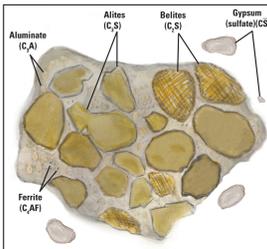


# Stages of Hydration

Cement compounds	
<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>	
<b>Calcium silicate hydrate (C-S-H)</b>	
<b>Calcium hydroxide (CH)</b>	
<b>Etringite (C-A-S-H)</b>	
<b>Monosulfate (C-A-S-H)</b>	
* 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.	

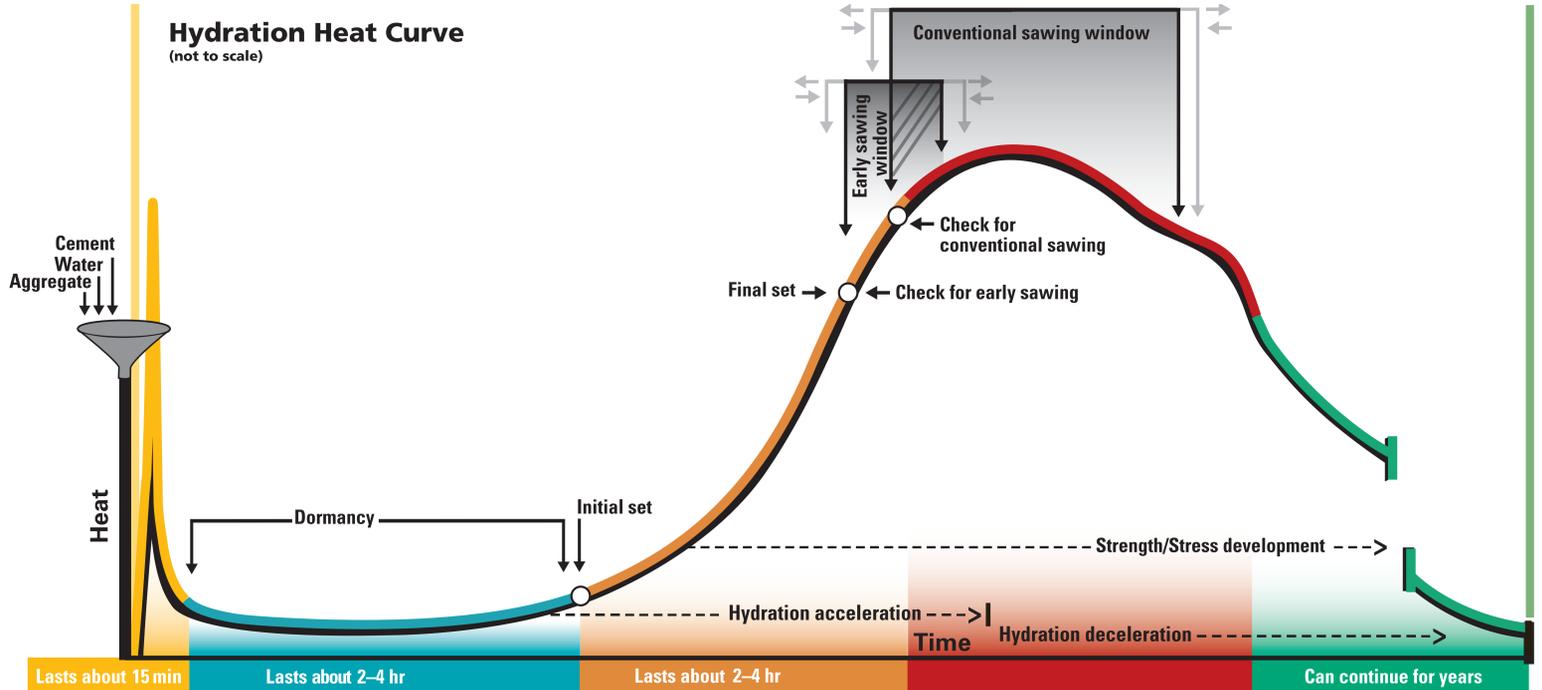
## Physical Changes in Cement Particles



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 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 the following events occur:</p> <ul style="list-style-type: none"> <li>The C-A-S-H gel 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 (alite (C<sub>3</sub>S) and belite (C<sub>2</sub>S)) slowly dissolve, calcium ions and hydroxyl (OH) ions accumulate in solution.</li> </ul>	<p>This stage is dominated by alite (C<sub>3</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 super-saturated with calcium ions (from dissolving alite (C<sub>3</sub>S) primarily), fiber-like C-S-H and crystalline CH start to form. This generates heat. Meshing of C-S-H with other solids causes the mixture to stiffen and set.</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>Acceleration is characterized by a rapid rate of hydration, significant heat, continued hardening, and strength development.</li> <li>The rates of reaction are faster for finer cementitious materials and for systems with higher alkali contents. Slower reacting systems will react longer and will generally provide a better microstructure in the long term.</li> <li>During acceleration, aluminate* and sulfate continue to react, and needle-like ettringite (C-A-S-H) crystals form.</li> <li>Final set—about when the concrete is hard enough to walk on—occurs before heat energy peaks (before alite (C<sub>3</sub>S) reactions begin to slow).</li> <li>After final set, tensile stresses start to develop due to temperature and drying effects, the mixture's increasing stiffness, and the slab's friction with the pavement base.</li> </ul>	<p>After final set, the rate of alite (C<sub>3</sub>S) reactions begins to slow, and the amount of heat generated peaks and begins to drop. This occurs because the buildup of C-S-H and CH interferes with contact between remaining water and undissolved cement grains.</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, sulfate, 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. (Monosulfate does not significantly affect concrete properties.)</li> </ul>	<p>This stage is critical for continued development of concrete strength and reduction of concrete permeability. (When concrete has low permeability, substances like water and dissolved salts cannot readily penetrate it and it is less susceptible to freeze-thaw damage.) The concrete must be kept moist as long as possible. Here's why:</p> <ul style="list-style-type: none"> <li>As long as alite (C<sub>3</sub>S) remains and there is water in the concrete, the alite 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>Belite (C<sub>2</sub>S), which reacts more slowly than alite (C<sub>3</sub>S), also produces C-S-H. After several days, in the presence of water, most of the alite has reacted and the rate of belite hydration begins to be noticeable. It is important to maintain sufficient moisture long enough for belite 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, as long as cementitious material and water are present. This process is affected by factors like cement type and fineness.</li> </ul>

## Hydration Heat Curve (not to scale)



## Effects of Supplementary Cementitious Materials

SCMs like fly ash and ground, granulated blast-furnace (GGBF) slag, are included in more than 65 percent of concrete mixtures in the United States. In general, they consist of the same basic elements—silicon, aluminum, and calcium—and perform basically the same function as cement. (Pozzolans require a source of calcium, usually provided by hydrating portland cement, to hydrate.) SCMs are used in concrete to take advantage of available materials and achieve desired workability, strength gain, and durability.



## Effects of Chemical Admixtures

Stage 1: Mixing	Stage 2: Dormancy	Stage 3: Hardening	Stage 4: Cooling	Stage 5: Densification
<p>If SCMs contain large amounts of calcium (for instance, 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 sulfate in solution.</p> <p>Fly ashes with high loss-on-ignition (LOI) (mass loss when heated to 1,000°C [1,830°F]) will likely interfere with development of the air-void system. That is because high LOI fly ashes contain unburned carbon that absorbs air-entraining admixture. 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>Like portland cement, during dormancy the silicates in SCMs are slowly dissolving and releasing calcium ions and hydroxyl (OH) ions.</p> <p>The amount of heat generated may be slightly later and lower, but heat generation may be extended longer.</p> <p>Mixtures containing retarders tend to have a finer, less permeable microstructure, leading to better long-term strength and durability.</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, while they start in this stage, they 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:</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 extended.</li> <li>Early strengths may be depressed.</li> <li>These effects may be especially significant for construction in cold weather.</li> </ul>	<p>The magnitude of the heat peak is often reduced in systems containing SCMs due to slower hydration rate (this results in less shrinkage later and, thus, potentially less stress). A second peak may be observed as the SCMs hydrate.</p> <p>Generally as a result of reducing the hydration rate and heat, 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>In the long term, 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. Permeability is often significantly reduced, thus improving potential durability.</p> <p>Systems containing GGBF slag and fly ash are reportedly more prone to frost damage. The extent of, and mechanisms behind, this perception are still under investigation.</p> <p>Low-calcium fly ash and GGBF slag are effective in reducing alkali reactivity of mixtures for three reasons. These SCMs:</p> <ul style="list-style-type: none"> <li>Reduce the mixture's alkali content.</li> <li>Reduce concrete permeability.</li> <li>Reduce the system's calcium/silica ratio.</li> </ul> <p>High-calcium fly ashes may have the same effect, and should be tested using the materials under consideration.</p>

## Implications of Cement Hydration for Construction Practices

<p><b>Water reducers.</b> Water reducers work by dispersing clusters of cement grains and releasing water trapped in the clusters, making more water available for workability. Water reducers may increase initial workability but may not slow slump loss with time. Polycarboxylate water reducers may increase air entrainment.</p> <p>In general, Type A water reducers increase the rate of aluminate* hydration (thus, the risk of flash set) and slow the rate of alite (C<sub>3</sub>S) hydration (slowing strength gain). High-range (Type F) water reducers are less prone to incompatibility.</p> <p><b>Air entrainers.</b> Air-entraining admixtures work by stabilizing small air bubbles in the paste. Several different chemical forms of air entrainers are available, all with differing stability and differing effects on bubble size. In general, the greater the slump, the easier it is for air to be entrained.</p> <p><b>Retarders.</b> Set-retarding admixtures may increase air content.</p>	<p><b>Retarders.</b> 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.</p> <p>The amount of heat generated may be slightly later and lower, but heat generation may be extended longer.</p> <p>Mixtures containing retarders tend to have a finer, less permeable microstructure, leading to better long-term strength and durability.</p> <p><b>Accelerators.</b> 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.</p> <p>Chloride-based accelerators increase the risk of corrosion of any steel embedded in the concrete.</p>	<p>After stiffening begins, do not work, vibrate, or consolidate the concrete. Segregation of the ingredients at this point will be permanent.</p> <p>Thoroughly apply curing compound to the concrete surface and edges as soon as possible after finishing, to reduce the rate of water evaporation from the concrete. Protecting the concrete with curing compound is critical because it results in stronger, less permeable concrete. (When water evaporates from the concrete, more cement remains unhydrated and fewer products form. Also, water evaporation leaves capillary pores behind, reducing concrete's durability because it is more susceptible to freeze-thaw damage and attack by aggressive fluids.)</p> <p>During this stage, prepare joint-sawing equipment. Beginning at final set, start checking concrete for readiness for saw cutting.</p>	<p>To prevent random cracking due to buildup of tensile stresses, saw joints during a brief sawing window:</p> <ul style="list-style-type: none"> <li>The sawing window begins when concrete is strong enough not to ravel when sawed, and ends before the concrete cracks in front of the saw—typically, no later than 24 hours after placement.</li> <li>Conventional sawing windows generally begin after final set but before the heat peaks, and end after the heat peaks; how long after depends on the specific mixture, cement, SCMs, ambient temperatures, etc.</li> <li>For early-age saws, the window may begin at or slightly before final set (stage 3) and will end earlier than for conventional sawing.</li> </ul> <p>Cover the slab, especially if temperatures will cool significantly during the first night. Insulation prevents extreme temperature and moisture variations within the slab that can lead to curling and warping and related cracking. Insulation also helps keep the slab moist and warm.</p>	<p>Keep concrete thoroughly covered and protected with curing compound as long as possible, at least for the first 72 hours after mixing.</p> <p>The longer the curing compound remains in place (that is, protected from equipment and construction traffic), the more moisture will be retained in the concrete for hydration and thus for development of strength and reduction of permeability.</p>
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## 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.

<p>If insufficient sulfate is in solution for the amount of aluminate* (from cement and fly ash), 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 sulfate may be needed to maintain an adequate shell around the aluminate* particles to control flash set.</p> <p>Excess sulfate 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. There is no effect on other hydration processes.</p> <p>The amount of sulfate in solution is controlled by the amount/form of sulfate in the cement. Gypsum dissolves slowly (increasing the risk of flash set). Plaster dissolves rapidly (increasing the risk of false set). Cement manufacturers normally balance these materials.</p>	<p>If calcium is consumed by poorly controlled aluminate reactions earlier in Stage 1, then supersaturation of calcium ions will be slowed and alite 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.</p> <p>Alite (C<sub>3</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.</p> <p>Alite 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.</p>	<p>When concrete sets at high temperature, increased stresses can develop because concrete cools (and so shrinks) more than concrete that sets at lower temperatures. The increased stresses may increase the potential for random cracking.</p>	<p>If setting is delayed, concrete may crack because it dries while the concrete is still too soft to start saw cutting.</p> <p>Faster setting may mean the concrete will crack before sawing can be completed because the sawing window is shorter than the time required for sawing.</p> <p>Cementitious systems with high alkali content, aluminate* content, and fineness may shrink more than other systems, therefore increasing the risk of random cracking.</p> <p>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.</p>	<p>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 shrink different amounts, resulting in curvature known as warping and curling. Depending on the support conditions and the extent of the curvature, stresses (self weight or traffic loadings) on the curved slab may result in cracking.</p>
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## Implications of Cement Hydration for Cracking

Materials tend to expand as they get warmer and shrink when they get cooler. Cement paste tends to move more with such volume changes than does aggregate. Cement paste also shrinks as it dries. Objects that are restrained when they move (shrink or expand) will be stressed, leading to cracking if the stresses exceed the strength. (Restraint comes from any connection with adjacent objects, such as friction with the subgrade.) It is therefore desirable to reduce paste content within a given mix, 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 tends to control the amount of thermal movement of concrete. If aggregate with a low coefficient of thermal expansion is used, the risk of problems will decrease. Concrete with high paste content and high fines content, due to improper aggregate gradation, will be at higher risk of cracking.

<p>Because chemical reactions are faster at higher temperatures, an increase in initial mixing temperature significantly increases the amount of heat generated (and corresponding stress development) in stage 3.</p>	<p>Drying, and consequent shrinkage, any time before final set may result in so-called plastic shrinkage cracking.</p>	<p>When concrete sets at high temperature, increased stresses can develop because concrete cools (and so shrinks) more than concrete that sets at lower temperatures. The increased stresses may increase the potential for random cracking.</p>	<p>If setting is delayed, concrete may crack because it dries while the concrete is still too soft to start saw cutting.</p> <p>Faster setting may mean the concrete will crack before sawing can be completed because the sawing window is shorter than the time required for sawing.</p> <p>Cementitious systems with high alkali content, aluminate* content, and fineness may shrink more than other systems, therefore increasing the risk of random cracking.</p> <p>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.</p>	<p>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 shrink different amounts, resulting in curvature known as warping and curling. Depending on the support conditions and the extent of the curvature, stresses (self weight or traffic loadings) on the curved slab may result in cracking.</p>
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## Implications of Cement Hydration for the Air-Void System

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

See Effects of Chemical Admixtures above.

<p>The air-void system develops during mixing. It is harder to entrain air in systems at high temperature, with low slump, and with very fine supplementary cementitious materials that have high loss-on-ignition (LOI) (mass loss when heated to 1,000°C [1,830°F]) and low alkali contents. Additional air-entraining admixture may be required for such systems. Set-retarding admixtures may increase air content.</p>	<p>The stability of the air-void system (i.e., the ability to prevent bubbles from breaking during handling) depends on the chemistry of the air-entraining admixture. Some air entrainers are more sensitive than others to the presence or dosage of other chemical admixtures or supplementary cementitious materials. (Methods are being developed to test the overall sensitivity of a paste system.)</p> <p>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 concrete mix.</p>	<p>The air-void system has been formed at this stage and is unlikely to change.</p>	<p>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 shrink different amounts, resulting in curvature known as warping and curling. Depending on the support conditions and the extent of the curvature, stresses (self weight or traffic loadings) on the curved slab may result in cracking.</p>	<p>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 shrink different amounts, resulting in curvature known as warping and curling. Depending on the support conditions and the extent of the curvature, stresses (self weight or traffic loadings) on the curved slab may result in cracking.</p>
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