Chapter 17
Cement, Ceramics, and Composites

17.1 Introduction

Cement and its applications as concrete (a composite of cement and aggregate) are known throughout the world. The most common cement used today is Portland, named after the gray rock of Portland, England, which it resembled. World production of Portland cement increased from 133 million tonnes in 1950 to about 1,000 million tonnes in 1985 and over ten times the 1950 value in 1995. The energy usage during this period dropped from 9.6 MJ/kg to about 5.7 MJ/kg in 1990. Table 17.1 shows the world and US production of Portland cement from 1970 to 2009. Research continues in all aspects of cement from quick setting to increase in strength—the predictability of which is still a major problem.

The history of cement starts in the earliest times when the Assyrians and Babylonians used clays to bind stones into massive walls. The Egyptians used a lime and gypsum mortar as a binding agent for the Pyramids. The Romans perfected such mortar and concrete for use in their structures, some of which still stand. They mixed slaked lime with volcanic ash from Mount Vesuvius to form a cement which hardened under water. The Mongols and Aztecs had developed a similar technology. However, the word "cement" is derived from the Roman "caemenium," meaning building stone.

This skill was lost during the Middle Ages and was not rediscovered until the scientific approach was taken by John Smeaton in 1757 when he built the Eddystone lighthouse on the southwest coast of England. He found that a good hydraulic cement was formed when the limestone used had clay impurities. We now know that aluminosilicate clays, when calcined with lime, form the desired cement. Between 1757 and 1830, the essential roles of the lime and silica were established by Vicat and Lisage in France and by Parker and Frost in England.

In 1824, Joseph Aspdin, a bricklayer and mason from Leeds, obtained a patent for a superior hydraulic cement which he called *Portland cement*. His process required the mixing and pulverizing specific quantities of limestone and clay and heating the mixture to a required temperature forming clinkers. Unfortunately, all details are missing, including the kiln Aspdin used. Two major improvements were introduced about 1890: (a) the addition of gypsum ($CaSO_4 \cdot 2H_2O$) to the clinker grinding step to act as a set retardant and (b) higher burning temperatures to permit higher lime and silicate content which results in more rapid strength development in concrete.

Portland cement presently constitutes over 60% of all cement produced and is a carefully apportioned combination of the oxides of calcium, silica, aluminum, and iron.

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Table 17.1 The World and US production of Portland cement—million metric tons[a]

Year	US production	US imports	US exports	World production
1970	62.4	1.99	0.144	571.8
1980	68.2	3.04	0.169	883.1
1990	70.0	10.3	0.503	1,043
1995	76.9	10.9	0.750	1,450
2000	87.8	24.6	0.738	1,660
2005	99.3	30.4	0.766	2,350
2009	63.9	6.21	0.884	3,060

[a]US geological survey 2010

17.2 Cement Nomenclature

Special notation is used by cement chemists to denote the various ingredients in cement. These are listed in Table 17.2 with the approximate concentrations used. Thus, tricalcium silicate is represented as $C_3S(3CaO{\cdot}SiO_2)$. Portland cement is a mixture of minerals: C_3S, 42–60%; C_2S, 15–35%; C_3A, 5–14%; C_3AF, 10–16%; and C and M. The minerals are formed in the kiln during the burning of limestone and the silicate clay which are usually readily available and inexpensive materials. The relative energy expended in producing various materials is given in Table 17.3. The advantages of cement in an age of rising energy costs are obvious.

17.3 Manufacture of Portland Cement

Portland cement is made from readily available and cheap raw materials (limestone, sand, and clay). The components in an appropriate composition are mixed as a wet slurry and passed into the top end (500°C) of a rotary iron kiln which is lined with firebrick, about 150 m long, and at a 15° angle to the horizontal. A diagram of the flow process commonly used in the manufacture of cement is shown in Fig. 17.1. The following reactions occur in the kiln as the temperature increases:

1. Free water is evaporated.
2. Combined water from the clay is released.
3. Magnesium carbonate is decomposed, and CO_2 is released.
4. Limestone is decomposed to form lime and CO_2.
5. Lime and magnesia combine with the clays and silica to form “clinker.”
6. Cooled clinker is then ground, and some 20% gypsum is added to prevent the cement from setting too rapidly.

A common accelerator which speeds up the hydration process is $CaCl_2$, but its corrosiveness makes it unacceptable in steel-reinforced concrete.

An alternate process which is gaining popularity is to introduce the ingredients into the kiln in the dry state and so reduce the energy required to drive off the water present in the wet slurry process.

Table 17.2 Components and nomenclature of Portland cement

Symbol	Compound	Cement (%)	Clinker (%)
C	CaO	60–67	67
S	SiO_2	18–24	22
A	Al_2O_3	4–8	5
F	Fe_2O_3	2–5	2.6
N	Na_2O	0.1–1	0.2
K	K_2O	0.1–1.5	0.5
M	MgO	1–2	
S	SO_3	2–3	
C	CO_2	3	
H	H_2O	3	

Table 17.3 The relative energy content of various materials

Material	Relative Energy (vol.)
Portland cement	1.0
Flat glass	3.0
Polyvinyl chloride	3.8
Polyethylene (low density)	4.2
Polyethylene (high density)	4.4
Polystyrene	6.0
Steel	19.2
Stainless steel	28.8
Aluminum	31.8
Zinc	34.8

17.4 Setting of Cement

The *setting* of Portland cement consists of the hydration of the various silicates and aluminates as well as the compound $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ (a process which occurs over a long period). Attempts to reduce setting time and time to maximum strength have included resistive heating, accelerated microwave, and RF drying as well as the use of additives. Evidence of gel formation with fibrillar growth during the dehydration has also been obtained.

Hardened cement is a porous solid with a density of about 2.5 g/mL and a surface area of 100–300 m^2/g. Such pores can be fully sealed by polymer impregnation that has numerous applications.

The compressive strength of cement increases from 10^2 N/m^2 when initially set to 10^7 N/m^2 after a few days, reaching 70% of its final strength value (10^8 N/m^2) after 28 days. Further, small increases in strength are observed even after 1–2 years. Thus, the normal working stress, with the appropriate safety margin, is restricted to about 10 MPa. The tensile strength, σ, of a solid (measured in bending) can be given by the Griffith relationship

$$\sigma = (ER/\pi c)^{1/2} \tag{17.1}$$

where E is Young's modulus of elasticity, R is the surface fracture energy, and c is the crack length. A reduction in particle size of the cement and the removal of all the air bubbles create a macro-defect-free (MDF) cement which results in a strength of up to 150 MPa, a value comparable to aluminum and its alloys. The high setting strength of MDF cement is illustrated by the coiled cement spring in Fig. 17.2 which is shown in the relaxed and extended states.

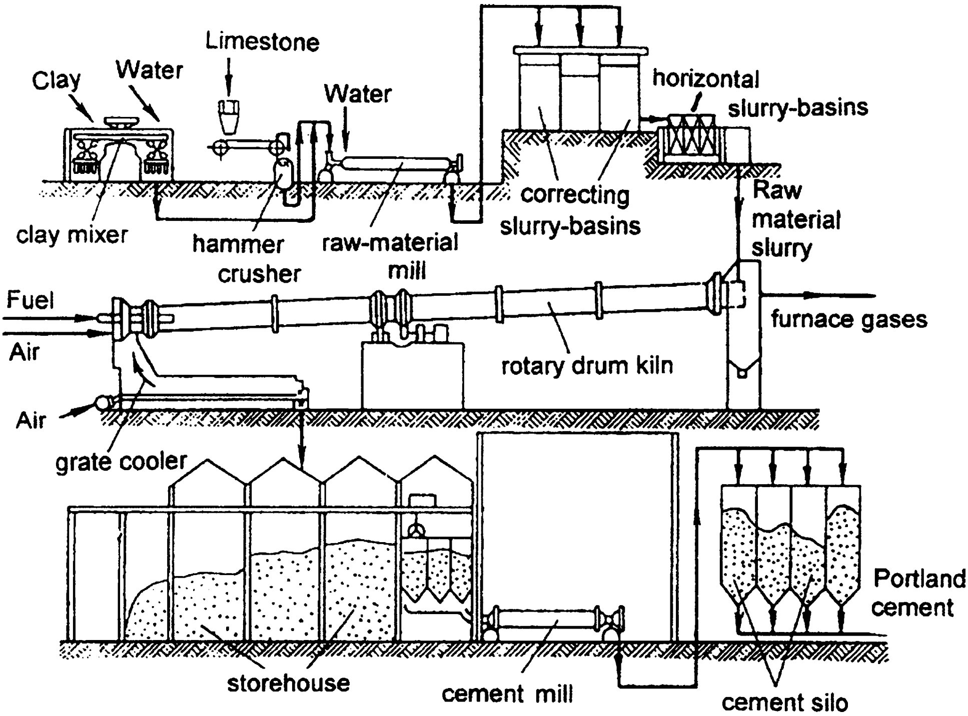

Fig. 17.1 Flow diagram for the manufacture of Portland cement by the wet process. The limestone is crushed, mixed with wet clay, and ground to a fine slurry in a mill. This raw material is stored and corrected for composition by blending before being fired in a rotary kiln where the process of water evaporation, mineral dehydration, limestone dissociation, and chemical reaction proceeds. Clinker formation forms finally at 1,450 °C and is cooled and ground with additives before storage

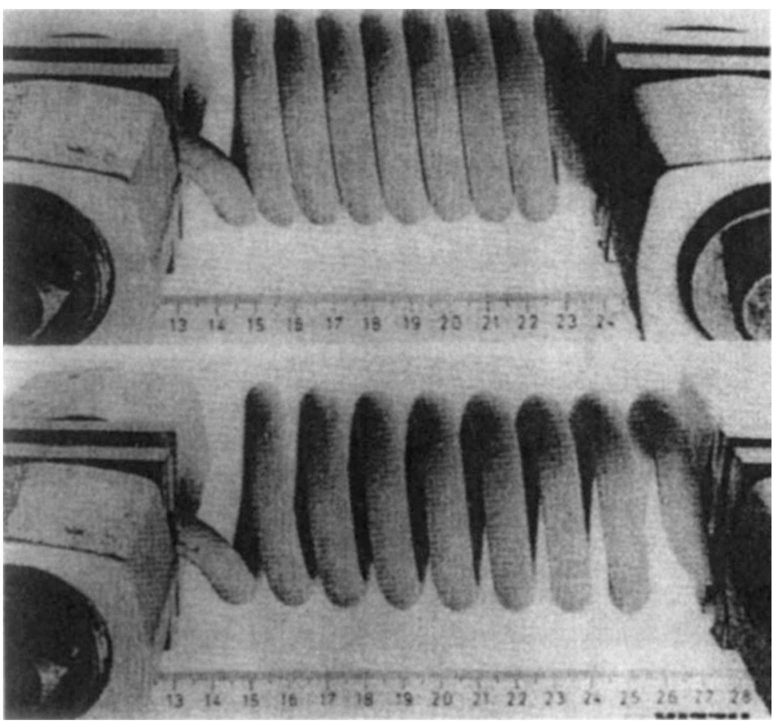

Fig. 17.2 Coiled high-strength micro-defect-free (MDF) cement spring in relaxed and extended positions

17.5 Concrete

Concrete is composed of cement and filler, or aggregate, which can be gravel or stones. A proper concrete is composed of aggregate of different sizes which permits better packing and fewer voids. For lightweight concrete, the aggregate can be vermiculite, perlite, or other low-density filler. The concrete must be vibrated as it is poured. The tensile strength of concrete can be increased by embedding iron rods, called *rebar,* and iron wire mesh in the slurry before it sets. The coefficient of expansion of concrete and steel are similar, and thus, temperature changes do not disrupt the structure—though corrosion of the iron must be avoided if long-term strength is to be maintained.

The strength of polymer-impregnated concrete is determined by the glass transition temperature, T_g, of the polymer. Above the T_g, the reinforcement is lost and the concrete is less resistant to salt penetration.

A patented invention (1995) has described how a conducting concrete can be made by adding conducting carbon fibers and particles to the cement. An electrical current through the concrete can heat the material. This can have a broad application for deicing in areas where freezing temperatures occur and cause traffic accidents. Airport runways, bridges, and highway intersections are other important locations where ice-free surfaces are desirable. Another application is as a secondary anode in existing cathodic protection systems.

The cement content of 28-day dried concrete is normally determined by dissolving the cement in hydrochloric acid (HCl), leaving the insoluble aggregate. A simpler and rapid determination can be carried out using differential thermal analysis (DTA) of a thoroughly ground and mixed sample (mesh <80). A typical DTA trace is shown in Fig. 17.3 where the area of the cement peak is directly proportional to the amount of cement in the concrete. It remains to determine the ultimate strength of concrete while the cement is still slurry in the cement truck. Though several methods have been proposed, none has, as yet, had any success.

17.6 Ceramics

Ceramics are inorganic solids, usually oxides, which contain ionic and covalent bonds. The material, formed by sintering at high temperatures, ranges from amorphous glass-like material to highly crystalline solids, from insulators to conductors or semiconductors. They include earthenware, which is fired at 1,100–1,300 K and a porosity of about 8%; fine china or bone china, fired at 1,400–1,500 K with a porosity of less than 1%; stoneware, fired at over 1,500 K with a porosity of about 1% before glazing; and porcelain which is fired at over 1,600 K and has a much finer microstructure than either stoneware or bone china.

One of the most noteworthy ceramics is the high-temperature superconductors that were first described is 1988 and show superconductivity at temperatures as high as 90 K.

The superconductor $YBa_2Cu_3O_7$ ($T_5 < 90$ K), known as the "1-2-3" compound, is prepared by mixing powdered Y_2O_3, $BaCO_3$, and CuO in the appropriate stoichiometry and heating to 950°C. The cooled solid is then pressed and sintered again at 950°C to bond the grains and to increase the density of the pellet. Final heating is in the presence of oxygen at 500–600°C followed by slow cooling to room temperature.

The glass or vitreous state of matter is a solid with the molecular random structure similar to that of a liquid. Such a state is not limited to inorganic substances since many organic compounds and mixtures can form transparent glasses. Glass can be translucent or opalescent due to the presence of small crystalline material in the glass. However, the term "glass" normally refers to a solution of inorganic oxides with silica (SiO_2) as the basic material.

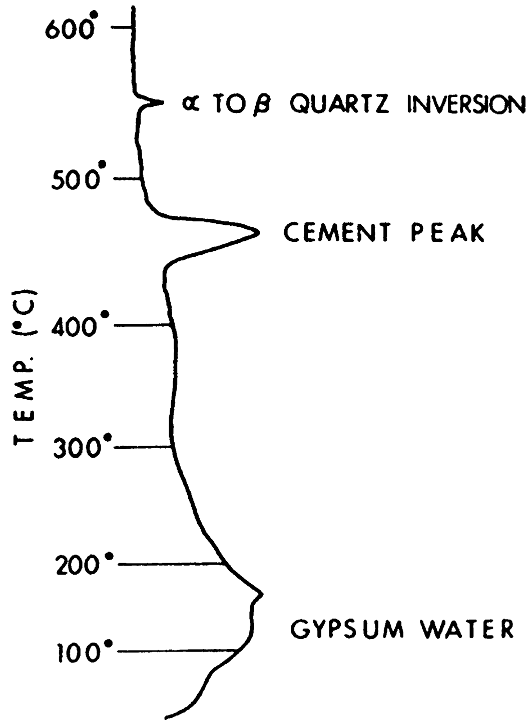

Fig. 17.3 Differential thermal analysis (DTA) of concrete sample ground to <80 mesh. Area of cement peak is proportional to amount of cement in sample

Ceramics can be cast prior to heat treatment or, like glass, can be formed by the sol-gel process, a recent development whereby a glass can be formed without first forming the melt. The oxides are converted into a colloidal gel which can also be formed from the organic alkoxide and M(OR), where *n* is the valency of the element M. The controlled hydrolysis reaction in an organic solvent such as methanol forms the hydroxide gel:

$$M(OR)_n + nH_2O \rightarrow M(OH)_n + nROH \quad (17.2)$$

When hydroxide gel is dried slowly in air, a xerogel is formed which is porous, often transparent, and usually smaller and more dense than the original gel. If the solvent is removed under supercritical conditions (temperature and pressure above the critical point), the shrinkage is minimal and the solid is called an *aerogel*. This is shown in Fig. 17.4. Aerogel has a very low thermal conductivity (10 mW/m, K), which is slightly lower than that of a xerogel and much lower than polyurethane foam (28 mW/m, K). A recent silica xerogel produced in Norway had a bulk density of 0.26 g/cm^3 and a thermal conductivity of 18 mW/m, K. These materials are being studied for possible use as insulating windows because of their high degree of transparency.

The possibility of blending, doping, or mixing various materials in the gel state makes the resulting homogeneous solids very easy to prepare to exact specifications. When a xerogel or aerogel is heated, the pores collapse, forming the oxide solid at a temperature much lower than that required if formed from the melt.

An interesting glass ceramic, MACOR, manufactured by Corning, is a two-phase machinable crystalline solid composed of mica and glass. Heat treatment converts the amorphous glass into a crystalline structure (please see http://www.ortechceramics.com/). A comparison of the properties relative to other ceramic materials is given in Table 17.4. Its machining characteristics are compared to some metals and nonmetals in Table 17.5. Such excellent properties are unique to ceramics and ceramic-like materials.

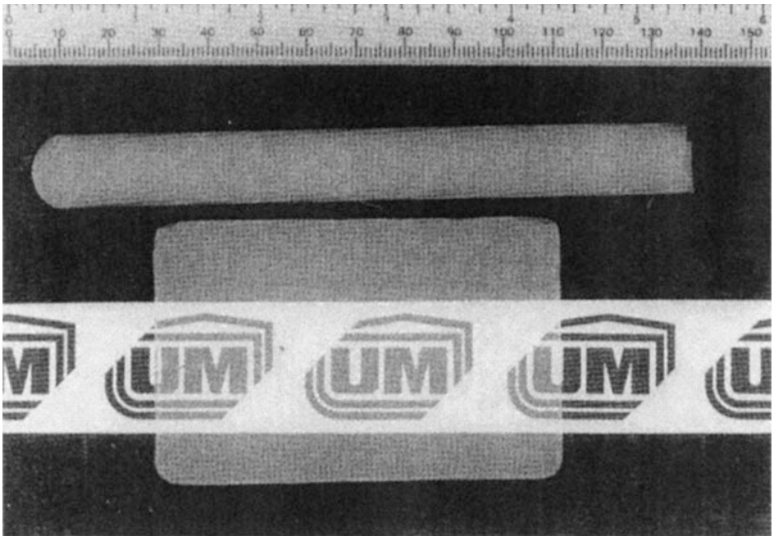

Fig. 17.4 Photograph of two aerogels prepared from the hydrolysis of tetraethylortho silicate in methanol and dried under supercritical conditions

Table 17.4 A comparison of macor with other common ceramic materials

Property	Units	MACOR™ machinable glass ceramic	Boron nitride 96% BN	Alumina nominally 94% Al_2O_3	Valox thermoplastic polyester
Density	g/cm^3	2.52	2.08	3.62	1.31
Porosity	%	o	1.1	0	0.34
Knoop hardness	NA	250	<32	2,000	NA
Maximum use temp,	°F	1,832	5,027	3,092	204°
(no load)	°C	1,000	2,775	1,700	140°
Coefficient of thermal	in/in (°F)	52×10^{-7}	23×10^{-7}	39×10^{-7}	530×10^{-7}
expansion	in/in (°C)	94×10^{-7}	41×10^{-7}	71×10^{-7}	934×10^{-7}
Compressive strength	psi	50,000	45,000	305,000	13,000
Flexural strength	psi	15,000	11,700	51,000	128,000
Dielectric strength (ac)	Volts-mil	1,000	950	719	590
Volume resistivity	Ω-cm	$>10^{14}$	$>10^{14}$	$>10^{14}$	$>10^{14}$

17.6.1 Composites

Composite materials were described in the Bible (Exodus), where straw was required and used in the preparation of reinforced bricks. The Inca and Maya people mixed plant fiber with their pottery to reduce cracking while being dried. Concrete is a composite structure, and most children are familiar with papier maché of paper and a glue made of flour and water. The Egyptians mixed their old papyrus manuscripts with pitch to wrap their mummies.

Table 17.5 Machinability index for various materials[a]

Material	Machinability index (MI)
Graphite	1
Teflon TFE	2.5
MACOR (glass ceramic)	25
Free-machining brass	36
Aluminum 2024-T4	50
Copper alloy no. 10	97
Cold-rolled 1018 steel	111
AISI 4340 steel (Rc46)	206
304 stainless steel	229

[a]The index unit (MI) is arbitrary and increases with difficulty of machining. Its approximate value is 1 $HP/in^3/min = 200$ MI

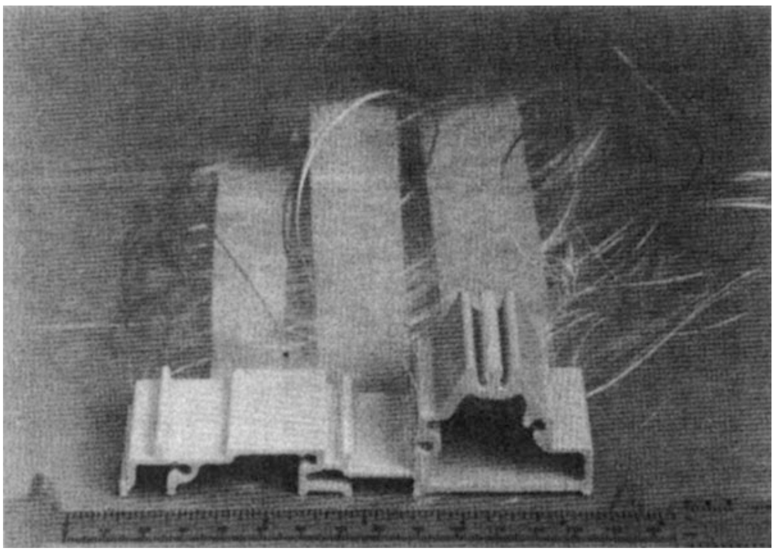

Fig. 17.5 Photograph of a short section of a polystyrene-fiberglass window frame prepared by the continuous exuding process of styrene-fiberglass and fiberglass mats

A durable and popular composite, *transite,* was asbestos with up to 15% cement. In the form of boards and sheets, it was a substitute for wood, and in severe climates, was used for roofing, fence materials, and other structures because it weathers as extremely well. *Transite* with asbestos is no longer available. Its replacement, *silica*, has limited applications because of health concerns. Other composites are continuously being developed to serve the needs of industry. Other *composites* include linoleum (linseed oil and jute), Bakelite (phenol-formaldehyde resin and cellulose fiber), plywood, and vehicle tires.

The more recent composites are the fiber-reinforced plastics and resins. The fibers include glass, Kevlar, and carbon fiber. Glass fibers used to reinforce plastics were introduced during World War II. The fibers are from 5 to 10 μm in diameter and have a tensile strength of about 3,000 MN/m^2. The glass fibers are treated with coupling agents to prevent the fibers from bundling and to bond the fibers to the plastic or resins. Because the fibers are about 100 times stronger than the plastic, the strength of the composite is proportional to the fiber content. An example of an extruded section of a polystyrene window frame which is reinforced with glass fiber is shown in Fig. 17.5. Molded fiberglass-reinforced polyester is the material of choice for boats though reinforced cement boats have also been built.

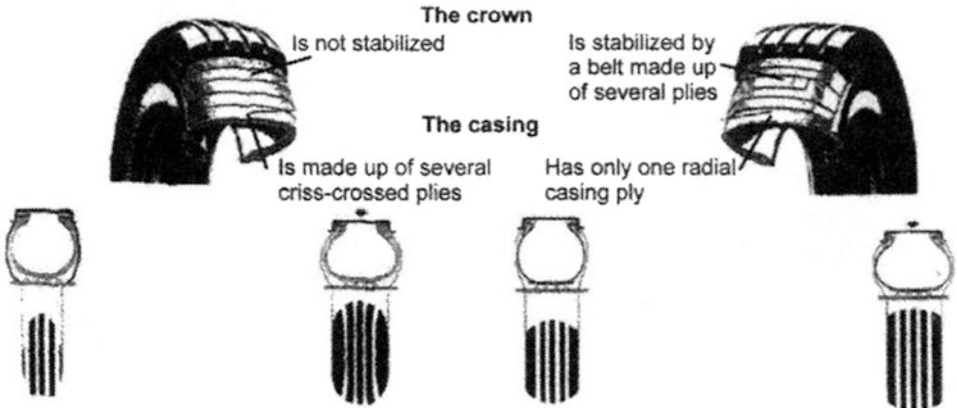

Fig. 17.6 A comparison of the diagonal-ply construction and the Michelin X radial tire

Carbon fibers were used about 100 years ago by Edison for his electric lamps. In 1964, the carbonized polyacrylonitrile (Orion) fibers were first produced with a tensile strength of about 2,000 MN/m^2 and a high modulus of over 400,000 MN/m^2. Thus, carbon fiber-reinforced resins are very stiff and have found wide application in artificial limbs, golf clubs, tennis rackets, skis, and many aircraft parts. However, the composites are not especially strong in tension.

Vehicle tires are another example of a composite, which are composed of rubber cord plies and beads, which hold the tire to the wheel. The cord plies are usually nylon, rayon, polyester, fiberglass, and steel wire. The construction of the tire was initially bias belted, with the cords running from bead to bead, crossing the tread at an angle with the number of plies determining the strength of the tire. Addition of two stabilizing belt plies below the tread increased traction and resistance to punctures. The radial-ply tires, manufactured first by Michelin in 1948, had cords, which ran from bead to bead with no bias angle (i.e., 90° to the longtitudal tread). This is shown in Fig. 17.6. Tread design has reduced planing on wet pavement and increased the life of a tire to approximately 80,000 miles.

New composites are constantly being developed to meet specific requirements with specified strengths, many to satisfy the aerospace industry.

Exercises

1. What are the primary components of cement?
2. What reactions occur in the kiln?
3. What reactions occur during the hydration process?
4. The lime (C), silica (S), and alumina (A) phase diagram is shown in Fig. 17.1a as mol%, and where the area of Portland cement and high alumina cement are indicated. Identify on the phase diagram the location for the following minerals found in (a) Portland cement clinker, C_3S, C_2S, and C_3A; (b) found in high alumina clinkers, CA, and CA_2.
5. In Fig. 17.1a, locate the positions of the substances listed in Exercise 4a and 4b assuming that the scale of the diagram is in units of wt.%.
6. Identify the composition of points *x*, *y*, and *z* on the phase diagram (Fig. 17.1a) for both a mol% and wt.% scales.
7. The silicate garden in which metallic salts grow colored “trees” when crystals are dropped into water glass (aqueous sodium silicate) is analogous to the fibrillars developed during the hydration process in cement. Explain.

8. In what way is polymer-impregnated concrete an important improvement?
9. It has recently been shown that the treatment of concrete with linseed oil (in dilute solutions of an organic solvent) extends the life of the concrete. Explain.
10. What advantages would there be in using fatty acid methyl esters of linseed oil instead of oil (triglyceride) to treat concrete?
11. Distinguish between cements, ceramics, and composites.
12. What is the difference between xerogels and aerogels and how are these materials used?
13. How is a ceramic or glass formed from the xerogel or aerogel?
14. What are the ideal properties of a fiber for reinforcement used in a composite?
15. Explain how the modern radial tire is an example of a composite structure.
16. Why is the addition of $CaCl_2$ to steel-reinforced concrete not to be recommended?

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