the dominant countries in the past, persons from the high part of the income distribution (who presumably are the most able and highly motivated) have less incentive to emigrate, whereas the persons in the bottom part of the income distribution have increased incentives to emigrate [G. J. Borjas, "Immigration and self-selection: An analysis of intercountry differences" (Univ. of California, Santa Barbara, 1986), mimeograph].

35. Several persons have asserted but have not shown that persons coming in through family visas do worse in the labor market than persons who come in through occupational visas [E. Abrams and F. S. Abrams, *Public Interest* **38**, 3 (1975)].
36. See Borjas in (*33*).
37. Computed from G. J. Borjas (*33*), tables 1, 4, 5, and 6.
38. The base referred to in Table 3 is the native group of like national origin as the immigrant group. For example, Mexican immigrants are compared to persons of Mexican origin born in the United States, black immigrants are compared to black native persons, and so on. The differentials reported control for differences in socioeconomic characteristics between immigrants and natives.
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45. We thank S. J. Walsh, D. Duesterhoeft and G. Heisserer for technical assistance, and L. Uhr for editorial assistance. This research was supported by grants from ASPE of the Department of Health and Human Services to the Institute for Research on Poverty, from the U.S. Department of Agriculture (Hatch Act) to the Department of Rural Sociology, from the Ford Foundation to the National Bureau of Economic Research, and NSF grant SES-8603973 to the University of California, Santa Barbara. We gratefully acknowledge helpful comments on an earlier draft from F. Bean, R. Freeman, L. Jensen, D. Massey, A. Portes, and several anonymous reviewers.

New Strong Cement Materials: Chemically Bonded Ceramics

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New cements developed in recent years have strengths that are greater by an order of magnitude than those of conventional hydraulic cements. These low-temperature materials, whose strengths approach those of many traditional high-temperature ceramics, are termed chemically bonded ceramics. The different routes to generating strong cementitious materials, including warm pressing, chemical modification, high-shear mixing with polymer additions, and the making of fiber and particulate composites, are reviewed. Strength, toughness, durability, impermeability, and abrasion resistance of these new materials have been greatly improved, as have certain electrical and acoustical properties.

NEW DEVELOPMENTS IN THE MAKING OF VERY STRONG cements have resulted from (i) modifying cement compositions (and the associated hydration, consolidation, and densification processes) and (ii) manipulating the microstructures. Together, these developments have produced about tenfold enhancements in their properties which approach those of many traditional ceramics or modern composites. These materials are called chemically bonded ceramics (CBCs) which refers to the bonding that takes place in a chemical reaction at low temperature, as opposed to fusion or sintering at elevated temperature. The bonding in such CBCs is a mixture of ionic, covalent, and van der Waals bonding, with the ionic and covalent dominating; in traditional cement hydration products, van der Waals and hydrogen bonding dominate. In this article I discuss first conventional cements and then different types of CBCs and the new brittle matrix composites. Finally, a brief perspective on the future of these materials is presented.

Portland and other cements—and the concretes made by combining them with different kinds of aggregates—are used in larger quantities than any other man-made materials (*1, 2*). Such cements offer modest strength and stiffness in compression but are weak in tension and severely lacking in toughness. Yet even with the extremely primitive cement technology that prevailed in ancient times, Greek cisterns and the remarkable Colosseum and Pantheon in Rome have lasted for 2000 to 3000 years (*3*).

Normal hydraulic (or portland) cement powder has four major components: tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_6$), and calcium aluminoferrite solid solution ($Ca_2Fe_xAl_{2-x}O_5$). Small amounts of gypsum ($CaSO_4{\cdot}2H_2O$) and other minor components, such as alkali sulfates, are also present. When mixed with water, cement undergoes an exothermic hydration-hydrolysis reaction. Immediately after the paste is formed, there is a period of time—several hours—in which to finish shaping the desired object in a simple fashion at room temperature, before the setting reaction precludes further handling.

The reaction rate and consequent rate of heat evolution are a function of the total chemical composition, the crystal chemistry of the cement minerals, the fineness of the powder, and the temperature of setting. Setting and hardening are the result of a complex sequence of processes (Fig. 1). Hardened cement paste has a finely intergrown microstructure dominated by the major binding component, a very high surface area, and submicrometer-sized noncrystalline fibers or particles of calcium silicate hydrate (CSH). These grow between and link together larger crystallites and residual anhydrous cement grain cores and their perimeters, leaving a microporous material with minimal interconnected capillaries.

The solidification of cement paste is a constant-volume process. When high-density cement particles are mixed with low-density water, they react to form a solid hydration product consisting of solids of intermediate density and interspersed residual porosity.

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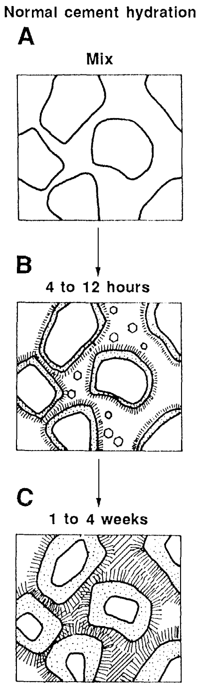

Fig. 1. Schematic development of normal cement paste microstructure with setting and hardening. (**A**) Cement grains (Ca_3SiO_5, Ca_2SiO_4, $Ca_3Al_2O_6$, $Ca_2Fe_xAl_{2-x}O_5$, and $CaSO_4 \cdot 2H_2O$) dispersed in water. (**B**) Set cement paste at 15 to 20% hydration. CSH noncrystalline fibers of submicrometer size form a reticulate structure, which links larger crystallites and anhydrous cores to form a highly porous material. (**C**) Fully hardened cement paste at 60 to 70% hydration. CSH fibers fill most of the large pores; these fibers and crystalline hydrates bind the now smaller anhydrous cores. Large and small pores remain to yield moderate porosity.

The strength of hardened cement paste increases as the ratio of water to cement (*w/c*) is reduced. Because the residual porosity, its distribution, and the excess molecular water cause most of the limitations on the properties of conventional hardened cement paste (*2, 4, 5*), many attempts have been made to reduce the amount of water. There is a practical limit if the mixture is to remain workable. Some decades ago it was discovered that increased workability at a constant *w/c* ratio could be achieved with admixtures that contain a small amount of chemicals such as lignosulfonates and related dispersants. However, the setting is retarded when such admixtures are made. New chemical admixtures (made with superplasticizers) provide much better control of the setting of cement paste and improve the properties of the concrete (*2*).

Nevertheless, the utility of these porous hydraulic cement products has been limited by their low tensile strength (~3 MPa) and low work of fracture [~20 J/m^3 (*6*)], despite compressive strengths of ~30 MPa. In addition to the presence of spherical pores and air voids, cement pastes with a normal *w/c* ratio ($\geq$0.40) may undergo shrinkage during drying, which induces microcracking when the material is exposed to low-humidity environments. This is one source of "Griffith flaws" (*7*), which initiate fracture under loading.

Since 1970 cement matrix composites have been developed (*8*). Four major advances have taken place: (i) the formation of specially densified or warm-pressed cement pastes that have properties approximating those of fired ceramics; (ii) modification of the chemical composition of the cement; (iii) the formation of macrodefect-free cements prepared by special processing; and (iv) the manufacture of a variety of cement-based composites.

Dense Warm-Pressed Cement Pastes

For decades uncertainties have existed regarding the factors that limit the theoretical strength of hydrated cement paste, or the strength a cement paste could achieve if it could approach the theoretical density. The bonds limiting the strength of cement paste are thought to be weak van der Waals forces. One might expect materials prepared under conditions involving dissolution and diffusion reactions which result in a dense interlocking microstructure as hydration takes place simultaneously with pressing, to be slightly stronger. However, the crystal chemistry and physics of the polycrystalline aggregate suggest a different answer. Set cement can be idealized as a polycrystalline "chemically bonded" aggregate of a silicate phase, CSH-I [a hydrated calcium silicate, schematically represented as Ca-Si-O-(OH)]. Drawing upon analogies to silicate minerals and assuming that there are no pronounced anisotropies (as in mica; none are known), one concludes that the "theoretical" strength of such a ceramic material could be in the range of similar oxide and natural silicate materials [dense polycrystalline nephrite $Ca_2(Mg,Fe)_5(Si_4O_{11})_2(OH)_2$ or jadeite $NaAlSi_2O_6$]. The mechanical properties of these materials are comparable to those of the best ceramics.

Very high strength through warm pressing. Before 1970, the potential strength of cement paste at theoretical density (possibly related to Powers "intrinsic strength") (*5*) had never been approached, because considerable porosity (20 to 30% or more total porosity) always remained after complete hydration of the cement. In 1971, I undertook research aimed at achieving very high strengths by "warm pressing" (applying heat and pressure simultaneously) of cement pastes (*9–11*). Some modest increases in strength had been achieved earlier by application of pressure alone (*12*).

Strengths an order of magnitude higher than those of normal cement pastes were achieved by warm pressing different types of cements, such as portland varieties, calcium aluminate cements, and individual cement compounds. Compressive strengths (σ_C) up to 650 MPa (compared to the typical 30 MPa, see Fig. 2), tensile strength (σ_T) up to 68 MPa, and values of Young's modulus (E) up to 40 GPa (10^6 N/m^2) were attained (*9–11*). These dense cement pastes are microcomposites consisting of about 50% residual anhy-

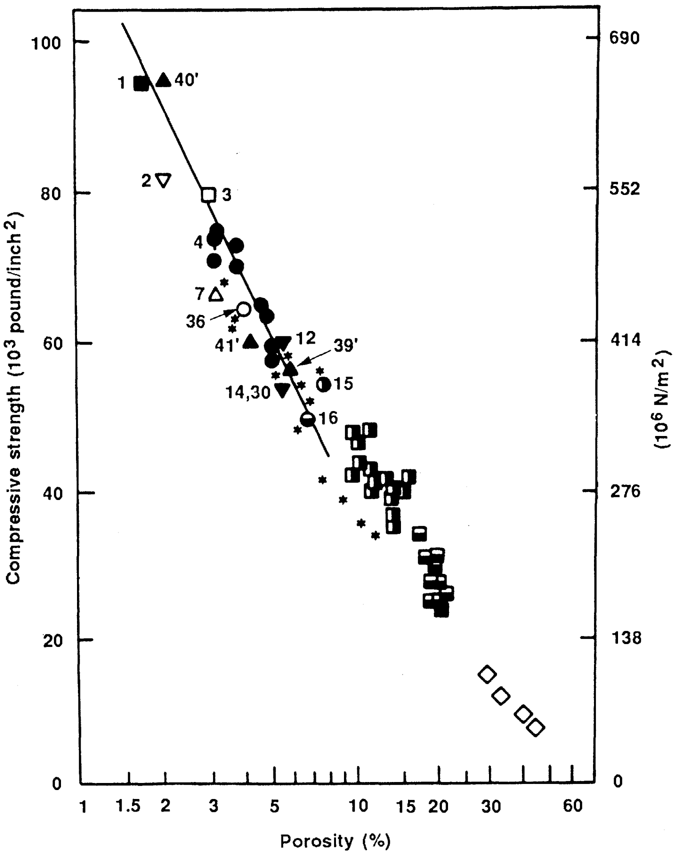

Fig. 2. Compressive strength versus the logarithm of porosity for mature cement pastes. The results for warm-pressed pastes are shown as the data near the line, whereas normal cement pastes are shown in the lower right corner as open diamonds. [Adapted from (*10*)]

drous phases surrounded by about 50% interstitial hydrous calcium silicates and aluminates of both crystalline and noncrystalline varieties. Enormous increases in strength resulted from the removal of most of the porosity and the generation of very homogeneous, or fine, microstructures. Porosities as low as about 1.7% were achieved; the microstructures were relatively featureless and dense. In polished sections micrometer-sized flaws appear occasionally, for example, along residual grain boundaries. Figure 3 illustrates the microstructures characteristic of warm-pressed cement pastes, as compared with ordinary and with high-strength macrodefect-free pastes.

Effects of processing parameters and particle packing. The effects of temperature, pressure, variations in their rates of application, time, *w/c* ratio, and particle characteristics have also been investigated in detail. In contrast to normal cement dehydration, the densification and strength generation mechanisms were believed to result from the following reaction sequence: (i) rapid initial compaction; (ii) an abbreviated induction period as temperature began to rise, with minimal hydration; (iii) a rapid hydration period—hydration products (very fine particles) are mechanically rearranged as they are formed and fill intergranular positions; and (iv) final stages of hydration, densification, and microstructure development. The dense structures formed were partially the result of a bimodal particle size distribution which developed during processing (*11*). The fine hydrated crystallites which formed and consolidated under the applied stress around residual anhydrous cores were welded into a monolithic mass. Occasional selvages of hydration products integral to the anhydrous grains, which penetrate into the interstitial matrix microstructure, generated a dense, well-bonded product.

The importance of the bimodal particle size distribution has been further demonstrated through the deliberate incorporation of a second colloidal phase of fine particles. When properly dispersed, the fine material filled interstices, which decreased the flaw size. The addition of colloidal alumina or silica markedly enhanced the tensile strength, which increased with the proportion of colloidal material added (*11, 13–16*). The highest tensile strength (68 MPa) was measured immediately after warm pressing a material that had a composition of 88% cement, 3.6% colloidal solids, and 8.4% water. This strength represented a 50% increase over that of an equivalent material formed without added colloidal particles. Further improvements occurred after curing such materials from 1 to 28 days, which allowed additional pore filling (*14*). Remarkable strength enhancement was produced by the incorporation of such fine particles in materials prepared even at lower pressures (*13–16*). The effects of such particles were much greater than those of new surface modifiers (superplasticizers) (*13–17*). Other investigators (*18*) have demonstrated that addition of small amounts of fine particles (colloidal or near colloidal) improved the rheological properties and densification of ceramics.

The microstructures as viewed by scanning electron microscope (magnifications up to ×10 to ×20,000) were very dense and homogeneous: features such as large $Ca(OH)_2$ crystals typical of ordinary pastes [which would be weaker than interlocking small crystals and which could act as Griffith flaws (*7*)] were absent. These enormous increases in strength with warm-pressed cement pastes demonstrated that very strong ceramic-like materials could be made at or near room temperature with the CBC process.

Modifying Chemical Composition

At the same time, Brunauer and his colleagues took a different route and used chemical aids to enhance grinding, to control setting, and to permit the formation of pastes with lower *w/c* ratios (*19*). They eliminated gypsum, the conventional grinding aid and setting controller. In one case, they used diethyl carbonate as a grinding aid, and added lignosulfonate–alkali bicarbonate mixtures to control setting and reduce the water needed. The resulting pastes had lower porosity and substantially higher strength than normal, and are called "low-porosity cement pastes." These had porosities of 16 to 20%, and compressive strengths after 28 days as high as ~240 MPa in cement pastes with a *w/c* ratio of 0.20. Finer cements (8000 cm^2/g surface area) developed greater strengths compared with normal cements (4000 cm^2/g); this increased strength is probably caused by the different porosity of the finer cements (very fine micropores as

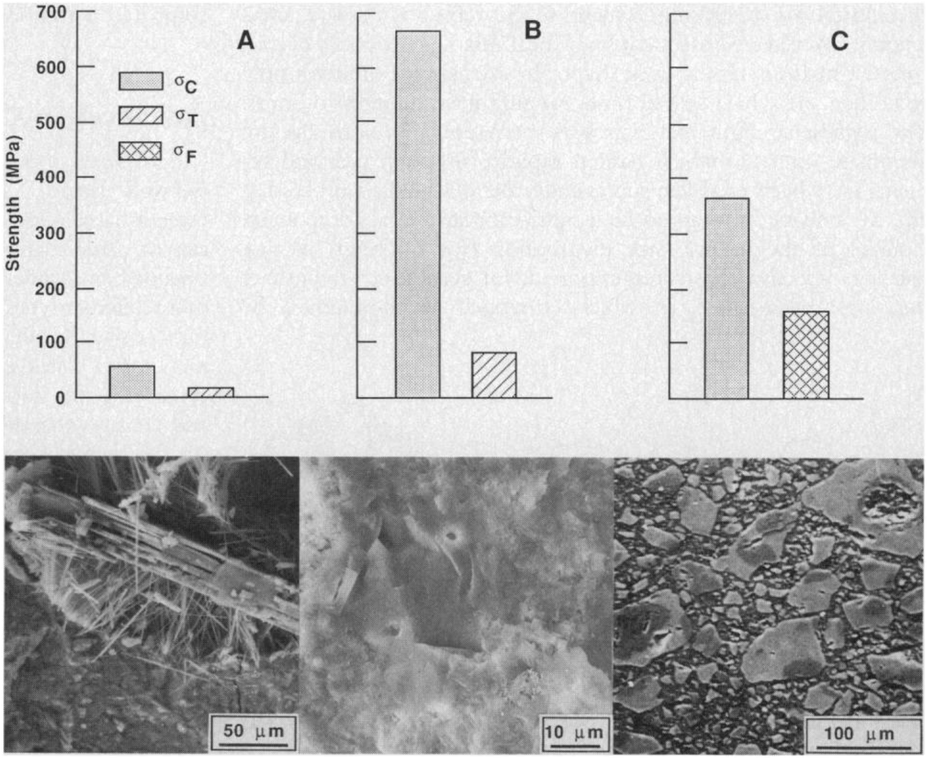

Fig. 3. Comparison of the strength and porosity of (**A**) normal cement paste, (**B**) warm-pressed cement paste, and (**C**) MDF Ca-Al cement paste. (**Top**) σ_C, σ_T, and σ_F are compressive, tensile, and flexural strengths. (**Bottom**) Comparison of porous (A) and dense (B and C) microstructures. Porosity of (A) is about 0.3; the pastes in (B) and (C) have porosities of about 0.01. Images in (A) and (B) were obtained with a scanning electron microscope (secondary electron image), whereas (C) is an electron backscattering image.

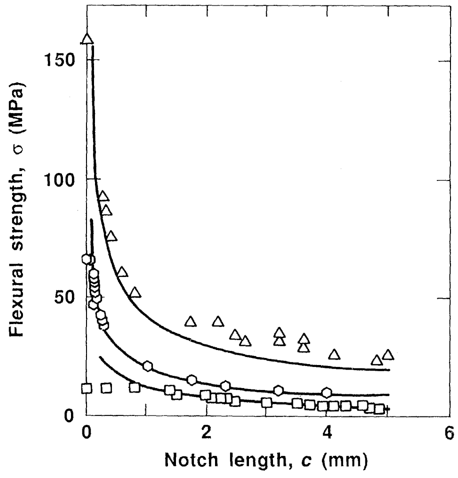

Fig. 4. Notched beam test of the flexural strength of cement pastes. Curves are theoretical fits to the data. Bottom curve (squares) normal portland cement paste, middle curve (hexagons), portland MDF; upper curve (triangles), calcium aluminate MDF.

opposed to macropores). The pastes had lower drying shrinkage than normal cement pastes, but their total porosity was significant, and their properties did not approach those of the warm-pressed materials.

Macrodefect-Free Cement (Pastes)

Although the warm-pressed cements were successful, they were not easy to produce in large amounts. The engineering of a new class of high-strength materials [the so-called macrodefect-free (MDF) cements] was pursued originally by Birchall and co-workers at Imperial Chemical Industries and Oxford University (*20–24*). MDF refers to the absence of relatively large voids or defects which are usually present in conventionally mixed cement pastes (Fig. 1) because of entrapped air and inadequate dispersion. Such voids and defects limit the strength that can be achieved by acting as stress concentrators (*20–24*). In the MDF process 4 to 7% of one of several water-soluble polymers (such as hydroxypropylmethyl cellulose, polyacrylamide, or hydrolyzed polyvinylacetate) is added as a rheological aid to permit cement to be mixed with very small amounts of water. Subsequent high-shear mixing produces a plastic, cohesive mixture which can be shaped by extrusion or other forming technique and which sets in times ranging from minutes to hours. The highest strength materials have been prepared with calcium aluminate cements, which harden rapidly, although portland cements have been used less successfully. Besides being a processing aid, the polymer appears to be a significant structural component. Control of the particle size distribution (for optimum particle packing) was also considered important for generating strength. A final processing stage, in which entrapped air is removed by applying modest pressure (~5 MPa), resulted in a paste that is free of all large defects. [Additional processing details are given in (*22–24*).]

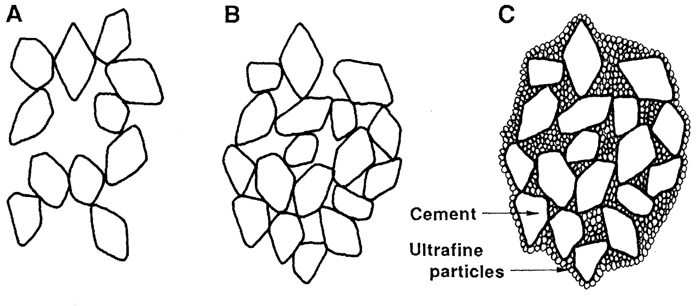

Fig. 5. Packing of DSP (silica fume) pastes. (**A**) Flocculated ordinary cement paste. (**B**) Better packing achieved with dispersant (superplasticizer). (**C**) Cement, silica fume, and superplasticizer. [Adapted from (*35*)]

The mechanical properties of MDF cements are remarkable as compared with those of normal cements. In Fig. 4 strength measurements of MDF portland cement paste bars are shown (*20*). The strength at any given flaw size was higher than for normal cement pastes because the MDF cements had a higher elastic modulus (~40 GPa) and higher fracture surface energy (~200 J/m^2). The results departed from the predicted Griffith relationship when visible holes or flaws were ≤90 μm in length, and showed no further increases in strength beyond ~66 MPa compared with a similar test on ordinary portland cement paste.

Materials prepared with different compositions and additional processing steps achieved even higher strengths, as, for example, a calcium aluminate cement mixture, that was press-molded (at ~5 MPa) to remove bubbles and heated at 80°C. A volume decrease of 9% occurred, which could be the result of the polymer shrinkage. This reflected a collapse of the colloidal porosity. Very low porosities were achieved (<1%) (*23*) at considerably lower pressures than in earlier warm-pressing studies (*9–11*), as well as flexural strength of ~150 MPa (Fig. 4), a compressive strength of ~300 MPa, and a Young's modulus of 50 GPa.

The Griffith criterion σ, which is normally defined as $(ER/\pi C)^{1/2}$ [where R is the fracture energy and C is the crack (pore) length], can be modified to incorporate porosity (p) (*23*), to yield

$$\sigma = \left[\frac{\mathrm{E_0 R_0}\ (1 - p)^3 \exp(-\mathrm{k}p)}{\pi C}\right]^{1/2} \qquad (1)$$

where k is a constant and $\mathrm{E_0}$ and $\mathrm{R_0}$ are E and R for a nonporous reference state. The data on the MDF cements in Fig. 4 agree with this theory fairly well.

Some of the complexities involved in interpreting the fracture behavior of both normal and high-strength cement pastes have been pointed out by others (*6, 25*), and there are some problems concerning water sensitivity of MDF materials (*24*). Nevertheless, the severalfold increases in strength and toughness achieved, as compared with normal cement pastes, are striking.

Advances in Cement-Based Composites

Particulate composites with reactive, partially reactive, and latent hydraulic particles. In the last decade a second major family of cement-based composites has emerged which incorporate fine particles of oxide materials. Enhanced strength and durability can be obtained by deliberately blending hydraulic cements with one or more different types of particulates, such as ground granulated blast furnace slag, fly ash, or silica fume (*26–31*). When combining two or more particulates in a cementitious composite, it is necessary to consider (i) the initial particulate characteristics (such as size, shape, and density) that affect rheology and optimal particle packing and (ii) the chemical reactivity of the particles.

When two monodisperse powders with large and fine grains, respectively, are mixed, the finer will pack within the interstices of the larger. In real polydisperse systems, soluble species from the fine particulate and the surfaces of the larger cement particles react within hours. A colloidal particulate, such as 0.2-μm silica fume (*30*) initially reacts with the alkaline cement solution (*31*) but apparently much unreacted residue remains as slow reactions produce ultrafine CSH reaction products. This decreases the mean pore size. This phenomenon has been discussed with respect to warm pressing (*9–11*) where, despite the simultaneous occurrence of reaction and pressurized consolidation (Figs. 2 and 3), additional strength gains can be achieved after long-term curing.

Because of this type of reaction, the microstructures and pore structures (*26–29*) developed from composites of cement with fine glassy slag or silica fume, or both, are much finer and possess lower ionic diffusivities than normal cements (*27–29, 32*), and are much more chemically resistant and durable (*33*). The combined physical and chemical effects cause enhanced resistance to chloride-enhanced corrosion and increased durability of steel-containing cementitious composites such as in highways and bridges. Proper particle packing also achieves very high strengths and stiffnesses (*27–29*). Tables 1 and 2 give the properties and formulations of several cement particle composites, as compared with those of normal cement paste.

Fine- or fumed-silica cements and concretes. Quite striking properties can be achieved when silica fume (also called condensed silica fume or microsilica) is substituted for portland cement in amounts ranging up to 25% (*11, 13–16, 34–36*). Concretes containing 5 to 15% silica fume have high compressive strengths (up to and above 100 MPa), flexural strengths (up to 12 MPa), and Young's moduli [up to 34 GPa (*37–40*)], and also have very low permeabilities to water (10^{-9} μm^2). The microstructure of the critical interfacial zone between cement paste and the aggregates in concrete is more dense and uniform than when conventional pastes are used (*39*), and the bond between paste and other embedded materials such as aggregates and fibers appears to be improved.

The most striking results have been found with silica fume–substituted pastes [the so-called densified systems with fine particles materials] illustrated in Fig. 5. Compressive strengths of up to 270 MPa with Young's moduli up to 80 GPa were achieved in preparations with up to 20 to 25% silica fume at a water to solids (*w/s*) ratio of 0.12 to 0.22 through mechanical compaction (*36*). A dense but fairly fluid paste is formed by the combination and chemical dispersion of particles that have dissimilar size ranges. No major air voids remain in products that are processed properly as hydration proceeds, and only a few very small "capillary" pores exist. Shrinkage upon drying of the cement hydration product is limited, and the residual cement grain cores act as a strong internal filler or "microaggregate."

Dense silica fume–based cementitious composites are used to resist severe mechanical erosion in impeller screws for moving coal and fly ash and in flooring to industrial areas (*36*). Another version is commercially available as a tooling and molding material in applications where vacuum tightness or mirror finishes are required. The latter material (Table 1, last column) retains a compressive strength of ~300 MPa up to about 500°C and ~200 MPa at about 700°C.

Fiber-reinforced cements. One approach to toughening brittle ceramic materials is to incorporate strong fibers into the microstructure. This can be done with cement pastes. The lack of ductility and the low tensile strength of cementitious materials have long been remedied on a gross scale by the use of steel reinforcing bars. In a typical highway application, steel rods make up less than 1% by volume of the concrete. Steel wire fiber-reinforced cement (*41, 42*) in concrete has further refined the means of increasing the tensile or flexural load-bearing capacity. On a much finer scale, composites of cement incorporating asbestos fiber have been used since about 1900 but are now unpopular because of asbestos hazards, despite their outstanding tensile properties and durability. Other important types of fibers investigated (*42–45*) include glass (*46–49*) and polypropylene (*50*).

Glass fiber–reinforced cements. The reinforcement of cement paste by glass fibers initially was limited by the poor resistance to corrosion of glass fibers in the highly alkaline environment in the pores, which contain water in contact with very fine $Ca(OH)_2$ ($pH \geq 12$) (*51*). The advance that stimulated the field again was the development (by Majumdar and associates at the Building Research Station in Britain) of alkali-resistant glass fibers (*46–49*) with a high ZrO_2 content which can resist the degrading effects of the cement paste environment for some years. Still unresolved is the long-term (10 to 100 years) stability of the fibers, which once assured will lead to their widespread use.

Table 1. Mechanical properties of cement particle composites. Formulations for the last three composites are given in Table 2.

Cement particle composite	σ_T (MPa)	σ_F (MPa)	E (GPa)	σ_C* (MPa)
Ordinary cement	~5	6	15	40
MDF cement		40–150	35–50	100–300
Warm-pressed dense-fume mortar	68		27–41	300–650
Slag mortar 81-20†			48	180
Steam 82-11‡			50	250
Steel aggregate steam-cured mortar§		28	49	250–350

*Flexural strength. †See (*27*). ‡See (*28*). §See (*40*).

Table 2. Particulate composites prepared for high-strength, optimum particle packing, and thermal stability. Each composite contains trace quantities of superplasticizer and defoamer.

Component	Mean particle size (μm)	Percentage by weight of each component in the following composites		
		83-01, 82-11*	81-20†	DASH-47‡
Hydraulic cement	30	23.73	21.2	24.3
Fine quartz SiO_2	<5 (~2)	19.0	10.3	11.8
Silica fume	0.2		2.89	3.3
Slag	8	14.2		
Sand	150–1180	28.5	55.7	
Steel	710–2000			34.8
	150–180			18.7
Water		14.0	9.55	6.2

*See (*28*); 83-01 is made with basaltic sand. †See (*27*). ‡See (*40*).

Incorporation of fine fibers into brittle materials increases their tensile strength severalfold and their toughness by orders of magnitude. Aveston, Cooper, and Kelly (A-C-K) (*52*) provided the now classical model for the strength and toughness of a fiber-reinforced brittle matrix composite for the case of cement paste. The strength of such cement pastes can be increased by reinforcement with a fiber (such as carbon) according to the relation (*44*):

$$\sigma_{cu} = \frac{V_f \tau_0}{K}\left[1 - \frac{r}{Kl} \ln\left(1 + \frac{Kl}{r}\right)\right] \tag{2}$$

where σ_{cu} is the strength of the composite, V_f is the volume fraction of fibers, τ_0 is the shear strength of fiber-matrix interface, l is the fiber length, r is the fiber radius, and K is a constant. A critical discussion of this and later models of constrained cracking is given in (*45*). Ultimate tensile strengths of about 15 MPa are common, while modulus of rupture (MOR) values of 35 to 40 MPa are observed, similar to those of glass fiber–reinforced cement composites (GRC) (*46–49*).

The work of fracture, or toughness, increases more substantially. The theory assumes that after the first matrix crack has appeared there are sufficient fibers and adequate bonding to support the load. The stress-strain curves of carbon fiber–reinforced cements (*52*) with fiber contents above a certain critical volume fraction of fibers

Table 3. Properties of cement composites containing about 5% glass fiber (CEMFIL 2). [Adapted from (*48*)]

Composite (% by weight)	Aging and treatment	Modulus of rupture (MPa)	Tensile strength (MPa)	Micro-strain (ppm)	Tensile Young's modulus (GPa)	Izod impact strength (kJ/m^2)
70% cement and 30% sand	28 days	38	15	11,000	30	21
	Natural weathering (U.K.) for 2 years	36	13	8,000	33	20
	Wet aged at 50°C for 180 days	24	9	870	33	8
70% granulated slag and 30% cement	28 days	35	13	9,800	22	21
	Natural weathering (U.K.) for 2 years	36	15	9,000	23	19
	Wet aged at 50°C for 180 days	37	13	9,500	33	20
Plain paste cement (*6*)	28 days	7	3.5		12	0.01*

*Fracture toughness is 0.03

fit the A-C-K theory very well. The energy per unit area (W^1) needed to pull out fibers that do not break is calculated (*48*) for fibers with $l \geq l_c$ (l_c = critical fiber length, ~15 mm for carbon fiber):

$$W^1 = \frac{1}{6\pi}\,\tau_d\,\frac{r^2}{l}\left(\frac{\sigma_F}{\tau_s}\right)^3 V_f \qquad (3)$$

where τ_s is the bond opposing slipping. τ_d is the frictional bond over slipping fibers, and σ_F is the flexural strength. Elastic strain energies of ~25 kJ/m^2 (compared with 0.01 to 0.03 kJ/m^2 for cement paste) have been calculated and agree with measured impact strengths of young nondegraded GRC samples.

Accelerated aging tests of GRC in hot water have been carried out (*47*). The results have been integrated with strength retention data obtained from long-term external exposures under different climatic temperature regimes. A normalized Arrhenius plot of temperature-accelerated experimental results was proposed to predict long-term durability. The time to degrade MOR values from greater than 35 MPa to less than or equal to 15 MPa (to remain constant thereafter) varied from about 1000 days at a mean annual temperature (MAT) of 25°C to about 10,000 days at a MAT of 10°C. Additional aging tests have been performed on GRC made with an improved alkali-resistant glass fiber (Table 3). When 5% fiber is used, high tensile Young's modulus (30 to 33 GPa) and a high tensile strain (up to 1%) at failure are found. Substitution of granulated blast furnace slag in the cement successfully extended the tensile and impact strength performance under wet conditions, which normally induce alkaline degradation (*48*).

Interface microstructural studies (*49, 53*) have emphasized the nature of the critically important region between fiber and cement paste in explaining strength and performance of GRC composites. Both silica fume and slag used in the composites are effective in improving the properties (*53*).

Other fiber composites. Polypropylene and other deformable polymer fiber reinforcements have the advantage of greater durability in the alkaline pore solutions of a cementitious matrix (*43, 50*). Such polymer fiber–cement composites have high impact resistance but a low modulus of elasticity. They exhibit poor fiber-matrix bonding and soften and lose strength with heating (fire tests). Other approaches have made it possible to use normal borosilicate glass (E-glass) fibers. The addition of about 15% of an acrylic polymer to the cementitious matrix provided resistance to the alkaline cement solution and retained strength (*48*). Composite strengths in steel fiber–reinforced cements have been increased by prepacking the molds with fibers before impregnation with a slurry and increasing the volume percentage of fibers (*54*).

Fiber-reinforced MDF cements. Spectacular advances in strength and toughness were achieved by both reducing porosity and "adding" fibers. Macrodefect-free cements have been reinforced with fiber laminates of glass, nylon, and Kevlar to increase their toughness and work of fracture (*55*). Mechanical properties were measured in tests on single-edge notched beam samples and unnotched samples (Table 4). A small to moderate decrease in tensile strength and Young's modulus was observed as compared to a reference sample of MDF. No systematic change in critical stress intensity factor occurred, but there was a major increase in the work of fracture and the Charpy impact energy. The impact energies of nylon and Kevlar MDF cements are high compared with Kevlar-reinforced normal cements [17 kJ/m^2 (*46–49*)]. The higher volume fraction of fibers increased the impact energy and work of fracture but decreased strength and modulus.

Other Applications

Nuclear waste solidification and encapsulation. Because of their versatility and low cost, cementitious materials have been extensively used for encapsulating low and intermediate level nuclear waste (*56–60*) to prevent release of radionuclides into the environment. As cementitious materials that have more ceramic-like qualities were developed, their potential for high-level-waste solidification was investigated (*15, 57–61*). Room-temperature processing, which has been an obvious advantage of cement, has attracted attention in radioactive waste management. The prime focus has been their leaching and dissolution behavior.

Portland cement paste composites have outstanding properties with respect to low leach rates of plutonium (*61*), and other transuranics, rare earths, and uranium (*15, 57–60*). Warm pressing was found to further diminish their leachability (*15, 57*). However, one of the readily soluble fission products, Cs$^+$, was not well retained in ordinary paste. The synthesis of an insoluble family of cesium compounds, the cesium zirconium phosphates, provided a

Table 4. Physical properties of MDF fiber composites. [Adapted from (*55*)]

Fiber	σ_F (MPa)	E (GPa)	K_{Ic}* (MPa m$^{1/2}$)	G_{Ic}† (kJ/m^2)	Impact‡ (kJ/m^2)
Glass A	123.8	42.8	2.54	2.62	13.4
Nylon A	119.5	46.9	2.99	15.9	38.1
Unreinforced	150.3	52.4	3.29	0.2–0.4	4.34
Nylon C	54.2	31.1	2.78	44.4	121.2
Kevlar 29 B	94.2	37.4	5.25	78.6	88.6

*Critical stress intensity factor. †Work of fracture across nominal cross-sectional area. ‡Impact measured using Charpy test.

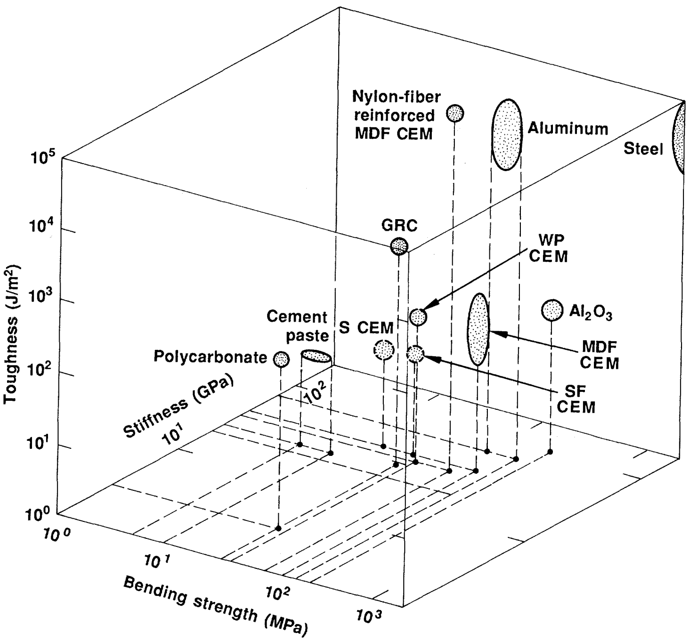

Fig. 6. Strength, toughness, and stiffness of conventional cement paste and modified cement composites as compared with plastics, alumina, aluminum and steel. Abbreviations: CEM, cement; S, slag; SF, silica fume; WP, warm-pressed; GRC, glass-reinforced; MDF, macrodefect-free. [Adapted from (*64*)]

possible fixation mechanism. The powder product, when solidified in a cement-matrix composite, had a very low release rate of cesium. The best cementitious matrix formulations contained blast-furnace slag and silica fume. The lowest Cs^+ leachabilities were found in warm-pressed specimens (*58–60*). The crystalline cement mineral tobermorite also has ion-exchange properties, and has a strong preference ~2000 times greater than for potassium for cesium in its structure (*62*).

Oak Ridge National Laboratory has developed a cement waste form in which a slurry of cement and special additives is mixed with a waste solution. The "grout" is pumped about 1000 m down into hydrofractured shale rock strata and thus permanently disposed.

High-grade cementitious materials are also important in other nuclear waste management applications, such as the sealing of shafts, boreholes, and fractures upon closure of a deep geological waste repository (*60*). Candidate materials should be highly durable, compatible with the host environment, as thermodynamically stable as possible, thermally stable, and very impermeable, and should have some of the properties important for waste encapsulation as well.

Electrical Properties. Chemically bonded ceramics have potential in electronic packaging. Certain cements have been found to have low relative dielectric permittivities and losses (*63*). A microfine cement, when pelletized or formed in sheets, showed relative permittivities (compared to air) of 7 to 8 depending on temperature (30° to 140°C) and frequency (1 kHz to 10 MHz). Under certain conditions the permittivity was as low as ~5, with a loss of only 0.4%, which shows that these materials have considerable potential as insulating substrates. Acoustic applications have similar potential (*55*).

Conclusions

Major advances have been made in several properties of cement materials critical to modern technology. Figure 6 illustrates the key mechanical properties of a representative set of materials. It may astonish nonspecialists that a nylon-reinforced cement is almost as tough as aluminum. Such materials are already being used in novel applications. The challenge remains to better understand the mechanisms involved in generating strength and toughness, the effects of compositional and microstructural modifications, and the range of feasible processing parameters which control the properties of such composites.

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Programmed Gene Rearrangements Altering Gene Expression

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Programmed gene rearrangements are used in nature to to alter gene copy number (gene amplification and deletion), to create diversity by reassorting gene segments (as in the formation of mammalian immunoglobulin genes), or to control the expression of a set of genes that code for the same function (such as surface antigens). Two major mechanisms for expression control are DNA inversion and DNA transposition. In DNA inversion a DNA segment flips around and is rejoined by site-specific recombination, disconnecting or connecting a gene to sequences required for its expression. In DNA transposition a gene moves into an expression site where it displaces its predecessor by gene conversion. Gene rearrangements altering gene expression have mainly been found in some unicellular organisms. They allow a fraction of the organisms to preadapt to sudden changes in environment, that is, to alter properties such as surface antigens in the absence of an inducing stimulus. The antigenic variation that helps the causative agents of African trypanosomiasis, gonorrhea, and relapsing fever to elude host defense is controlled in this way.

GENE ORDER IS A STABLE CHARACTERISTIC OF ALL ORGANISMS analyzed. Each virus, bacterium, plant, and animal has a genetic map, shared by all members of the species. If the β-globin gene is on chromosome 11 in one representative of *Homo sapiens*, it is likely to be there in all. Genes do move around, however. Such DNA rearrangements are of two types, programmed and incidental (also called unprogrammed or mutational) (*1*). The incidental rearrangements arise from errors in DNA replication, repair, or recombination; from the movement of mobile elements, such as transposons; or from the insertion or excision of plasmid DNA, viral DNA, or other immigrant DNA. The exact outcome of these incidental rearrangements is unpredictable, but most of them are deleterious to the individual affected by them.

In contrast, programmed gene rearrangements are part of the normal developmental program of an organism and its progeny. The outcome of these rearrangements is largely predictable; the process is usually carried out by specific recombination enzymes and is developmentally regulated. Such programmed (or developmental) rearrangements can be grouped in three categories: (i) amplification or deletion of genes; (ii) assembly of genes from gene segments; and (iii) DNA rearrangements that alter gene expression.

This review will mainly deal with the third category, the gene

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