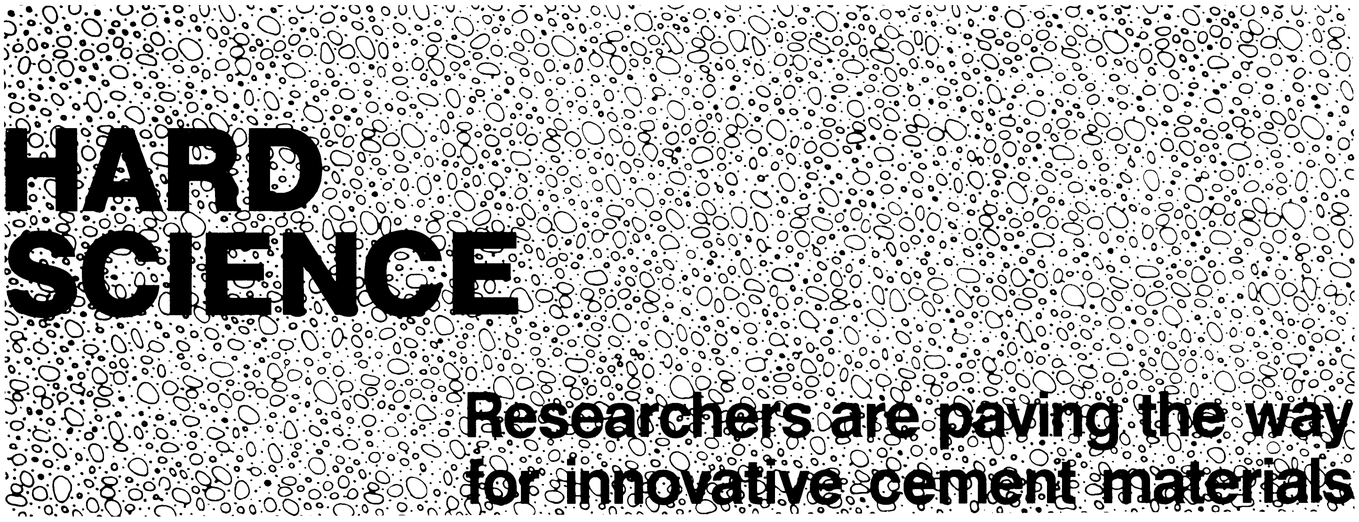


HARD SCIENCE

Researchers are paving the way for innovative cement materials

By STEFI WEISBURD

Concrete is the very foundation of civilization. The Egyptians held together their pyramids with a cement-like mortar, and the Greeks lined cisterns and built walls with a primitive concrete. The Romans, having discovered that adding volcanic ash gave their cements superior strength and water resistance, erected the Colosseum, the Pantheon and a multitude of other concrete buildings and underwater structures. Centuries later, these stand as some of the world's most durable examples of concrete architecture.

Today our houses, roads, runways, bridges and skyscrapers depend on concrete. So do dams, cooling towers, factories and some of the tallest television and radio towers. Concrete pipes carry water and sewage. Concrete bins store everything from grain to coal. There are concrete boats and barges, and every year the American Society of Civil Engineers sponsors concrete canoe races and concrete Frisbee contests.

At a cost of a penny a pound, concrete — a mixture of binding cement, gravel, sand and water — is the cheapest, most plentiful and most commonly used building material. Annual world consumption totals roughly 1 ton for every person living on the planet. In the United States alone, the value of all concrete-based structures has been estimated at $6 trillion.

Yet our concrete world is crumbling from corrosion and poorly made and maintained materials. According to a 1987 National Research Council report, it will cost $50 billion to repair or replace deteriorating bridges alone and an estimated $1 trillion to $3 trillion over the next 20 years to fix all U.S. concrete structures.

"Because we don't understand it correctly, we are spending a lot of money in maintenance and repair and replacement of concrete," says Surendra Shah, director of Northwestern University's Center for Concrete and Geomaterials in Evanston, Ill. "We take concrete materials for granted. They have a low-tech image."

Such statements, however, should not be cast in . . . well, concrete. After 5,000 years of concocting cement and concrete recipes largely by trial and error, scientists in Europe, Japan and the United States are coming closer to understanding the fundamental chemistry and physics of cements and are designing concrete materials that will last longer, stand up to environmental forces better and achieve greater strength, flexibility and toughness.

Scientists are exploring specialty cements that can be shaped into springs, be formed into blades for jet engine turbines, replace teeth or bones, store nuclear wastes or be used to make integrated circuits. Cements also are being designed to withstand the corrosive effects of seawater and salt, and the crumbling power of earthquakes and explosive blasts.

Researchers "have a chance to create a revolution in our ways of using cement-based materials," says J. Francis Young, director of the University of Illinois Center for Cement Composite Materials in Urbana-Champaign. "The concrete industry is not the world's most progressive and it has not been using the potential of cements to anywhere close to what they can do. That's what we're trying to do — to see just how far you can create high-performance materials using the cement reaction."

Most concretes used today are based on portland cement, which was patented in 1824 by an English bricklayer after he burned limestone (calcium carbonate) and clay (aluminosilicates) together in his kitchen stove. (He named the new material after the gray stone quarried on England's Isle of Portland.) When mixed with water, cement powder takes on a mud-like consistency. Then it hardens in a process that can take months or even years. Concrete hardens not by drying but by hydration — chemical reactions in which the five or so major compounds in cement incorporate water molecules into their structures.

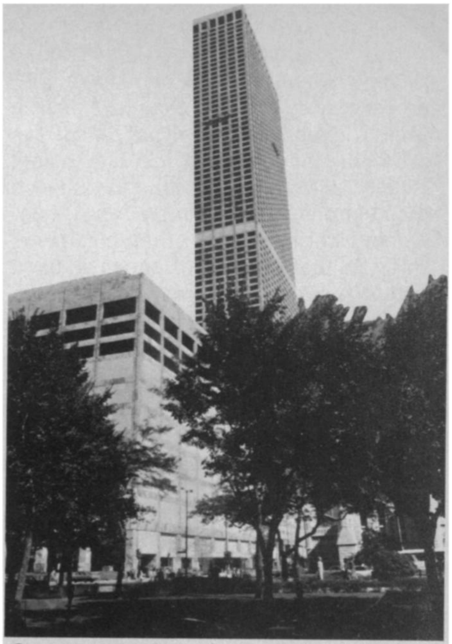
The most important chemical reaction occurs when water and tricalcium silicate combine to form calcium hydroxide and a calcium silicate hydrate. The latter precipitates out as a gelatinous material that coats cement grains and bridges them together. The calcium silicate hydrate can grow into spiny and densely packed tendrils that stick out from cement grains like porcupine quills, or it can form a structure resembling crumbled foil. The resulting interwoven network binds together all the hydrated cement crystals, unreacted cement grains and the sand and gravel in the concrete. This network is primarily responsible for a cement's strength.

But cement has an Achilles' heel. Its main source of weakness is the little pockets of air and water dispersed throughout the material, which dilute its strength after it hardens. The culprit in high porosity is water. Water need account for only about 20 percent of a cement's weight for the hydration reactions to take place. But in practice, workers typically add much more in order to make the liquid cement easy to work and finish, says Jan P. Skalny at W.R. Grace and Co. in Columbia, Md. Excess water that freezes and thaws also cracks concrete. As a result, the thrust of much cement research is to reduce the porosity and the amount of water required, without making the cement stiff and hard to shape.

One of the most important advances in construction concrete involves the use of "superplasticizers" such as sulfated organic chemicals, which make the cement more fluid with less water. With these compounds, "the maximum strength of ready-mix concrete has more than doubled in the last 15 to 20 years," notes Geoffrey Frohnsdorff at the National Bureau of Standards in Gaithersburg, Md. "We don't know what the limit is, but it is conceivable it could be doubled again."

Like most innovations in cement, however, the use of superplasticizers has

Courtesy of Construction Technology Laboratories



Some examples of concrete at its best include the Pantheon in Rome and the 859-foot-high Water Tower Place in Chicago, the world's tallest reinforced-concrete building.

been largely empirical; scientists know that the chemicals somehow change the surfaces of the cement grains, but they have yet to unearth the fine details of how superplasticizers work – details that might help them design even stronger construction concretes.

While research on construction concrete continues to creep along, scientists in the last few years have gotten unusually fired up over innovative work on specialty cements – materials too expensive to use in voluminous quantities for everyday building, but whose special properties make them ideal for a host of other applications. These materials are several times as strong as any cement used in civil engineering today.

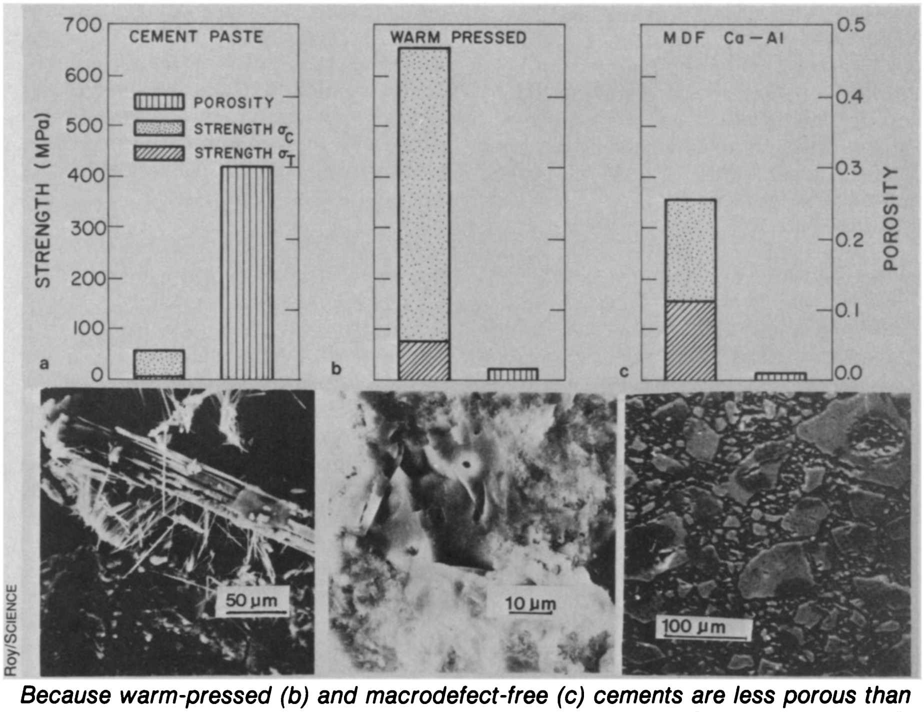
Moreover, their strengths are approaching those of traditional ceramic materials. The advantage of ceramics and cements (a class of "chemically bonded ceramics") is that they keep their shapes at high temperatures. But unlike most ceramics, cements are produced near room temperature with relatively simple, low-energy and inexpensive processes. "There are no other materials that become solid at room temperature and atmospheric pressure," Shah notes. "Glass and metal have to be melted first and ceramics have to be sintered at high temperatures."

One superstrong specialty cement, developed in Scandinavia, is known as "densified with small particles" (DSP) material. The DSP recipe blends cement grains with fine particles of silica fume – a by-product of silicon metal and alloy production – or other materials. The fine particles pack snugly between the cement grains, filling the voids to the maximum possible extent, decreasing pore size and reducing the amount of water needed.

The compressive strength of DSP cements ranges from 20,000 to 40,000 pounds per square inch (psi), Young says. Civil engineering cements typically withstand only several thousand psi of compression.

An added benefit of using silica fume or other silica particles is that they react with and eliminate calcium hydroxide crystals, implicated in the deterioration of concrete exposed to seawater. DSP-type cements are already used on bridge decks because their high densities and low porosities make them highly resistant to attack from the salt routinely used to melt ice. And because DSP cements resist abrasion, they are used in processing coal, fly ash and other abrasive powders. Researchers envision other applications too, from coatings on runways to nuclear waste disposal.

Young and his colleagues are investigating the *electrical* properties of DSP cements. "We're able to create a material that has dielectric properties very similar to alumina, which is used extensively as an insulating substrate in integrated



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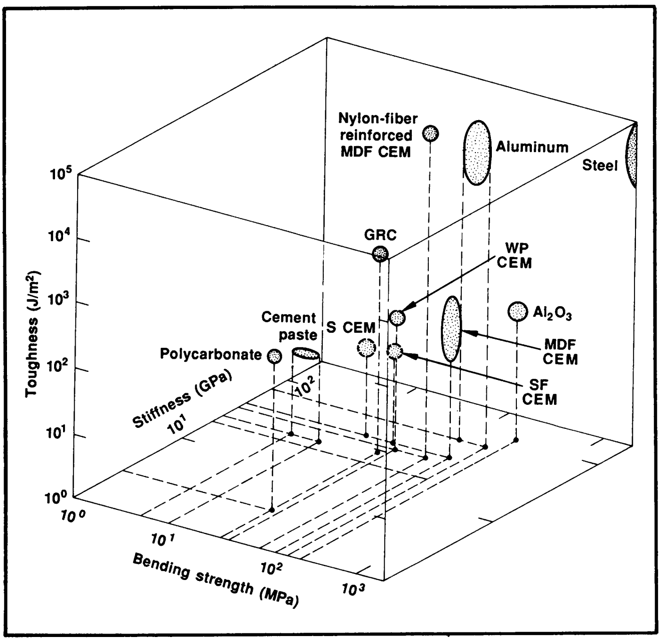
Because warm-pressed (b) and macrodefect-free (c) cements are less porous than normal cement paste (a), they have higher compressive (σ C) and tensile (σ T) strengths.



SCIENCE, fig. 6, p.657

With better understanding of the chemistry and physics of cements, scientists hope to custom-design materials having a wide variety of properties. Here, the mechanical properties of different cements are compared with those of plastics, alumina, aluminum and steel. (CEM = cement; S = slag; SF = silica fume; WP = warm-pressed; GRC = glass reinforced; MDF = macro-defect-free.)

circuits," he says. By adding hollow spheres, Young's group can make DSP cements more ductile than the brittle alumina substrates, many of which are lost to breakage during manufacturing. Because DSP substrates could be made at room temperature, this might enable device engineers to use other electronic materials that presently cannot be used because of their sensitivity to high temperatures. The one problem researchers face is making the materials more stable when exposed to moisture.

If any cement innovation has churned up interest in the last few years, it's the development of "macrodefect-free" (MDF) cement by scientists at Imperial Chemical Industries (ICI) in Runcorn, England. In the MDF process, water-soluble polymers are added to help keep the cement pliable, thereby requiring less water during mixing. The crumbly MDF dough is squeezed between two rollers to produce a dense, flexible plastic sheet that can be extruded into virtually any shape.

MDF cements have high compressive strengths, and their flexural properties are remarkable. Cement is notoriously weak under bending. But ICI researchers have reported a 40,000-psi compression strength and a striking 20,000-psi flexural strength. And Young says his group has doubled these numbers with some refinements in MDF processing.

Scientists envision all sorts of MDF applications – including relatively flexible pipes and fittings, window and door frames and table tops. ICI researchers have made turntables, stereo cabinets, bottle caps and springs out of MDF cement. Add metallic fibers, and "we'd have a material that would be good for isolating electronic equipment from electromagnetic interference such as might occur during blasts or nuclear tests," Young says. "This material is so new, there are all kinds of possibilities we haven't thought of."

Besides strength, another difficulty is that concrete cracks easily. To make less-brittle concretes, scientists mix in fibers, just as brickmakers used to mix in pieces of straw. "It's the same principle as building adobe houses, but now we've pushed it to a point where it's scientifically based on the properties of the material," says Antoine Naaman at the University of Michigan in Ann Arbor.

The fibers – made from steel, glass, polymers, asbestos and other materials – keep the concrete from crumbling and prevent any cracks that form from opening. Naaman's group has made steel-fiber cements that can withstand impacts up to 1,000 times more energetic than those withstood by ordinary cements.

One type of fiber cement, called slurry-infiltrated fiber-concrete, or SIFCON, is especially tough and has been considered for use in missile silos. Because it can be formed into complex shapes, researchers envision SIFCON replacing wood, cast iron, steel and fiber-reinforced plastics in a multitude of uses. Naaman is designing and testing SIFCON joints for the parts of buildings most vulnerable to earthquakes.

At the University of Texas in Austin, David Fowler and his colleagues are studying concretes bound together by polymers instead of portland cements. While such polymer concretes burn or lose their shape at high temperatures, they are stronger, more durable and more resistant to acids, salts and water than are portland cements at room temperature. Moreover, they set remarkably quickly. Fowler is also studying the structural properties of polymer concretes reinforced with steel, as well as how to recycle soda bottles and other plastics into polymer concrete materials.

In spite of such exotic cements, concrete engineering has progressed surprisingly little from the days of the Pantheon. In trying to design concretes that would safely entomb nuclear wastes, for example, Della M. Roy at Pennsylvania State University in University Park and her colleagues found that the chemical compositions of long-lasting Roman cements are very similar to what researchers currently predict to be the most durable materials on the basis of thermodynamic principles. The Romans' success, however, was largely grounded in a fortuitous choice of materials. Today scientists want to do better.

They want to uncover the molecular intricacies of the hydration process, much of which remains unsolved. Several kinds of chemical reactions occur, all of which depend on a confusing array of factors. These include the kinds of impurities in the raw materials, the different sizes of cement grains reacting with water and the different crystalline structures of cement compounds. Scientists have only begun to understand the physical forces that bind cements together, as well as how the microstructure and chemistry translate into macroscopic properties such as strength and brittleness.

"We still don't know very much about all these things," Frohnsdorff says. "But if we really want to control and predict the performance of cements, we need to understand how cement reacts with water in a more detailed and quantitative way."

As scientists unravel the chemistry and physics of cements and pave the way for inventing new materials, they must find ways to inject their new ideas into the conventional concrete industry. "We already have a tremendous amount of knowledge which we don't use," Skalny says. "One of the reasons is that the construction labor force is the lowest paid and least educated. . . . Moreover, very few civil engineering departments in the country even teach materials courses in concrete. Engineers know how to design a structure without understanding the material. You can get a PhD in civil engineering without knowing why concrete hardens."

Perhaps the exotic new cements emerging will challenge architects and structural engineers to stretch their horizons. "To use these kinds of [high-strength] materials in construction and civil engineering, we're going to have to rethink our approach to design and look at some quite revolutionary ways of using them," Young says. "We'll have to think of new ways of creating buildings." ☐