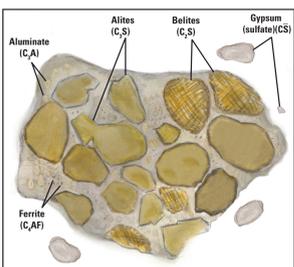


# Stages of Hydration

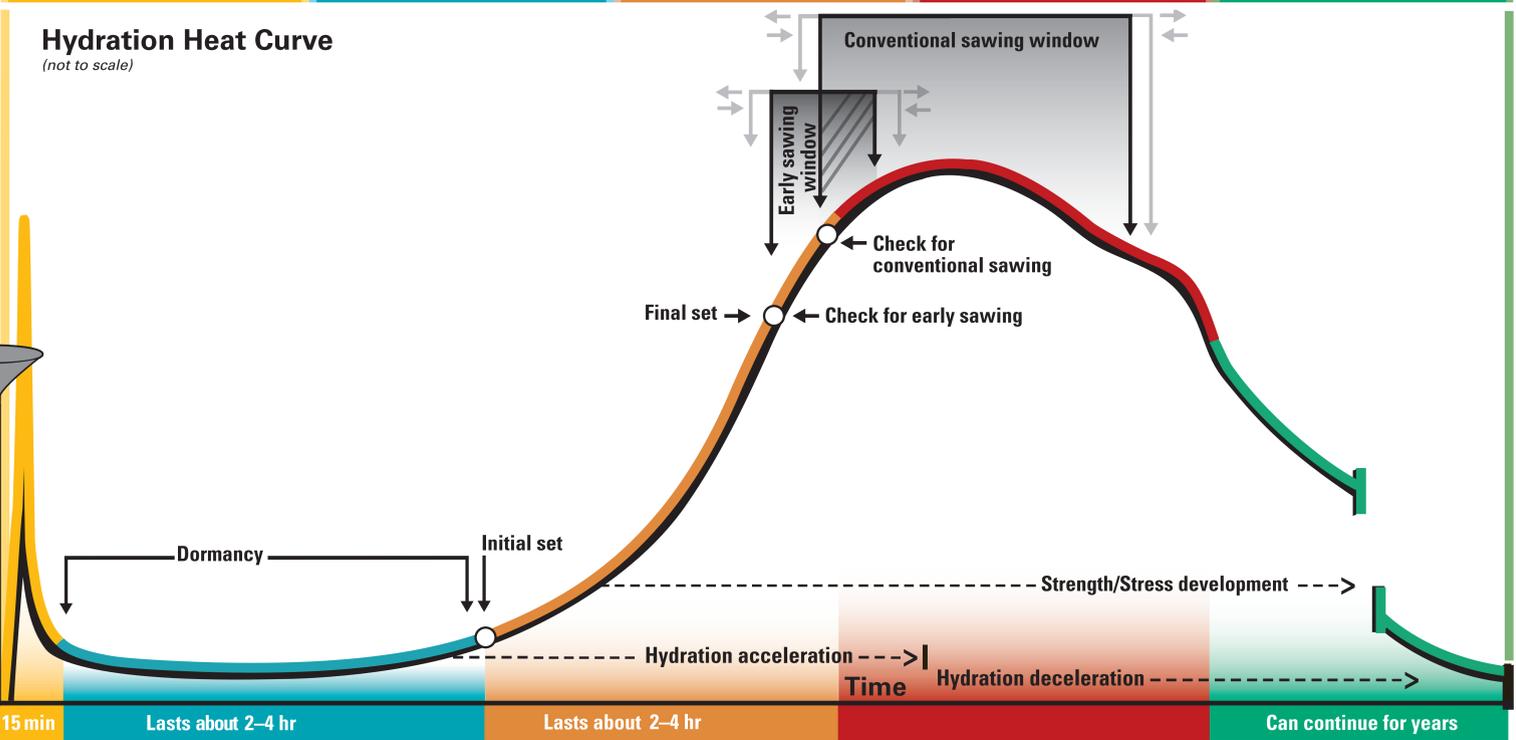
<b>Cement compounds</b>
<b>Silicates</b>
Alite (C <sub>3</sub> S)
Belite (C <sub>2</sub> S)
<b>Aluminates*</b>
Tricalcium aluminate (C <sub>3</sub> A)
Ferrite (C <sub>4</sub> AF)
<b>Sulfates (CS)</b>
Gypsum (dihydrate)
Plaster (hemihydrate)
Anhydrite
<b>Products of hydration</b>
Calcium silicate hydrate (C-S-H)
Calcium hydroxide (CH)
Etringite (C-A-S-H)
Monosulfate (C-A-S-H)
Carboaluminate (C-A-C-H)
(portland-limestone cements only)
<i>Carboaluminate is a minor compound formed in portland-limestone cement.</i>
<i>* In the Stages of Hydration chart, "aluminate" refers generically to tricalcium aluminate (C<sub>3</sub>A). Ferrite (C<sub>4</sub>AF) hydration does not contribute significantly to concrete properties.</i>

## Physical Changes in Cement Particles



Unhydrated cement

Stage 1: Mixing	Stage 2: Dormancy	Stage 3: Hardening	Stage 4: Cooling	Stage 5: Densification
<p>Within minutes of mixing cement and water, the aluminates start to dissolve and react, with the following results:</p> <ul style="list-style-type: none"> <li>Aluminate* reacts with water and sulfate, forming a gel-like material (C-A-S-H). This reaction releases heat.</li> <li>The C-A-S-H gel builds up around the grains, limiting water's access to the grains and thus controlling the rate of aluminate reaction. This gel formation occurs after an initial peak of rapid hydration and heat generation.</li> </ul>	<p>For about two to four hours after mixing, there is a dormant period, during which these events occur:</p> <ul style="list-style-type: none"> <li>The C-A-S-H is controlling aluminate* reactions. Little heat is generated, and little physical change occurs in the concrete. The concrete is plastic.</li> <li>During dormancy, as silicates (C<sub>2</sub>S and C<sub>3</sub>S) slowly dissolve, calcium ions and hydroxyl (OH) ions accumulate in solution.</li> </ul>	<p>This stage is dominated by C<sub>2</sub>S hydration and the resulting formation of C-S-H and CH crystals:</p> <ul style="list-style-type: none"> <li>When the solution becomes supersaturated with calcium ions from dissolving C<sub>2</sub>S primarily, fiber-like C-S-H and crystalline CH start to form. These hydration products nucleate on cement grains, SCM particles, and also ground limestone particles in portland-limestone cement (PLC). These hydration reactions generate heat. Meshing of C-S-H with other solids causes the mixture to stiffen.</li> <li>The increasing heat and stiffening of the cement paste mark the beginning of hydration acceleration, which lasts several hours. Initial set occurs early in this stage.</li> <li>Final set—about when the concrete is hard enough to walk on—occurs before heat energy peaks from C<sub>2</sub>S reactions begin to slow.</li> <li>After final set, tensile stresses start to develop.</li> </ul>	<p>After final set, the rate of C<sub>2</sub>S reactions begins to slow and the amount of heat generated peaks and begins to drop.</p> <p>During this stage, several things are occurring:</p> <ul style="list-style-type: none"> <li>The concrete is gaining strength, as the amount of C-S-H and CH increases. However, the concrete is still somewhat porous and should carry only light construction traffic.</li> <li>Tensile stresses may be building faster than tensile strength. At some point, stress will exceed strength, causing the concrete to crack. Unless joints are sawed to control crack location, random cracking will occur.</li> <li>Sometimes after the temperature peaks, C<sub>2</sub>S, which has continued reacting with aluminate* (see Stages 1 and 2), will be depleted. Any remaining aluminate* now reacts with ettringite to form monosulfate, which may be associated with a brief increase in heat.</li> </ul>	<p>This stage is critical for continued development of concrete strength and reduction of concrete permeability. The concrete must be kept moist as long as possible for the following reasons:</p> <ul style="list-style-type: none"> <li>As long as C<sub>2</sub>S remains and there is water in the concrete, the C<sub>2</sub>S will continue to hydrate. As the volume of hydration products grows, concrete porosity and permeability decreases, and the concrete gains strength. Eventually, the products—particularly C-S-H—will combine into a solid mass.</li> <li>C<sub>2</sub>S, which reacts more slowly than C<sub>3</sub>S, also produces C-S-H. After several days, in the presence of water, most of the C<sub>2</sub>S has reacted and the rate of C<sub>2</sub>S hydration begins to be noticeable. It is important to maintain sufficient moisture long enough for C<sub>2</sub>S reactions to occur.</li> <li>Hydration products will continue to develop, permeability will continue to decrease, and strength will continue to increase slowly for days, weeks, even years.</li> </ul>



## Effects of Supplementary Cementitious Materials

SCMs, like fly ash and slag cement, are included in more than 60 percent of concrete mixtures in the US. In general, SCMs consist of the same basic elements—oxides of silicon, aluminum, and calcium—and perform basically the same function as cement. Pozzolans require a source of CH to hydrate, usually provided by hydrating portland cement. SCMs are used in concrete to achieve desired workability, strength gain, and durability.



Fly Ash

Slag

Stage 1: Mixing	Stage 2: Dormancy	Stage 3: Hardening	Stage 4: Cooling	Stage 5: Densification
<p>If the SCMs contain large amounts of calcium (e.g., Class C fly ash), the calcium may be in the form of aluminate*, which will increase the risk of flash set if there is insufficient CS in the solution.</p> <p>Fly ashes with high loss-on-ignition (LOI) may interfere with development of the air-void system because high LOI fly ashes contain unburned carbon that adsorbs air-entraining admixture (AEA). Higher and more variable dosages of air-entraining agents may be required.</p> <p>Mixtures with SCMs may require less water to achieve workability.</p> <p>Mixtures using PLC may have a slight variation in water demand as compared to portland-only cements; it may increase or decrease (Tennis et al. 2011).</p>	<p>Like portland cement, during dormancy the silicates in SCMs are slowly dissolving and releasing calcium ions and OH ions. Contributions of ground limestone to PLC may slightly reduce the duration of the dormant period.</p>	<p>Silicates in the SCMs react with the CH from the cement reactions to form additional C-S-H, thus reducing porosity of the system and increasing strength and durability. These reactions are slow and may only be noticeable in Stage 5. They will continue for a long time and generally lead to higher long-term concrete strengths.</p> <p>In mixtures with SCMs, note the following:</p> <ul style="list-style-type: none"> <li>Setting time may be delayed, and working time may be extended. Heat and rate of hydration are often reduced, and the duration of hydration is extended.</li> <li>Cold weather construction may increase these effects.</li> </ul> <p>In mixtures using PLC, note the following:</p> <ul style="list-style-type: none"> <li>Setting time may slightly increase.</li> <li>The heat of hydration may be higher in the early stages of hydration but equal or lower at later stages of hydration.</li> </ul>	<p>The magnitude of the primary heat peak is often reduced in systems containing SCMs due to slower hydration rate. This generally results in less shrinkage later and, thus, potentially less stress. A secondary peak may be observed as the SCMs hydrate.</p> <p>Generally, as a result of reducing the rate and heat of hydration, SCMs influence the duration and timing of the saw-cutting window. The influence depends on the system chemistry and the environment. If SCMs are being used for the first time or if sources change, then close attention is required to prevent random cracking.</p>	<p>Silicates in SCMs chemically combine with CH from cement hydration to form additional C-S-H.</p> <p>Strength development may be slower initially but continues longer, normally leading to higher long-term strength.</p> <p>Permeability is often significantly reduced, thus improving potential durability.</p> <p>Portland-limestone cements may result in higher early strengths. Slightly reduced later strengths are possible at high limestone contents.</p> <p>Systems containing slag cement and fly ash are reportedly more prone to frost damage.</p> <p>Low-calcium fly ash and slag cement are effective in reducing alkali reactivity of mixtures for three reasons:</p> <ul style="list-style-type: none"> <li>Mixture's alkali content</li> <li>Concrete permeability</li> <li>System's calcium/silica ratio</li> </ul> <p>High-calcium fly ashes may have the same effect, and they should be tested using the materials under consideration.</p>

## Effects of Chemical Admixtures

Water reducers work by dispersing clusters of cement grains and releasing water trapped in the clusters. Water reducers may increase initial workability but may not slow slump loss with time. Polycarboxylate water reducers may increase air entrainment.

Type A water reducers increase the rate of aluminate\* hydration and, therefore, the risk of flash set. They also slow the rate of C<sub>2</sub>S hydration, slowing strength gain. High-range (Type F) water reducers are less prone to incompatibility.

**Air Entrainers:** Air-entraining admixtures work by stabilizing small air bubbles in the paste. The greater the slump, the easier it is for air to be entrained.

**Accelerators:** Accelerators will shorten the time required to reach initial set, and this fact should be considered when hauling freshly mixed concrete.

**Retarders:** Set-retarding admixtures may increase air content.

**Retarders:** Retarders work by forming a layer around cement grains, which causes the cement to dissolve more slowly. This delays initial set and the start of the acceleration period. The amount of heat generated may occur slightly later and be slightly lower, but heat generation may be extended longer. Mixtures containing retarders tend to have a finer, less-permeable microstructure, leading to better long-term strength and durability.

**Accelerators:** Accelerators shorten the dormant period, leading to earlier setting, and often result in a higher temperature peak. The mechanism behind the acceleration is not fully understood, although silicate hydration is faster. Chloride-based accelerators increase the risk of corrosion of any noncoated steel embedded in the concrete.

## Implications of Cement Hydration for Construction Practices

If using dump trucks or agitator trucks, mix the materials and place the mixture into the transport vehicle. Watch for stiffening during transportation (see early stiffening under Incompatibilities below).

If using ready-mix trucks, place materials into truck and mix during transport.

In both cases, ensure adequate mixing is provided in accordance with applicable specifications.

Transport, place, finish, and texture the concrete during the dormant period, before initial set, while the concrete is cool, plastic, and workable.

Use transport methods and equipment that will prevent segregation.

If visible bleeding occurs, finish the surface after bleeding has stopped and bleed water has evaporated. Do not work bleed water back into the surface because it increases porosity and permeability of the surface layer. In hot weather, bleeding may be helpful in reducing plastic shrinkage cracking.

If necessary (e.g., in hot, windy weather) apply a polymeric evaporation retarder before finishing to reduce the potential for plastic shrinkage cracking.

To prevent random cracking due to build-up of tensile stresses, saw joints during the sawing window:

- The sawing window begins when the concrete is strong enough not to ravel when sawed and ends before the concrete cracks in front of the saw, no later than 24 hours after placement.
- Using conventional saws, the sawing window generally begins after final set but before the concrete heat reaches a maximum.
- For early-age saws, the window may begin at final set (Stage 3) and will end earlier than for conventional sawing.

Cover the slab, especially if temperatures will cool significantly during the first night, to prevent curling, warping, and related cracking.

Keep concrete thoroughly covered and protected with curing compound as long as possible, at least for the first 72 hours after mixing.

The longer the curing compound remains in place (i.e., the concrete remains protected from equipment and construction traffic), the more moisture will be retained in the concrete for hydration, increasing strength development and reduction of permeability.

## Incompatibilities: Early Stiffening/Retardation

The risk of incompatibilities occurring is higher

- When using finer cementitious materials
- At low water/cementitious materials ratios
- At high temperatures

If solution has insufficient CS for the amount of aluminate\*, uncontrolled aluminate hydration may cause rapid, permanent stiffening or flash set. This is characterized by a temperature rise. Aluminate hydration is accelerated by some Type A water-reducing admixtures and high temperature; more CS may be needed to maintain an adequate shell around the aluminate\* particles to control flash set.

Excess CS in solution results in gypsum crystals being deposited out, prematurely stiffening the system, resulting in (temporary) false set. The gypsum eventually dissolves as the mixture is mixed, which is why false set is temporary.

If calcium is consumed by poorly controlled aluminate reactions earlier in Stage 1, then supersaturation of calcium ions will be slowed and C<sub>2</sub>S hydration retarded. This retardation can potentially continue for several days, severely delaying or even preventing setting. It is possible to have a mixture that exhibits false set, followed by severe retardation.

C<sub>2</sub>S hydration is accelerated by high temperatures, high alkali contents (from cementitious materials), and high cement fineness. This accelerates setting, which can accelerate the start of, and shorten the duration of, the saw-cutting window.

C<sub>2</sub>S hydration is retarded by some Type A water-reducing admixtures and low temperatures, slowing setting and thus delaying the beginning of the saw-cutting window.

## Implications of Cement Hydration for Cracking

Cement paste changes with temperature variations more than aggregate and also shrinks as it sets; drying will exacerbate this shrinkage. Objects that are restrained when they shrink or expand will be stressed, leading to cracking if the stresses exceed the material strength. It is desirable to reduce paste content within a given mixture, while still achieving workability and filling all the voids between aggregate particles.

The volume of aggregate is significantly larger than the volume of paste, and it tends to control the amount of thermal movement of concrete. If aggregate with a low coefficient of thermal expansion (CTE) is used, the risk of cracking problems will decrease. Concrete with high paste content and high fines content will be at higher risk of cracking.

Because chemical reaction rates generally increase at higher temperatures, an increase in the initial mixing temperature significantly increases the amount of heat generated, and corresponding stress development, in Stage 3.

Drying, and the consequent shrinkage, any time before final set may result in plastic shrinkage cracking.

When concrete sets at high temperature, stresses can develop because the concrete cools and shrinks more than concrete that sets at a lower temperature. The increased stresses may increase the potential for random cracking.

Drying, and the consequent restrained shrinkage, before sufficient strength gain may result in random cracking.

If setting is delayed, concrete may crack because it dries while the concrete is still too soft to start saw cutting.

Faster setting may result in the concrete cracking before sawing can be completed because the sawing window is shorter than the time required for sawing.

Cementitious systems with high alkali content, aluminate\* content, and fineness may shrink more than other systems, therefore increasing the risk of random cracking.

Modeling programs like HIPERPAV can be used to predict the sawing window more accurately for a given set of circumstances, helping to reduce random cracking.

After concrete has set, it tends to dry and cool more quickly at the top surface, setting up differential stresses through the thickness of the slab. This will cause the top and bottom surfaces to expand or contract different amounts, resulting in curvature known as warping and curling. Depending on the support conditions and the extent of the curvature, stresses on the curved/warped slab from dead weight or traffic loadings may result in cracking.

## Implications of Cement Hydration for the Air-Void System

A good air-void system is a uniform distribution of small, stable bubbles in the finished concrete, and it is necessary for concrete durability.

See Effects of Chemical Admixtures above.

The air-void system develops during mixing. It is more difficult to entrain air in systems at high temperature, with low slump, and with very fine SCMs that have high loss on ignition (LOI) and low alkali contents. An increased AEA dosage may be required for such systems. Set-retarding admixtures may increase air content.

The stability of the air-void system (i.e., the ability to prevent bubbles from breaking during handling) depends on the chemistry of the AEA. Some air entrainers are more sensitive than others to the presence or dosage of other chemical admixtures or SCMs.

Increased handling (e.g., transportation, placing, vibration, finishing) of unstable systems may reduce the air content and affect the quality of the in-place air-void system. Air content of concrete should be tested at the delivery point and after placing to assess the stability of the air-void system.

The air-void system has been formed at this stage and is unlikely to change.