. While not marketed as an accelerator, calcium nitrite will promote both accelerated set and early strength. Typically, the expected 28-day strength will be attained in about 7 to 10 days. If desired, a retarder can be used to offset the adverse effects of rapid setting, with no adverse effect on early strength gain.⁴

Type F – High Range Water Reducers and Type G – High-Range Water Reducer and Set Retarder

The principle difference between the high-range water reducers (HRWR) and high range water reducer and set retarders is the ability of the high-range water reducers to produce a highly fluid, flowing concrete at normal water-cement ratios or a workable concrete at greatly reduced water-cement ratios. When high-range water reducers are used, the admixture is measured and dispensed in accordance with the manufacturer's recommendations. Note that this may include adding all or a portion of the admixture at the job site.

HRWRs are relatively new admixtures, having first appeared on the market in the mid-1970s. Because of their ability to produce flowing concrete, they are often referred to as superplasticizers. Typically these HRWRs will be used for one of the following reasons:

- To create self-leveling, flowing concrete without increasing the water content and without sacrificing strength. When used to produce flowing concrete, a typical HRWR will transform a relatively stiff conventional concrete mixture with a ball penetration reading of 1 inch into a fluid, self-leveling mixture with a ball penetration reading of 4 inches or more.
- To produce high-strength concrete by reducing the water content and thus the water-cement ratio, but without any loss of workability. When used as water reducers, HRWRs permit the reduction of as much as 30% of the water in a conventional mixes with no loss of slump or workability.

⁴ Although several products are marketed commercially as corrosion inhibitors, only the calcium nitrite materials are also accelerators. Calcium nitrite inhibitors are furnished in liquid form. Because of the relatively large quantity required, the mixing water volume is reduced by the volume of admixture added.

- To save cement by reducing both the water and the cement content while maintaining the same water-cement ratio and the same degree of workability. When used to save cement, HRWRs will permit a reduction in cement of up to 15% while maintaining the same concrete strength.

HRWRs are made from the salts of organic sulfonates. Depending on their primary purpose, they are divided into two types. The pure water reducers (ASTM Type F) are formulated from formaldehyde condensates of naphthalene or melamine sulfonic acid. The HRWR retarders (ASTM Type G) are made by blending hydroxyl compounds and ligno-sulfonic acid. Both HRWR types may be used to obtain the water reduction required; however, the ASTM Type G admixtures will delay the initial set as well. Depending on dosage, the delay will range from 30 minutes to 2 hours, or more.

HRWRs function by dispersing the cement particles; therefore, they will function most efficiently in concrete that is rich in cement or contains a mineral additive such as fly ash

When an HRWR is added to a normal concrete mix to produce a high-slump, flowing mixture, the concrete often segregates and bleeds. To prevent this, the mix must be redesigned to thicken the sand-cement paste. This is usually accomplished by increasing the fine aggregate by 4 or 5% or by adding a pozzolanic material. Regardless of the fines content, there is a maximum HRWR dosage beyond which segregation is inevitable in a flowing mixture.

Segregation and bleeding will not be increased when an HRWR is used simply to reduce the water content of a mix that remains within the normal consistency and workability range.

HRWRs have an unpredictable effect on air content. In theory, the amount of air-entraining agent needed should be increased when the naphthalene or melamine-based water reducers are used and decreased when the lignosulfonate-based retarders are used. However, this does not always occur in practice, so frequent testing for air content is indicated.

All superplasticized mixes experience a rapid loss of slump after the admixture is added. As the slump loss occurs, the mix gradually returns to its original consistency. Depending on temperature, humidity, cement characteristics, and other factors that affect slump loss, the slump change achieved by the superplasticizers is usually lost within 45-60 minutes or sooner, if the mix temperature is above about 70°F. If slump loss occurs because of delayed concrete placement or some other reason, the intended characteristics of the superplasticized mix can be restored by one or more additional dosages of the admixture. However, each additional dosage reduces the amount of entrained air by 1 to 1.5%, so that an additional dosage of air-entraining admixture may be required as well.



Other than loss of air content, increasing the dosage to offset slump loss will have no detrimental effect on the concrete if an ASTM Type F admixture is being used. If a water-reducing retarder (ASTM Type G) is being used, however, the set retardation time will be increased proportionally to the amount of admixture added. Accordingly, some caution is advisable when considering an increase in the dosage of any Type G admixture to offset actual or anticipated slump loss.

Because the effect of the HRWRs is lost so quickly, they are usually added at the site rather than at the batch plant. When transit mixers are being used, the admixture should be mixed with a small quantity of water, and then added to the concrete at the front of the mixing drum through a pipe or hose placed inside the drum. Any additional air-entraining agent should be added at the same time. (Note that the mixer drum must be stopped while the admixtures are added.) Adding admixtures to the concrete at the discharge end of a transit mixer drum is not recommended because this procedure does not ensure a uniform dispersal of the admixture throughout the mixture. In view of the many uncertainties associated with the use of HRWRs, the use of one or more trial batches is recommended to determine the amount of admixture needed to achieve the intended results and, if air-entrained concrete is required, to ascertain the effect of the HRWR on air content.

Type S – Specific Performance Admixtures

Performance requirements outside the bounds of water reduction and set modification are classed as Type S admixtures. The dry-cast concrete industry uses a no-slump concrete that is compacted into precast molds by extreme vibration, packing or centrifugal spinning. Specific performance admixtures are added to dry-cast concrete for plasticizing, water repulsion, and efflorescence control. With transportation structures, specific performance admixtures (Table 2-9) are used to produce concretes with additional properties.

Table 2-9. Type S (Specific Performance) Admixture Working Characteristics.

Admixture Purpose	Advantages	Disadvantages
Shrinkage Reducing	Reduces surface tension of water to reduce cracking associated with drying shrinkage during early age curing by reducing water mass loss.	May delay set-time and reduce early strength. Requires optimization with air entrainment. High cost.
Corrosion Inhibitor	Blocks corrosive action of chlorides on reinforcing steel. Decreases permeability. Interrupts creation of galvanic response.	May accelerate initial set. Cracking reduces effectiveness.
Alkali-Silica Reaction Inhibitor	Reduce ASR by forming non-expansive gel with reactive aggregate. Requires SCM use to mitigate excess heat of hydration.	Accelerated hydration, heat generation, and set time. May increase shrinkage and reduce workability. High cost.
Viscosity Modifier	Controls bleeding. Reduces segregation while flowing through formwork. Improves workability. Promotes uniform surface appearance.	Overdosing leads to decreased workability, retarded set, and coarse air bubbles. Underdosing leads to low viscosity, bleeding and segregation. May require HRWR to retain workability.
Rheology Modifier	Improves placement, consolidation and finishing in low slump and slip-form mixes that could result from use of ultra fine SCMs, manufactured aggregate, or reduced water. Reduces concrete pump pressure requirements.	Similar to Viscosity Modifiers