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- Slabs on Grade

That Pesky Moisture Gradient, Part 1

By:

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Ideally, it should only take about 3 gallons of water to hydrate a sack of cement. To obtain adequate workability, however, a mix design must typically employ between 5 to 6 gallons of water per sack—even when a water reducer is used. Strictly in chemical terms, therefore, every slab mix is always going to contain somewhere between 67% and 100% too much water. The necessary inclusion of this additional water of convenience has enormous consequences. Indeed, it is the root cause of all of the “Big Three” slab performance problems: cracking, curling, and delamination.

This complex story begins with the character of the paste—the water and cement portion of the mix. Because portland cement does not dissolve in water, the paste is not a homogeneous solution, but rather a special kind of heterogeneous mixture—termed an emulsoid—wherein the tiny insoluble solid particles are both suspended in and strongly attracted to the dispersing liquid. Indeed, the ability of the cement particles to generate heat either by reacting with or adsorbing the water molecules in which they are immersed is the engine that drives the entire concrete hardening process. Critically, however, until it becomes involved with the cement in such hydration chemistry, any “free” water molecule can be mechanically removed from the system at any time, for example, by evaporation.

A dimensional perspective on the two bits of matter that make up the paste may be helpful. A single water molecule measures about 1/100 of 1/1000 of 1/1000 of an inch across. The suspended cement particles, in contrast, are gigantic in comparison—most spanning between 20,000 and 200,000 individual H₂O molecules. Each irregularly shaped cement particle is itself just a colossal conglomeration of different molecules—the four principal ones being oxides of calcium, silicon, aluminum, and iron. These molecules are not present in isolation, but rather are variously combined to form the four distinct compounds that comprise portland cement: tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. The basic picture of fresh paste, then, is one of massive solid cement chunks suspended in a sea of miniscule water molecules with which the four different molecules at the surfaces of the chunks very much want to combine.

Now nobody knows for sure exactly what happens next. Although we know what we start with, and end up with, precisely how we get from one to the other remains one of those fortuitous mysteries—like the way a car battery works—that is best viewed as simply miraculous. This much is known: for the necessary chemical processes to occur at the surfaces of the cement particles, the reacting water and surface molecules must be in contact. Because the newly created cement + water molecules at the particle’s surface occupy less volume than do the constituent

cement and water molecules individually, voids tend to be created around the cement particles as the free water molecules get used up. Unless additional water molecules from the surrounding pools of surplus liquid continue to move into contact with the particle surfaces, the relative humidity at the surfaces will drop below 100%, and the cement's hydration will be starved into inactivity.

The process by which the cement's hydration persists in depleting the supply of adjacent free water molecules is called "self desiccation," and in the absence of wet curing, this internal drying will inevitably lead to less than optimal conversion of the raw cement. Once the water-cement ratio reaches 0.50, however, enough surplus water is available for the hydration to continue at the same rate obtained with wet curing. But even under these most favorable conditions, because each bit of hydrate that forms at the cement particle's surface creates a new barrier between the surrounding free water molecules and the raw cement inside the particle, the rate of hydration always will continue to decrease irregularly. It is entirely normal, therefore, for a large amount of raw cement to remain unhydrated for years.

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That Pesky Moisture Gradient, Part 2

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Although the raw cement particles contain four different molecules eager to combine with water, only tricalcium and dicalcium silicates (C3S and C2S) precipitate into the crystals of calcium silicate hydrate (C-S-H) that form the magic glue around which our professional lives revolve.

In commercial portland cements, neither of these two molecules exists in pure form. Both are contaminated by various amounts of impurities, including the so-called alkali oxides of potassium and sodium that react expansively with certain silica-containing aggregates causing the concrete to disintegrate. With proper testing, such destructive alkali silica reactions may be avoided with the use of low-alkali cement, or by a 30% to 40% fly ash or 40% to 50% GGBS replacement.

The impure versions of tricalcium- and dicalcium silicate actually in the cement are called alite and belite. Because alite reacts with water to form C-S-H much faster than belite, its hydrolysis accounts for about 90% of the cement's strength gain during the first 28 days. Thereafter, the alite's reaction rate falls off, and the much slower hydrolysis of the belite into C-S-H drives the long-term strength gain. It takes about a year for the compressive strengths of both hydrates to become about equal.

The slaked lime, or dissolved calcium hydroxide, that makes cement caustic is a byproduct of both the alite and belite hydrolyses. It is a remanifestation of the quicklime, or calcium oxide, created in the kiln when the raw crushed limestone, or calcium carbonate, was heated initially to drive off its constituent carbon dioxide. This purposeful thermal decomposition of limestone is

the process, in fact, that gives the manufacture of portland cement such a large carbon footprint. Adding in the carbon dioxide released in heating the kiln and generating the electricity, about 1 pound of CO₂ gas is created for every 1 pound of portland cement produced. Concrete's caustic character is certainly one of its fortuitous features, however, particularly with regard to the protection against rusting that it affords to any embedded steel.

The third bits of material on the cement particle's surface—the tricalcium aluminate (C3A) molecules—are the ones most ready to combine with water. Though relatively few in number, accounting for only about one in 10, owing to their rapid, even violent reactions, they create serious set rate issues. If unchecked, these are the molecules that will cause the paste to flash set, or stiffen immediately after the water is added. It is precisely to prevent such flash setting that gypsum (calcium sulphate hydrate) is added to the cooled clinker in carefully controlled amounts before grinding. In solution, the gypsum prevents the C3A from hydrating directly by forcing the formation of unstable intermediate products that bind up the C3A and temporarily shield it from the water. But add too much gypsum and upon hardening, the cement will expand enough to fracture the paste. Add too little gypsum, and the C3A molecules will hydrate before the C3S molecules, creating a weak porous structure on which the later reaction products must form.

The fourth and final significant bits on the cement particle's surface that react with water are the tetra-calcium aluminoferrite (C4AF) molecules. Also accounting for about 10% of the total, these aluminum and iron containing molecules are mostly just along for the ride, because they neither perform a useful function nor create any particular problems.

Portland cement is made from a cheap stew of commonly available calcium- and silicate-rich minerals: primarily limestone and clay. Because the desirable clays are all aluminum silicates, however, the generation of the troublesome C3A is practically unavoidable. Fortunately, the presence of the aluminum is not wholly without benefit; both it and the iron do act as fluxes in the kiln to significantly reduce the amount of heat required to sinter the clinker.

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That Pesky Moisture Gradient, Part 3

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The material ultimately created by the cement's hydration—the gray stuff we know as hardened cement paste—is called a colloidal gel—a curious sort of “permanently damp solid” wherein very tiny bits of liquid (the molecules of water and dissolved ions of calcium and hydroxide) are evenly dispersed throughout a porous random nanostructure of insoluble hygroscopic solid material (the precipitated crystalline hydrates).

In the same way that the precise chemistry of the cement's hydration remains a mystery, nobody knows for sure exactly how hardened cement achieves its strength. It is known that each leaf-like

crystal of calcium silicate hydrate (C-S-H) remains exceedingly small; most measure less than 1/125 of 1/1000 of an inch. And though the bits of C-S-H do interlock, their mere physical entanglement does not appear to be the principal source of the paste's strength.

The particles in a pound of dry portland cement powder have a total surface area of about 5000 square feet. In contrast, the much smaller C-S-H crystals which form on the surfaces of all these particles once they are immersed in water have a total area of about 1,000,000 square feet. This 200-fold increase in the internal solid surface area brought about by the cement's hydration appears to be most significant factor leading to the strength development. It is this property, in concert with the conjoined water, that makes the paste behave like super-stiff Jello.

A pound of portland cement powder and a third of a pound of water each occupy about 9 cubic inches. The 1 1/3 pounds of 0.33 water-cement ratio (w/c) paste created by mixing the two together will have a volume of about 18 cubic inches—half of which will be solid material and half of which will be liquid water. If this paste were somehow able to avoid self-desiccating (see "That Pesky Moisture Gradient, Part 1" in the December 2010 issue) and hydrate completely, the volume of the resulting C-S-H gel would be enough to fill the entire mass; there would be no space left for anything else. A w/c of about 0.33 thus represents something of an ideal minimum, because it is around this value that all of the mix water is needed to convert all of the raw cement into gel.

If the w/c is above 0.33, increasing amounts of unused, and thus evaporable, water will be leftover after the cement has fully hydrated. Some of this unused water will occupy the remaining capillary pores in the paste that have not been filled by the newly created gel. The capillary pores are irregularly shaped, randomly distributed, and widely varying in size. Although most measure less than 400 water molecules across, a few do get as much as 10 times larger. The lingering interconnections that exist between the capillary pores in mature paste create the concrete's permeability and consequent susceptibility to freeze/thaw damage.

Some of the leftover evaporable water—though in a much less mobile state—also will occupy the much smaller gel pores within the C-S-H itself. C-S-H gel is, in fact, highly porous—being riddled with myriad minute voids that comprise almost a third of its volume. Having nominal diameters in the range of only 8 to 12 water molecules, the gel pores are 1 to 2 orders of magnitude smaller than the capillary pores. The porosity of C-S-H gel remains fairly constant regardless of w/c or the degree of hydration: the more the hydration, the more the gel pore formation. The situation regarding the capillary pores is just the inverse: the more the hydration, the less the capillary pore volume.

Regardless of the actual w/c employed, the theoretical maximum volume to be occupied by the C-S-H gel upon complete hydration always will be about twice the volume of the raw cement powder. This makes the percentage of the fully hydrated paste occupied by the evaporable water solely a function of w/c: **Percent of Paste Volume Containing Evaporable Water = 100 [1 - 2/(3 W/C + 1)] %**

With regard to curling, cracking, and delamination, it is this remaining removable portion of the original mix water that causes all the problems.

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That Pesky Moisture Gradient, Part 4

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Portland cement paste shrinks primarily in response to the removal of free water from its capillary and gel pores. Immediately after mixing, while the paste is a murky fluid, its volume will be reduced as gravity forces the solid cement particles to settle. In this initial stage, the lost paste volume equals the volume of water bled to the surface. Once the paste's solid structure begins to form, its reduction in volume changes to a decreasing fraction of the water lost. Logically, the mechanisms that give rise to the lion's share of the paste's shrinkage throughout the hardening process must involve the replacement of the original liquid water with a gaseous mixture of air and steam (i.e. water vapor).

The shrinkage associated with self-desiccation is termed autogenous shrinkage. It is strictly an internal process that begins as soon as the water is introduced to the mix and persists as long as the cement continues to hydrate. The shrinkage associated with the loss of water to the surroundings is termed drying shrinkage. It is strictly an external process that persists as long as water is able to escape from the paste. Of all factors, evaporation is by far the most significant contributor to the paste's long-term shrinkage.

Here is the overall picture: All practical portland cement concretes contain large amounts of surplus water, and all start out as grossly aerated, solid-in-liquid suspensions. At water-cement ratios, all the mix water fully occupies two different kinds of spaces within the paste: the capillary pores and the very much smaller gel pores. From the moment of batching, and continuing essentially to eternity, both internal and external processes—self-desiccation, base wicking, bleeding, and evaporation—act to replace the liquid water originally permeating the paste with air (sucked in from the nearest entrapped bubbles) and vaporized water. It is the persistent substitution of humid air for liquid water within the paste's capillary and gel pores that leads inexorably to the paste's, and thus the concrete's, drying shrinkage.

There are two ways that this gas-for-liquid replacement is believed to force the paste's skeleton to contract: loss of disjoining pressure between adjacent C-S-H crystals and compression of the capillaries by surface tension. For complicated reasons, in an emulsoid (remember that hydrated cement paste is just really hard gelatin), the pressure in the liquid filling the space between two closely adjacent particles is higher than the pressure in the liquid surrounding the particles. Because this higher pressure tends to push the particles apart, when it is relieved by the liquid's replacement with a gas, the particles tend to move toward one another and thereby shrink the paste's solid structure.

At equilibrium, six factors determine the height and shape of the boundary—called the meniscus—that forms between two immiscible fluids in an open vertical capillary tube. Four of the factors—the particular surface tensions characteristic of the three interfaces that exist

between the various materials present (i.e. the water, steam, and C-S-H), and the radius of the capillary tube itself—are conceivably modifiable.

Given the colossal value that would attend the development of a practical method for eliminating drying shrinkage, this last observation immediately suggests the existence of at least four sure-fire get-rich schemes. Indeed, all you have to do is find an inexpensive way to do just one of the following:

1. Eliminate the surface tension between water and steam.
2. Equalize the surface tensions between water and C-S-H, and air and C-S-H.
3. Equalize the surface tensions between water and C-S-H, and water and steam.
4. Make the capillary and gel pore radii large enough to flatten out the menisci, but still small enough to allow the paste to gain strength.

Although schemes 1 and 4 have already been tried using shrinkage reducing admixtures and autoclaving, schemes 2 and 3 have yet to attract commercial interest.

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That Pesky Moisture Gradient, Part 5

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The surplus paste water is the most mobile and least dense of the four principal concrete components, and the only one capable of changing phase from liquid to gas. Immediately following placement, this surplus water starts to percolate upward, and the slab begins a process of sedimentation wherein the solid particles of cement, sand, and stone sink to the bottom while the lighter liquid water works its way, or bleeds, to the top.

Starting with the largest capillary pores, bleeding and self-desiccation combine to dewater the paste. While the larger pores are being emptied and the menisci forming that remain are more than 400 water molecules wide, very little horizontal shrinkage occurs. Though strongly adhered to the surrounding solids, these larger menisci are just too large to translate their surface tensions into enough force to pull the sides of the pore inward. Once the dewatering process reaches the pores that are less than 400 water molecules wide, however, the surface tensions of the smaller menisci being formed do become sufficient to draw in the pore walls. The aggregation of these myriad local surface tension-induced microcontractions is the phenomenon that makes the concrete shrink en masse.

Rule No. 12a: Drying shrinkage is caused by what happens inside the pores that are less than 2 millionths of an inch across.

Once the bleed water has made its way to the top and removed, the paste at the surface is exposed directly to the air. If the air's temperature is higher than the dew point, then the air's relative humidity will be less than 100% and the paste water will start to evaporate. Then the vaporization rate will be determined by four main factors: the air's relative humidity, the air's movement, the paste's surface roughness, and the paste's temperature. Indeed, every experienced finisher knows that his Window of Finishability—the imaginative term coined by Bill Phelan 25 years ago—always will close as the environment gets more arid, the concrete gets hotter, the wind blows harder, and/or the surface is left more open.

Rule No. 12b: In the first two years, a slab's top layer will shrink about 1/32-inch for every 5 feet of its uninterrupted length.

Suppose a new plain, portland cement concrete slab is cut into 15x15-foot squares. If the concrete exhibits normal shrinkage and no visible cracks develop, the average sawcut width increases by about 3/32 inch. If a high-shrinkage concrete is used instead, the average joint grows about 5/32 inch. Conversely, if the concrete is of the low-shrinkage variety, then the sawcut widths only grow about 1/32 inch. Relative to the joint growths that are normally expected, the practical performance differences between high and low shrinkage concretes are barely significant—especially because any amount of joint growth, no matter how small, immediately raises the specter of stability problems. In short, the hand wringing that often attends consideration of a mix's shrinkage potential is largely pointless.

Rule No. 12c: Regardless of slab thickness, at age D days the drying shrinkage experienced t inches from the top surface will approximately equal $\{-E+[t(E-t)]^{1/2}\}/10,000$ inches/inch, where $E=5\{1-\exp[-D/90]\}$.

The figure shows this formula plotted at $D=360$ days. The fact that this curve is unaffected by the slab's depth has profound implications regarding the proper use of embedded reinforcement.