

# Letters

## PORTLAND CEMENT HYDRATION

The article “Amount of Water Required for Complete Hydration of Portland Cement” by Bryant Mather and William G. Hime (*Concrete International*, V. 24, No. 7, June 2002, pp. 56-58) should have been written ages ago. It summarizes, to some extent, the ultimate finality and essence of cement hydration, in part because there has been the belief by many that after moist curing for 28 days (and even poor curing for 28 days), hydration of portland cement is essentially, if not entirely, complete. Therefore, the authors, along with many others who have had the opportunity to do so—including us—are chided for not having summarized the subject much sooner.

As usual, because of the complexity of portland cement compositions, and sometimes of necessity, there is a need, to some extent, to simplify compound compositions in terms of “theoretical composition,” and that is typically done based upon calculations using Bogue equations. In reality, as many of us know, the portland cement compounds do not exist in the proportions so calculated, and that they also vary in crystal size and actual chemical composition as has been extensively documented.

Our comments are divided into two parts: 1) a pictorial showing photomicrographs of polished sections; and 2) a narrative on other aspects of cement hydration or incomplete hydration. Let's take the latter first.

The authors state that there are “...at least two possibly undesirable consequences of a concrete having all of its cement hydrated...there can be no autogenous healing of microfractures...” and “...it will have a higher modulus of elasticity, be more brittle, and crack at a lower strain level.” Let us comment on the latter. Residual portland cement particles act as “micro-aggregates.” They also have a high modulus of elasticity and thus should help minimize drying shrinkage because, in a sense, they reduce the volume of the hydrated cement components, which upon drying cause shrinkage.

The strongest components of the paste are residual portland cement particles. The following concept has been expressed in the past. As the volume of residual portland cement particles in the paste progressively increases, the strength of the “paste” approaches the strength of portland cement clinker, which is thought to be in the neighborhood of 50,000 to 60,000 psi. As a consequence, drying shrinkage and creep should progressively decrease because there are less cement hydration products to shrink and also to “creep.” In

addition, due to drying shrinkage, these residual “micro-aggregate” particles are put in compression and peripheral hydrated cement components are put in axial tension. The paste thus becomes brittle. This is one explanation for a higher modulus of elasticity and increased brittleness with decreasing water-cement ratio ( $w/c$ ), and is a different concept than the increase in brittleness as hydration proceeds as described by the authors. The amount of residual portland cement is dependent upon the  $w/c$ , size of the coarser cement particles, and length of curing and curing conditions. Even under good curing conditions, it is unusual for most of the ferrite phase to hydrate as based upon microscopical examinations of varieties of pastes in laboratory and field concretes. The concept by the authors that increased cement hydration increases strength is true but, as they conclude, only to the extent that hydration products fill original water-occupied space.

Back to Item 1, we believe there has always been agreement that the actual compound composition of portland cement may be somewhat like, but nowhere near, that identified by the Bogue equations. We do believe that reported “average” compound compositions are sometimes taken at their face values for the different types of portland cement as given in Table 2 of the authors' article. It may be of interest to provide the high and low values for the major compounds in addition to the mean value for Type I portland cement from the same reference (Gebhardt) used by the authors. These are shown in the table.

**TABLE 1:**  
SPREAD OF COMPOUND COMPOSITIONS OF THE MAJOR CEMENT COMPOUNDS FOR 1994 TYPE I PORTLAND CEMENTS (BASED UPON DATA GIVEN BY GEBHARDT)

	Amount, %				Blaine fineness, cm <sup>2</sup> /gm
	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	
<b>Greatest</b>	59.6	25.6	13.0	10.0	410
<b>Lowest</b>	47.0	9.1	8.0	5.8	321
<b>Mean</b>	51.8	18.2	10.6	7.4	374

The range of compositional values, which obviously makes up the average values for Type I cement given in the authors' Table 2, means that the amount of water needed to completely hydrate the different cements must be quite variable and not a specific value as indicated in that table. In addition, the spread in Blaine fineness (from the table) does not

# Letters

reflect particle size distribution, which can be quite different at the same Blaine fineness so that the size and distribution of particles between cements can vary significantly. The variations in particle size distribution are somewhat conveyed in the Gebhardt compilation by the amount of minus 325 mesh (45  $\mu\text{m}$ ) material, which for Type I portland cement is reported to be from 81.0 to 96.9%. For a given cement, the particle size distribution will dictate the amount of cement that has hydrated at any particular time (that is, a finely ground cement will have hydrated more completely than a coarser ground cement because there is more surface area to react).

We present some pictorial examples of clinker “mineralogy” that will help explain some of the other things that we have been discussing.

Bernard Erlin and Dipayan Jana  
The Erlin Co.  
Latrobe, PA

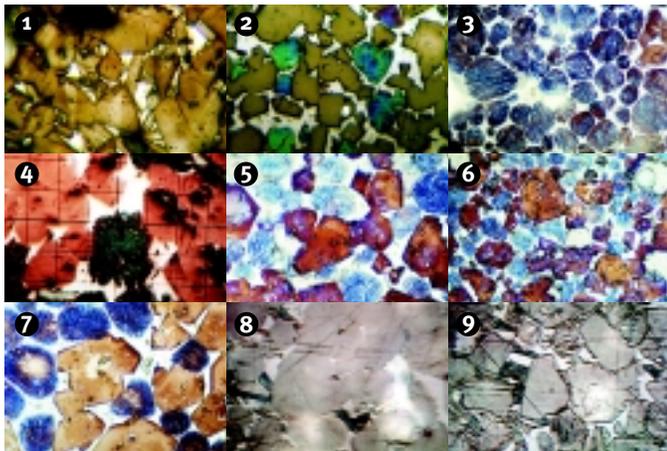


Fig. 1: Photomicrographs of polished sections (at comparable magnifications) that show variations of composition and crystal size of the compounds in different clinkers used to make Type I portland cement. The surfaces have been etched using nitric acid (1-7) and water (8, 9)

## AUTHORS' RESPONSE

The letter from Erlin and Jana discussing our article contains many kind words that are appreciated. Unfortunately, the discussion seems to have missed our point regarding the disadvantageousness of “hydrating all the cement.” We made it clear, we trust, that our data agree with those of Powers that if the  $w/c$  is not at least about 0.4 by mass it will be impossible to hydrate all of the cement. It has been our experience that many people in the concrete industry, who should know better, talk about how “there must be enough mixing water to hydrate all the

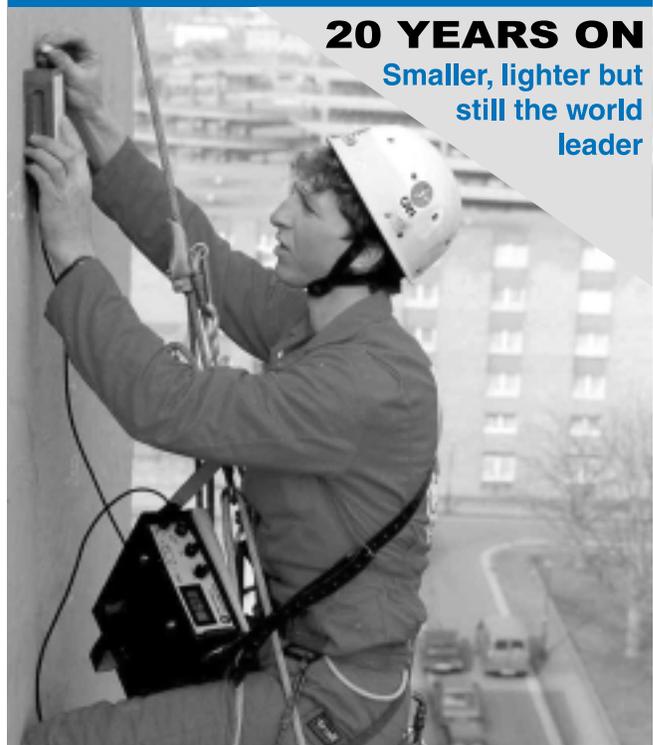
cement.” This is, of course, not true; nor is it true that when the  $w/c$  is more than about 0.4 that all the cement will hydrate. It can't practically be so because 100% is only achieved if kept moist for infinite time.

If all the cement has not hydrated in a given concrete at a given time and water is available in the paste and the original mixing water-filled space remains available to accept hydration products, hydration will continue. If not, it will stop, often with a  $w/c$  greater than 0.4, and unhydrated cement particles will remain embedded in the paste and presumably they will act to raise the elastic modulus of the concrete above what it would have been otherwise. However, in the real world, if there is some concrete made at  $w/c$  over 0.4 that under “normal” conditions is supplied no curing water after 28 days and therefore dries and no more cement hydrates, it will not be as strong and will not have as high a modulus of elasticity at later ages as it would if it were kept moist

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and allowed to go on gaining strength and brittleness (modulus), which it doesn't need to serve the function for which it was manufactured.

Getting a much higher brittleness than one needs to put up with is not a benefit. Hydrating all the cement that can hydrate may be a benefit if one needs to do that to get the strength and impermeability that is needed in a particular case—but that is not “hydrating all of the cement” for its own sake.

We believe we are quite as aware as are the discussers of the variation in composition of the phases (not “compounds”) by fractional mass or volume in cement samples all meeting the requirements of ASTM C 150 for Type I. This simply illustrates one of portland cement's more user-friendly features. One can make acceptable concrete at a wide range of chemical compositions. We are equally aware that calculated phase composition based on chemical analysis only

approximates the proportions of the actual amounts of each phase that is present in a sample. We did not regard it as sufficiently relevant to the points we attempted to make to emphasize that in our article.

We did not deal with expansive cements but Mr. Mather was involved with the ACI report on concrete curing and wrote in a version of that report that if all mixing water was retained during concrete curing, additional water would need to be supplied only if the  $w/c$  was significantly below 0.4 or the concrete was made with expansive cement. The committee withdrew the second part at the request of a maker of expansive cement whose cement was being used in concrete in airfield paving very satisfactorily with membrane curing. When it was pointed out that the customer was only getting half the expansion he was paying for, the producer replied: “He knows that, but he's happy.”

The discussion mentions the role of fineness (particle size distribution) in hydration. However, since our article dealt with how much water it takes to hydrate all of the cement, the particle size has no effect. Regardless of fineness of a given cement, it will take exactly the same amount of water to hydrate. After 150 years or more, some cement will probably remain unhydrated (as was the case in Joseph Aspdin's fence posts). George Verbeck once told Mr. Mather that he'd finally seen a cement paste in relatively old hardened concrete that had been made into fine cement—it had hydrated so that no unhydrated cement particles had been found in it. Mr. Mather has never seen one.

To summarize, the discussers make two proposal points—one has to do with the effect of full hydration on modulus of elasticity and the other has to do with the accuracy of the equations for determining phase composition:

1. Modulus of elasticity and full hydration of cement—That increased hydration of cement in a given concrete results in higher strength and higher modulus of elasticity of that concrete, up to a limit, seems to be an established truth based on tests on concrete specimens. The discussers' argument that hydrated cement paste has a lower modulus than unhydrated cement paste is convincing but seems relevant only on a microscopic scale. The modulus of elasticity of concrete, being a bulk property, is dependent not only on the modulus of the solid phases but also on the contribution from the porosity of the concrete. For a given concrete, at low levels of cement



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# Letters

hydration, the cement fraction has a higher modulus, but because the amount of porosity is relatively high, the net effect apparently is a lower bulk modulus. As hydration proceeds, the modulus of the cement fraction decreases but, because the porosity is decreased, apparently the net modulus of the concrete increases; and

2. Accuracy of the equations—The discussers' points here are granted, but we had intended the major point of the article to show that the amount of water required to fully hydrate portland cement is about 0.40, and that this number does vary with phase composition, but not in a major way over a reasonable range of values. The point was not to try to show how the exact water required for full hydration can be accurately calculated from a given phase composition. Had that been the point of the article, then the discussers' criticism of the accuracy of the calculations would be relevant. The assistance of Toy Poole in preparing this summary is acknowledged with appreciation.

Bryant Mather  
ERDC  
Vicksburg, MS

William G. Hime  
Wiss, Janney, Elstner  
Associates, Inc.  
Skokie, IL

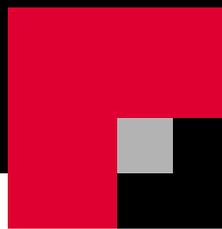
## SULFATE ATTACK

I read with interest Harvey Haynes' recent article ("Sulfate Attack on Concrete: Laboratory versus Field Experiences," *Concrete International*, V. 24, No. 7, July 2002, pp. 64-70). The article contains a good summary of the issues and potential mechanisms associated with sulfate attack. However, I

would like to correct a misstatement in the article. Mr. Haynes refers to a field study conducted by PCA, in cooperation with CALTRANS, in

which test beams were immersed in 68,000 ppm sulfate solutions for 16 years and comments that PCA "overlooked an opportunity" to study

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