How SCMs may affect hydration

- Often slow hydration, extending working time and delaying set, strength gain, and sawing window.
- Reduce heat peak.
- Extend heat generation.

Potential benefits of SCMs

- Less water required to achieve workability.
- Increased long-term strength.
- Reduced permeability.
- Reduced early-age cracking.
- In hot-weather concreting, maximum heat of hydration is moderated.
- Less alkali-reactive mixture (with fly ash or GGBF slag).

Potential problems with SCMs

- Possibly significant delay in early strength gain, especially in cold-weather concreting, that can affect sawing operations.
- Increased risk of flash set with class C fly ash because it is high in calcium aluminates.
- Interference with development of air-void system (especially very fine fly ashes with high loss-on-ignition).
- Perhaps increased potential for frost damage (with fly ash or GGBF slag).

Water Reducers

How they work

Disperse cement clusters, freeing trapped water which can then react (hydrate) with cement.

How they affect hydration

More of the mix cement is hydrated, resulting in a greater volume of hydration products.

Potential benefits

- Possibly increased initial workability.
- Possibly increased air entrainment (polycarboxolate water reducers only).
- Reduced concrete permeability; increased durability.

Potential problems

- May slow the rate of alite hydration and thus of strength gain.
- May accelerate initial aluminate reactions, increasing the risk of flash set.

Set Retarders

How they work

Coat cement particles so they dissolve more slowly.

How they affect hydration

- Slow hydration.
- Reduce heat peak and extend hydration and heat generation (similar to water reducers).

Potential benefits

- Generally result in a finer, less permeable microstructure, increased strength, and durability.
- Lower heat of hydration can be useful in hot-weather paving projects.
- Extended haul times or other accommodations to production cycles.

Potential problems

Possibly reduced rate of alite hydration and thus strength gain.

Set Accelerators

How they work

Reduce time required for supersaturation of calcium ions.

How they affect hydration

- Earlier initial and final sets.
- Increased heat generation; higher maximum peak on the hydration curve.

Potential benefits

Promote hydration and strength gain; can be useful in cold-weather paving projects.

Potential problems

Possibly short sawing window, increasing the risk of cracking.

National Concrete Pavement Technology Center

CP Tech Center

August 2007

This technical summary is based on chapter 4 of the IMCP Manual (Taylor, P.C., et al. 2006. *Integrated Materials and Construction Practices for Concrete Pavement: A State-of-the-Practice Manual*, Ames, Iowa, Iowa State University [FHWA HIF-07-004] [www.cptechcenter.org/publications/imcp/]) and was sponsored by the Federal Highway Administration. (References for any citations in this summary are at the end of the chapter.)

CP Tech Center Mission

The mission of the National Concrete Pavement Technology Center is to unite key transportation stakeholders around the central goal of advancing concrete pavement technology through research, tech transfer, and technology implementation.

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4a

A summary of chapter 4 (pages 69–104) of the *IMCP Manual* (reference information on page 4)

Cement Hydration: The Basics

This document is one of a set of technical summaries of chapters 1 through 10 of the *Integrated Materials and Construction Practices for Concrete Pavements: A State-of-the-Practice Manual* (IMCP manual). The summaries provide an overview of the manual and introduce its important concepts. To be useful for training, the summaries should be used in conjunction with the manual.

This summary covers material in chapter 4, the basic characteristics of cement hydration and its significance for concrete performance. It identifies the primary compounds in cement and those resulting from cement hydration. It illustrates the stages of hydration on a time vs. heat curve, describing reactions occuring during each stage, their effect on concrete performance, and the effects of supplementary cementitious materials and chemical admixtures.

What is Cement Hydration?

Cement hydration is a series of irreversible chemical reactions between cement and water. During hydration, the cement-water paste sets and hardens, "gluing" the aggregate together in a solid mass.

Why is it Important?

Cement hydration is central to the formation of concrete. It influences how the plastic concrete behaves when it is being placed and finished and governs how strong and durable the hardened concrete becomes. During the first 72 hours after mixing, concrete can often gain 50 percent of its strength or more. During that time, it is especially susceptible to stresses that may cause cracking because it has not gained its full strength.

Understanding the basics of hydration will help readers recognize and mitigate the stresses to control and/or prevent cracking and to appreciate the importance of good curing and construction practices.

Primary Compounds in Cement

When portland cement is manufactured, limestone, clay, and shale are mixed in a kiln at very high temperature to produce clinker. The clinker is then ground with calcium sulfate (mostly gypsum) (figure 1).

Clinker consists primarily of *calcium aluminates* and *calcium silicates* (in this summary, *aluminates* and *silicates*):

- Calcium (as in teeth) aluminates (as in aluminum):
  - Tricalcium aluminate (C_3A); ferrite (C_4AF).
  - Aluminates reduce the amount of heat required for the manufacture of clinker.
- Calcium silicates (as in glass): alite (C_3S); belite (C_2S).

The *calcium sulfate* ([$C\overline{S}$] as in sulfur, the smell of rotten eggs) is primarily gypsum, but it is also present as plaster and anhydrate.

During cement hydration, products of aluminate reactions contribute to early stiffening of concrete; calcium sulfate controls the early aluminate reactions; and products of silicate reactions contribute to concrete's strength.

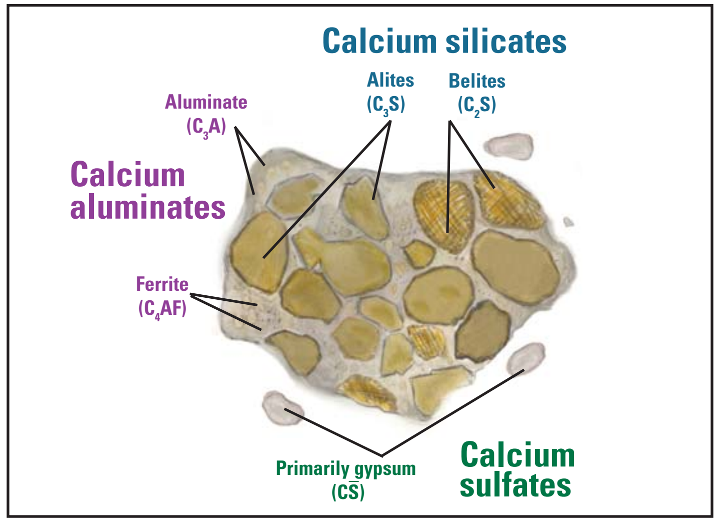

Figure 1. Portland cement: clinker particle ground with sulfate

Five Stages of Hydration

To simplify this discussion, chemical reactions between the various compounds in portland cement and water are described in five stages. The stages are illustrated by a curve that represents changes in heat during the first hours and days of hydration (figure 2).

Stage 1: Mixing (< 15 minutes)

What is happening

- Aluminates dissolve and react quickly, with high heat.
- Sulfate dissolves quickly, too. It reacts with aluminate and water, forming a gel (C-A-$\bar{S}$-H, a precursor to ettringite). The gel limits water's access to aluminate (figure 3). Reactions slow. Heat drops.
- Sulfate is included in cement primarily to control aluminate reactions as just described. However,
  - Too *little* sulfate in solution can result in immediate hardening of the mix, or flash set—rare but permanent.
  - Too *much* sulfate in solution can precipitate out, causing temporary stiffening of the mix, or false set. False set can generally be corrected by additional mixing.
  - Different *forms* of sulfate result in different amounts of sulfate ions in solution.

Implications

The correct balance of sulfate (amount and form of C$\bar{S}$) to aluminate is necessary to prevent flash set and false set.

Stage 2: Dormancy (2–4 hours)

What is happening

- While the C-A-$\bar{S}$-H gel controls aluminate reactions, the concrete is cool, plastic, and workable.
- During this dormant period, the silicates (alite and belite) slowly dissolve, releasing calcium ions in solution (figure 4).

Implications

During dormancy—before initial set—the mix can be transported, placed, finished, and textured.

Stage 3: Hardening (2–4 hours)

What is happening

- The solution eventually becomes supersaturated with calcium ions, triggering the formation of new compounds:
  - Calcium silicate hydrate (C-S-H, fiber-like particles), which adheres to aggregate and gives concrete its strength.
  - Calcium hydroxide (CH, crystals).
- Formation of C-S-H and CH generates heat, causing thermal expansion.
- "Initial set" occurs when enough C-S-H and CH form to mesh together, causing the mix to stiffen (figure 5).
- As these products continue to mesh, the concrete begins developing some strength.
- "Final set" occurs when the concrete achieves a defined stiffness, about when the concrete is hard enough to walk on.
- The gel-like C-A-$\bar{S}$-H transforms into a needle-like solid (ettringite) that contributes somewhat to early strength.

Implications

- It is critical to apply curing compound thoroughly (or conduct other curing practices) as soon as possible after finishing, before the concrete begins hardening.

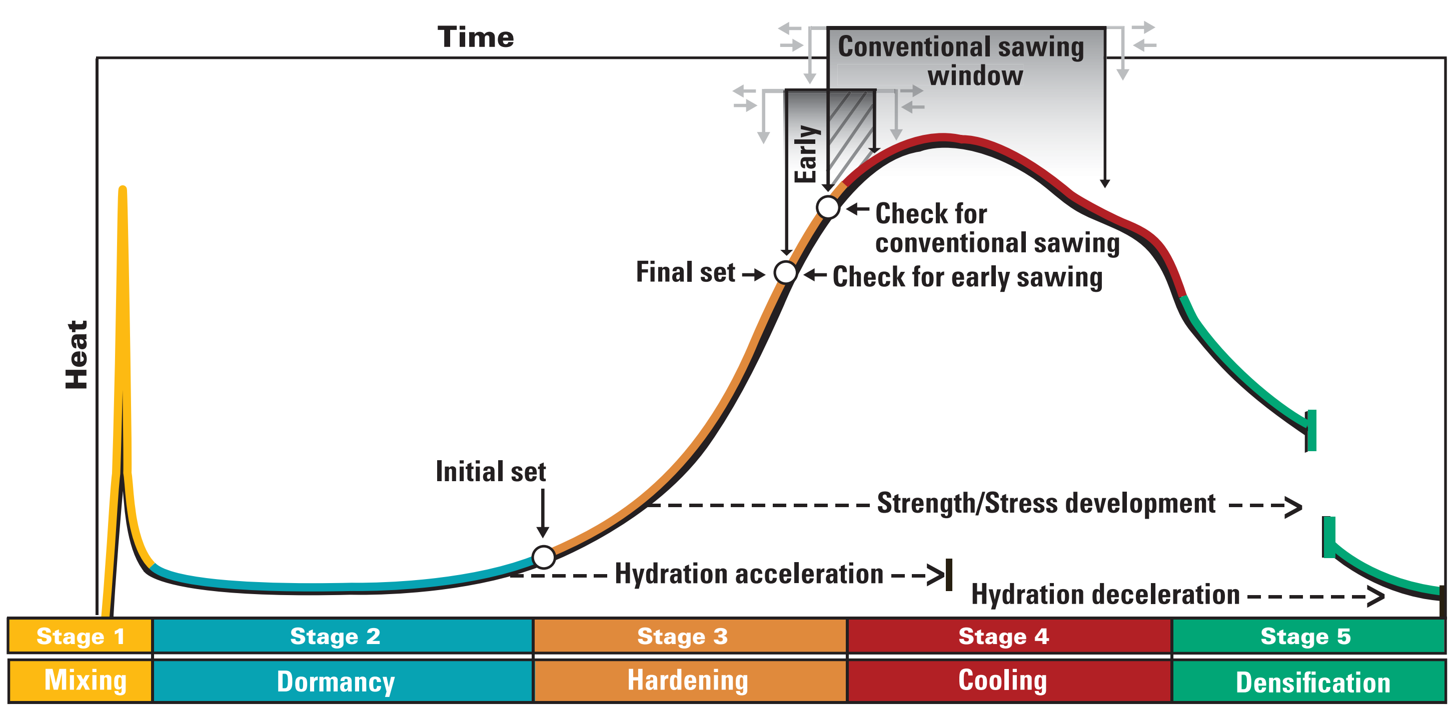

Figure 2. The five stages of hydration mapped on a heat vs. time curve

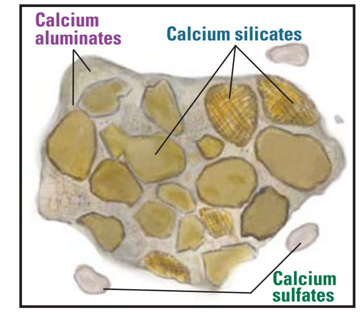

Figure 1. Cement particle (see also page 1)

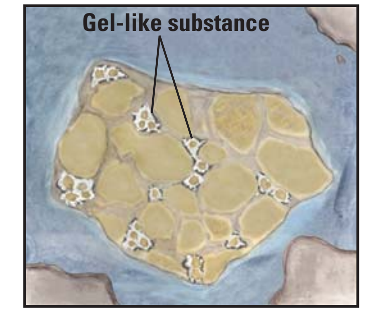

Figure 3. Controlled aluminate reactions in stage 1

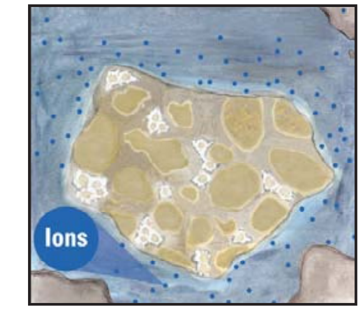

Figure 4. Cement particle dissolving during stage 2

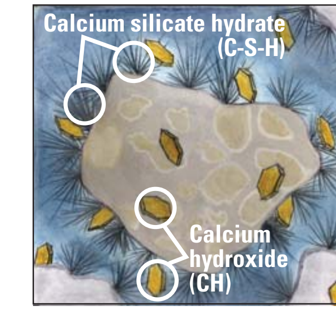

Figure 5. New hydration compounds during stage 3

Curing slows water evaporation from the pavement surface, retaining mix water for hydration and reducing the risk of plastic shrinkage cracking.

- Do not trap bleed water by finishing the surface too early, and so weakening the surface.
- The sawing window generally begins about the time of final set (figure 2).

Stage 4: Cooling (several hours)

What is happening

- Soon after final set, the buildup of C-S-H and CH begins to limit access of water to undissolved cement (figure 6). Silicate reactions slow. Heat peaks and begins to drop.
- As it cools, concrete contracts. Movement of the contracting slab is restrained by the subgrade, causing tensile stress to develop in the slab.
- At some point the stress will become greater than the concrete's strength. The concrete will crack.

Implications

- Before the concrete cracks randomly, joints must be sawed to control the crack locations.
- For early-age saws, the "sawing window" may begin slightly before final set. For conventional saws, the window generally begins after final set.

What else is happening

During this stage, the sulfate will be depleted. Any remaining aluminate then reacts with the C-A-$\bar{S}$-H. This has little effect on concrete properties except for a brief increase in heat.

Stage 5: Densification (can continue for years)

What is happening

- Belite dissolves and reacts more slowly than alite. During stage 5, belite reactions start to have an impact on the slab. They can continue for years.
- Belite reactions also produce C-S-H and CH, forming a solid mass (figure 7).
- The longer the cement in concrete hydrates (that is, belites and any remaining alites react with water),
  - The greater the concrete's strength.
  - The lower its permeability.
  - The greater its potential durability.

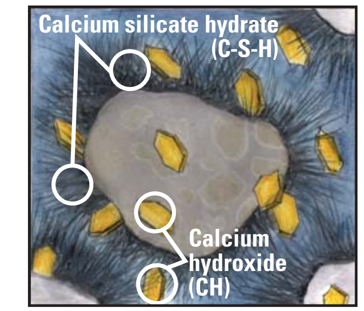

Figure 6. Hydration compounds during stage 4

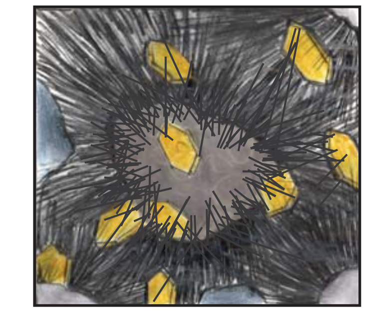

Figure 7. Hydration compounds during stage 5

Implications

- To promote continued hydration, moisture must be retained in the slab as long as possible.
- Therefore, after fininshing, curing compound should be applied uniformly and at recommended coverage rates, then protected from weather and construction traffic as long as possible.

Effects of Other Materials on Hydration

Most mixes today include **supplementary cementitious materials (SCMs)**, economical materials that can enhance certain concrete properties. These may include class C fly ash, class F fly ash, and/or ground, granulated blast-furnace (GGBF) slag. Other common admixtures are **water reducers**, **set retarders**, and **set accelerators**.

Certain combinations of perfectly acceptable SCMs and chemical admixtures may react in undesirable ways. Such materials incompatibilities are described in Technical Summary 4b.

SCMs

How they work

In general, SCMs convert CH (a somewhat less desirable product of hydration) into C-S-H (which gives concrete its strength).