Engineering Concrete Performance

Comparing chemical and physical options for producing desired properties

BY DALE P. BENTZ

Ever since the first concrete bridge, concrete street, and concrete high rise were built in the U.S. in 1889, 1891, and 1903, respectively, people have attempted to engineer the performance of concrete.[1] Performance-related characteristics (mainly strength) were initially engineered by varying the proportions of cement, water, sand, and coarse aggregate, and important parameters such as the water-cement ratio (w/c) were soon recognized.[2,3] Gradually, the important physical characteristics, such as particle size distribution, relative density, and shape, were also recognized for concrete's three main particulate components. While the chemistry of aggregates can be important in specific cases, such as alkali reactivity, the chemistry or phase composition of cements is always influential, particularly in terms of hydration and properties of the hardening concrete.

As with all materials, the performance of concrete is strongly influenced by its physical structure. Parameters such as the volumetric mixture proportions and particle size distributions will strongly influence the initial packing of the three-dimensional structure, and thus concrete's density and flow properties in the fresh state and its strength, shrinkage, and durability in the hardened state. For example, the particle size distribution or fineness of the cementitious materials has been recognized as having a large influence on durability,[4] autogenous volume change,[5,6] hydration kinetics,[7,8] setting time and heat release,[9] and strength development.[10,11]

From their earliest origins,[1] the performance of cement-based materials has been controlled by the judicious addition of supplemental chemicals. For example, the Romans used animal fat, milk, and blood as admixtures to enhance performance of their lime/pozzolana mortars.[1] Over two millennia later, air-entraining admixtures were introduced in the 1930s to improve the resistance of concrete to freezing-and-thawing cycles. Currently, concrete designers and technologists can select from a wide variety of chemical admixtures including air-entraining, accelerating, retarding, water-reducing, high-range water-reducing, viscosity modifying, shrinkage-reducing, corrosion-inhibiting, alkali-silica reaction mitigating, and anti-freezing admixtures; the list goes on and on.

From these examples, it's clear that the engineering of concrete performance has historically taken dual but parallel tracks using both physical and chemical approaches. Future engineering efforts will almost certainly maintain this tradition.

References for this article are available with the online version at www.concreteinternational.com.
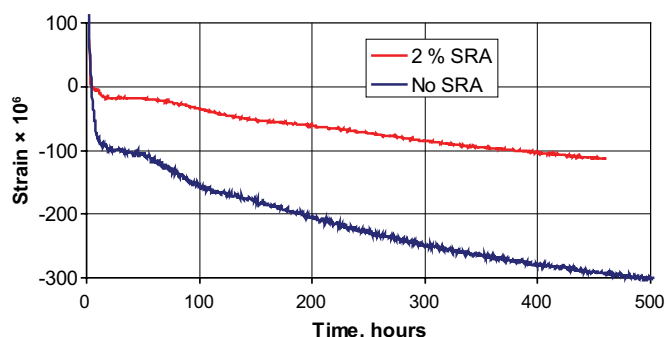
Fig. 1: Strain due to autogenous shrinkage obtained with and without the addition of 2% shrinkage-reducing admixture to a *w/cm* = 0.35 high-performance mortar[20]

SOME CONCRETE EXAMPLES
Rheological performance

In modern concretes, the use of both normal and high-range water-reducing admixtures is ubiquitous. These chemicals allow the proportioning of concrete mixtures with water-cementitious material ratios (*w/cm*) of 0.3 and even lower, leading to the production of higher strength and, it's hoped, higher performance concretes. While there are several classes of chemicals that function admirably in this role, in one way or another they all lead to a reduction in the interparticle forces between cementitious particles, avoiding the large degree of flocculation that occurs in a conventional system containing only water and cementitious material. This chemical approach to controlling rheology is quite sensitive to environmental conditions such as temperature. The retention of adequate rheological properties for the several hours required to haul, place, and finish concrete is a challenge. The benefits of these materials, however, far outweigh these occasional problems, and nearly all concrete mixtures are now proportioned with one or more water-reducing admixtures.

The particle size distributions and shapes of both the aggregates and the cementitious materials also have a strong influence on rheological properties. For example, finer cements are known to demand increased water to achieve the same flow properties as coarser cement. As another example, fly ash, with its usually spherically-shaped particles, has been noted to improve the rheological properties of pastes, mortars, and concretes in many instances.[12] This may also be due to its effects on inter-particle forces and the greater average interparticle spacing of the cement particles in a paste volume diluted by fly ash.[13] As pointed out in a comparison of gap-graded and well-graded mixtures,[14] the grading of aggregates also has a large influence on rheological properties such as finishability and pumpability. Slump is usually adjusted

by changing the dosage of the chemical admixtures. In cases where cement-admixture incompatibilities or problems with slump retention are encountered, however, the volumetric proportions, gradings, and shapes of the particulates comprising the mixture should also be considered and possibly modified to engineer an appropriate and sufficiently robust rheological performance.

Segregation in self-consolidating concrete

As self-consolidating concrete has moved from the laboratory to the field, a problem sometimes encountered in practice is the settlement of the larger aggregate particles to the bottom of the concrete and the concurrent formation of a mortar-rich layer at the top.[15] In addition to increasing the fines content of the concrete, this is often avoided by adding special viscosity modifiers and other chemicals to the mixture to slow or eliminate aggregate settlement. Though not as commonly employed, this problem could also be addressed from a purely physical approach by replacing the normalweight coarse aggregates with a prewetted lightweight coarse aggregate with a saturated surface-dry relative density similar to that of the paste component of the concrete. Minimizing the difference in density between paste and aggregates minimizes the driving force for the segregation.

Plastic shrinkage cracking

From a physical approach, significant reductions in plastic shrinkage cracking have been achieved in recent years with the introduction of distributed fibers.[16] For example, at volume fractions as small as 0.2%, fibers can reduce plastic shrinkage cracking to 10% of that exhibited by a control system with no fiber addition.[16] Even more recently, a new chemical approach to reducing plastic shrinkage cracking based on the use of shrinkage-reducing admixtures to reduce drying rates and internal stresses has been demonstrated.[17,18]

### Autogenous shrinkage and early-age cracking

Achieving the promise of high-performance concrete has been hampered by its increased autogenous shrinkage and accompanying propensity for early-age cracking. Mitigation of autogenous shrinkage can be accomplished by a variety of means, some chemical and some physical in nature.[19] Other than using expansive agents, the primary chemical means that can be used to reduce autogenous shrinkage is the addition of a shrinkage-reducing admixture (SRA) to the concrete. Conventionally used to reduce drying shrinkage, the presence of the SRA reduces the surface tension of the pore solution which, in a sealed system, leads to a reduction in the capillary stresses and strains exerted on the hydrating microstructure.[18,20,21] Figure 1 provides an example of the

autogenous shrinkage reduction obtained by the addition of 2% SRA (by mass of cement) to a w/cm = 0.35 mortar.[20] In this case, the long-term autogenous shrinkage is reduced by more than a factor of two.

There are also several available physical approaches to reducing autogenous shrinkage. For example, as mentioned previously, autogenous shrinkage is dependent on the fineness of a cement. For a coarse enough cement, an actual autogenous expansion, as opposed to a shrinkage, may be observed at early ages.[6] As an example,[6] for a w/c = 0.35 paste, substantial autogenous shrinkage was observed for the same cement when ground to a Blaine fineness of either 387 or 643 m²/kg. Conversely, an early-age expansion was observed for the two cements produced with Blaine finenesses of 254 and 212 m²/kg. For these latter two pastes, the net deformation values were nearly zero even after 28 days of sealed curing, while the finer cements exhibited shrinkages of more than 500 microstrain and evidence of cracking.[6] A cement with a Blaine fineness of 250 m²/kg, however, is nowhere to be found in the U.S. in the twenty-first century as most cements are approaching or have exceeded 400 m²/kg.[22] To my knowledge, the coarsest Type I/II cement currently available in the U.S. has a Blaine fineness of about 310 m²/kg.

Another physical approach to reducing autogenous shrinkage is the incorporation of internal curing by adding physical internal water reservoirs to the concrete mixture.[23,24] These reservoirs can consist of prewetted lightweight fine aggregate, super-absorbent polymers, or prewetted wood fibers. Because they contain pores that are larger than those in the hydrating cement paste, water is preferentially drawn from the reservoirs to the paste during hydration. Thus, the small pores in the paste are maintained in a saturated condition, avoiding self-desiccation and the generation of large internal stresses and strains. The emptying of the larger pores in the internal curing agent does not cause significant shrinkage of the concrete, as the shrinkage stresses are inversely proportional to the pore radius.

Figure 2 provides an example of the reduction in autogenous shrinkage that is achievable by the addition of an internal curing agent (with an extra 8% internal curing water by mass of cement) to a blended cement mortar. Internal curing is especially important in blended cement systems due to their generally increased chemical shrinkage relative to conventional cement, which results in an increased demand for additional curing water. Blended cements also have a propensity to form a denser, less permeable pore system that can drastically reduce the efficiency of external water curing. For some internal curing materials, the reservoirs can be employed to distribute chemical admixtures, in addition to water, during the cement hydration process.[25]
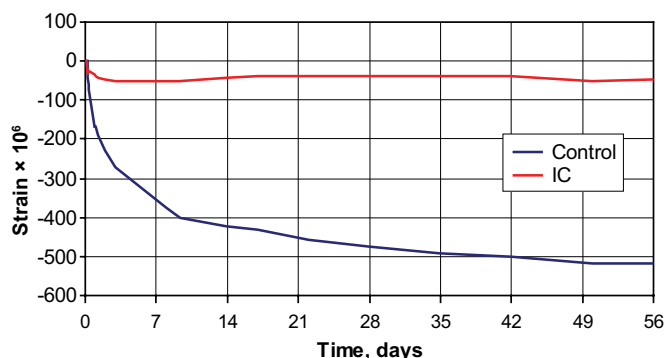
Fig. 2: Strain due to autogenous shrinkage obtained with and without the addition of internal curing with prewetted lightweight aggregates to a w/cm = 0.3 blended cement mortar containing 20% slag cement by mass of cement[24]

High early strength

High early strength has been an increasing concern of the construction industry in recent years, due mainly to the emphasis on fast-track construction and faster cycle times in the precast industry. In addition to conventional concretes, high early strength formulations have recently been engineered for self-consolidating concrete, repair products, and engineered cementitious composites.[26-28] It has long been recognized that the physical[10,11] and chemical properties of the cement are critical to strength development, as exemplified by the development of an ASTM standard classification, Type III, for high early strength cement. Since the 1950s, both the fineness and the chemical composition of cements have changed substantially. One result of these changes has been the increase by about a factor of three of the 1-day compressive strength of ASTM C 109 mortar cubes.[22]

Most cement manufacturers have moved from controlling Blaine fineness to controlling the complete particle size distribution of their products. With the newer high-performance separators (classifiers) in cement plants, it's now possible to produce a wider range of cement particle size distributions, such as a cement with basically no particles larger than 30 µm (1.2 mil) in diameter.[29] With present-day technology, cement manufacturers can now chemically and physically engineer cements for specific markets or even for specific seasons of the year. Pozzolans such as silica fume are another example of a combined chemical and physical approach to increasing early-age hydration and strength; the chemical effects are due to the pozzolanic reactions between the silica fume and the calcium hydroxide produced during cement hydration, while the physical effects are due to the extremely small particle size of a well-dispersed silica fume.

Chemical admixtures have long provided an alternate route to high early strengths. While the original calcium

chloride-based admixtures have lost favor due to their negative impacts on corrosion resistance and durability, a variety of nonchloride-based accelerators, such as calcium nitrates, have quickly filled this role.[26-28] The chemical admixture approach offers the advantage that the dosage and performance can be tailored to local environmental conditions that may be changing on a daily basis. If the cementitious components of the concrete are found to be too reactive at early ages, a retarding chemical admixture can also be added.

Resistance to freezing and thawing

As mentioned previously, air-entraining agents were introduced in the U.S. in the 1930s as a chemically-induced, yet physical means to increase concrete's resistance to cycles of freezing and thawing. They are employed to stabilize a microscopic system of entrained air bubbles in fresh concrete. Both the overall air content and the spacing factor that describe how the air bubbles are distributed within the three-dimensional concrete microstructure are critical to assuring adequate

TABLE 1:
Some freely available computational tools for predicting concrete performance

Tool name	Website	Functionality
HIPERPAV	www.hiperpav.com	HIPERPAV is user-friendly, Windows-based software designed to assess the influence of pavement design, concrete mixture proportions, construction methods, and environmental conditions on the early-age behavior of portland cement concrete pavements.
Life-365	www.corrosioninhibitors.org/life365.htm	Life-365 is a computer program for predicting the service life and life-cycle costs of reinforced concrete exposed to chlorides.
Curing	http://construction.asu.edu/cim/curing/curingfirstpage.htm	This program computes the evaporation rate for concrete according to nomographs in ACI 308-92, "Standard Practice for Curing Concrete." The air temperature, humidity, concrete temperature, and wind velocity are input to determine if conditions are favorable for plastic shrinkage cracking.
Internal curing	http://ciks.cbt.nist.gov/lwagg.html	Resources for internal curing, including mixture proportioning, three-dimensional simulation of water reservoir distribution, and an extensive bibliography.
CIKS	http://ciks.cbt.nist.gov/ciks.html	Computer Integrated Knowledge System for high-performance concrete includes mixture proportioning, chloride diffusion, service life prediction, and a virtual rapid chloride permeability test.
COST	http://ciks.cbt.nist.gov/cost	Concrete Optimization Software Tool is an online design/analysis system to assist concrete producers, engineers, and researchers in determining optimal mixture proportions for concrete.
VCCTL	http://vcctl.cbt.nist.gov	Virtual Cement and Concrete Testing Laboratory for simulation of hydration and microstructure development, including prediction of numerous physical properties including heat evolution, setting, diffusivities, and strengths.

performance.[30,31] The stability of this chemically-induced air void system during hauling, placement, and pumping has long been an issue, along with the detrimental influences of other components of the concrete on this stability, such as fly ash with a high carbon content.

A second possibility for obtaining resistance to freezing and thawing would be to distribute a physical set of air voids within the concrete. For example, prewetted lightweight aggregate used to provide internal curing may become empty during early-age hydration and then function successfully as part of an air void system in the hardened concrete.[32] While not conclusively proven by a detailed study, the empirical evidence provided by the excellent durability of lightweight concrete lends credence to this possibility.[33] Super-absorbent polymers used to provide internal curing may also provide a very controlled system of nearly monosize spherical air voids once their work as internal curing agents is completed.[34]

Unpublished research has also indicated that other porous materials such as spent fuel cracking catalyst may provide an adequate air void system in concrete. While this physical air should be immune to the detrimental influences of other admixtures or fly ash, it will likely be saturated either prior to its introduction or during its mixing in the fresh concrete. Thus, it will only function as air voids if this internal water is removed by either self-desiccation or drying during the hardening process. The spatial and size distributions of these air reservoirs will be of equal importance to their overall volume fraction.

Transport/reaction-based degradation processes

Many degradation processes in concrete require or are significantly enhanced by the ingress of a deleterious species such as chloride, sulfate, or alkali ions. There are two viable options for mitigating such degradation. The first is to provide a physical barrier to the ingress of the deleterious species. The second is to use a chemical admixture to avoid, reduce, or alter the degradation process. In the former case, the barrier may be provided by products such as sealers, coatings, and crystalline waterproofing[35] applied at the concrete surface; by products such as hydrophobic admixtures[36] mixed directly into the concrete; by the concrete itself through densification and transport reduction by the use of a low w/cm, a finer cement, or appropriate pozzolans; or at the location of the degradation as in epoxy-coated reinforcing bars. Examples of the latter approach would include the use of corrosion inhibitors[37,38] or ASR-mitigating admixtures such as lithium-based compounds.[39-41]

COMPUTATIONAL TOOLS

In the past 10 years, numerous computational tools have been developed and refined for predicting concrete performance as a function of materials and environmental conditions. These tools allow their users to conveniently investigate the influence of many of the chemical and physical approaches described in this article. Table 1 provides the names, websites, and descriptions of a number of freely available tools. Numerous other tools are available for a fee. Many of these tools have been developed in the Inorganic Materials Group at the National Institute of Standards and Technology. A convenient portal site for all of them can be found at **http://ciks.cbt.nist.gov/cmml.html**.

OPTIONS

"Better concrete through chemistry" is not that far from the actual recent headline and content of the article "Synthetic Chemistry Moves into Concrete" from the October 11, 2004, issue of *Chemical & Engineering News*. Chemistry has made and continues to make valuable contributions to endowing concrete with new and desirable properties, increasing durability, and expanding the range of construction applications. Robustness, environmental sensitivity, and detrimental interactions are all issues that will continue to arise as these chemical technologies are applied to variable materials in an even more variable field environment. When these issues do arise, it may be beneficial to consider the possibilities offered by the physical methods of engineering concrete performance in place of or in addition to the more commonly employed chemical means.

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References for this article can be found in the electronic version available at **www.concreteinternational.com.**

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