

Cementitious Materials—Nine Millennia and A New Century: Past, Present, and Future

Arnon Bentur¹

Abstract: Cementitious materials have been used in construction for several millennia and through several civilizations. Their use has been revitalized in the recent century, and they have become the major construction material for housing and infrastructure. The amalgamation of the science and engineering of these materials in recent decades has advanced the state of the art in their understanding and development. In a new century where sustainable construction is becoming an overriding consideration, the new scientific concepts can have direct impact on the way we use and formulate cementitious materials. On top of this, the scientific advances have provided the means for the potential use of the current portland cement as a platform to develop composite formulations of a high level of performance equivalent to and in some respects exceeding those of steel and ceramics. This may provide the basis for advanced and efficient construction techniques. The present article reviews the past, present, and future of cementitious materials and highlights the need for a comprehensive approach to maximize the advantages of the newly emerging cementitious materials and concretes.

DOI: 10.1061/(ASCE)0899-1561(2002)14:1(2)

CE Database keywords: Cements; History; Concrete.

Introduction

Construction has been an important element since civilization began and continues its vital role as a key industry in the rapidly changing modern society. It supplies the basic human need for housing and provides the infrastructure for industry and commercial activities, which are the driving forces for the advancement and well-being of society. Materials are at the heart of the construction industry. They determine the quality of the end product and the technology by which it is manufactured. Thus, advancement of the performance of a variety of types of structures and their efficient and industrialized production are directly related to the characteristics of the materials involved. Innovation in construction is highly linked with development of advanced construction materials.

Cementitious materials are a major class of construction materials that have been with us for more than nine millennia. To a nonexpert, they seem quite simple-a powder that is mixed with water, fillers, and aggregates to form a fluid mass that can be easily shaped and molded and thereafter hardens spontaneously in normal environmental conditions. This apparent simplicity is not matched by any other existing material and makes this class of materials unique.

Most cementitious materials can be considered calcareous, and their overall composition is defined within the ternary diagram CaO-SiO₂-Al₂O₃ shown in Fig. 1. The ancient cementitious materials were lime alone or lime in combination with natural pozzolans, as well as gypsum (the latter is outside the ternary diagram, as it is composed of calcium sulfates), while the modern ones are largely portland cement. The trend at present and in the foreseeable future is to increase the use of combinations of portland cement and large contents of mineral additives such as slag and fly ash.

The development of cementitious materials has a long historical record. In the early ages, their advent was to a large extent based on tradition and experience that crossed a range of civilizations. In the last century a major leap in the technology of cementitious materials has occurred, based on a unique bridging between the science and engineering of these systems.

The simplicity in production of components, engrained in the fresh fluid nature of the system, can be drastically improved using methods based on sophisticated concepts of surface chemistry and rheology. The properties in the mature state can be enhanced, approaching the level of "higher-grade" materials through control of microstructure and chemical reactions. The concepts of materials science are routinely applied in cementitious materials, providing the infrastructure for the development of systems with the superior performance and environmental friendliness required in this new 21st century. Among the various classes of cements, portland cement and composite cements based on portland cement are and will continue in the foreseeable future to be the main binder used in construction. The viability of this binder is demonstrated in the consumption trends for the last 50 years presented in Fig. 2. This article provides a review of the past and present and a projection of some future trends.

¹National Building Research Institute-Faculty of Civil Engineering Technion, Israel Institute of Technology.

Note. Associate Editor: Antonio Nanni. Discussion open until July 1, 2002. Separate discussions must be submitted for individual papers. To extend the closing date by one month, a written request must be filed with the ASCE Managing Editor. The manuscript for this paper was submitted for review and possible publication on June 20, 2001; approved on August 29, 2001. This paper is part of the Journal of Materials in Civil Engineering, Vol. 14, No. 1, February 1, 2002. @ASCE, ISSN 0899-1561/2002/1-2-22/\$8.00+\$.50 per page.



Fig. 1. Ternary diagram representing overall composition of calcareous cementitious materials

Historical Notes

The early beginning of cementitious materials dates back to 7000 B.C., to the Galilee in Israel, where a mortar floor was discovered in 1985 in Yiftah El (Malinowski and Garfinkel 1991; Ronen et al. 1991). It consists of several layers of $CaCO_3$ (upper finish of 5 mm and core of 50 mm), which was apparently manufactured from hydrated lime produced by burning of limestone and slaking thereafter. The microstructure of the binder is quite dense (Fig. 3), and the strength of the material evaluated in recent studies exceeded 30 MPa (Ronen et al. 1991). There is evidence for the use of similar cementitious floor construction on the Danube River, at Lepenski Vir in Yugoslavia, which dates to 5600 B.C. (British Cement Association 1999). The use of lime implies that ancient society had the technology required to burn limestone, and this is confirmed by several archeological findings.

A more intensive use of cementitious materials dates back to the ancient Egyptian civilization, at about 3000 B.C. It was suggested that the stone blocks used in the construction of the pyramids were bonded by cementitious materials, including gypsum (burned gypsum) and lime (burned limestone) [e.g., Snell and Snell (2000)]. It is believed that this technology was diffused around the Mediterranean countries, to be adopted by the Greeks and later by the Romans.



Fig. 2. Consumption of portland cement in recent 50 years



Fig. 3. Microstructure of 7000 B.C. lime revealed in Yiftah El, in the Galilee, Israel. Right-hand side is top layer and left is bottom layer (after Ronen et al. 1991)

The Romans, during the period between 300 B.C. and 200 A.D., improved this technology (Vitruvius 13 B.C.; Malinowski 1979; British Cement Association 1999). They used slaked lime in a mixture with volcanic ash (called pozzolana) found near Pozzuoli at Naples Bay. It is likely that the first use of this mixture resulted from observation that when ash was added as a fine filler (sand replacement), the hardened material performed better. The experience that led to this discovery resulted in what is known as pozzolanic cement, where improved properties in the hardened state are based on chemical reactions between hydrated lime (slaked lime) and the amorphous aluminosilicates. In his handbook for Roman builders, Vitruvius (13 B.C.) described this material as one that hardens both in air and underwater.

During the Roman Empire, this pozzolanic cement served for the construction of such large-scale structures as the theater in Pompeii in 75 BC, as well as infrastructure components such as aqueducts and sewers (Malinowski 1979). The Romans also developed the concept of lightweight concrete by casting jars into wall arches as well as the use of pumice aggregate, which was obtained by crushing a porous volcanic rock (British Cement Association 1999). The arches of the Colosseum and the Pantheon dome were made with such materials.

The art of using cementitious materials and making concretes was essentially lost after the fall of the Roman Empire. The reemergence of cementitious materials dates largely to the 17th and 18th centuries (Klemm 1989; Idorn 1997; Blezard 1998; British Cement Association 1999). A significant step toward the development of modern portland cement was made by John Smeaton in England in 1756, when he was involved in the reconstruction of the Eddystone lighthouse. He was driven by the need to develop a masonry construction that would be durable in a marine environment. His concept was to carry out experiments in order to produce a binding lime mortar that would not dissolve in seawater. For that purpose he burned different types of limes and mixed them later with a trass ("tarras") that possessed pozzolanic characteristics. He discovered that argillaceous limestone, namely limestone that contains some clay, provided better performance than "pure white chalk." This class of materials may be defined as hydraulic limes and can be considered as midway between slaked lime and modern portland cement. Additional improvements of this class of binders by Bay Higgins in 1779 and James Parker in 1796 followed thereafter (Klemm 1989).

Evolution of Modern Portland Cement

A significant step toward the development of modern portland cement was made by Louis-Joseph Vicat in France in his publi-

cation, "Recherches experimentales sur les chaux de construction," in 1818. He discovered that hydraulic lime can be made not only from argillaceous limestone, but also by burning an artificial mixture of clay with a high-grade limestone or quicklime (i.e., burned limestone before slaking—CaO). The latter mode of production was preferred and was named "artificial lime twice kilned." Various patents and products that may be defined as hydraulic limes or perhaps low-grade hydraulic cements were issued in that time period by Maurice St. Leger in 1818, John Tickel in 1820, Abraham Chambers in 1821, and James Frost in 1822 (Klemm 1989).

A three-stage process for producing hydraulic cement was first developed by Joseph Aspdin in 1824: calcining the limestone, burning it with clay, and recalcining the mixture to obtain the final product. This process has some similarities to Vicat's "twice-calcined" product. The Aspdin process is more adaptable to a variety of raw materials and assumes more intimate and efficient reaction between the raw ingredients during the firing stages. This process was patented as "an improvement in the modes of producing artificial stone," which was claimed to be similar to portland stone, considered one of the best quarried building stones in England. Aspdin called this product "portland cement," and he was quite successful in marketing it to the construction industry, convincing them that it performed better than the variety of hydraulic limes.

Portland cement was introduced in the United States around 1870, and the first plant was established by David O. Saylor, in Coplay, Pa. It is of interest to note that prior to that time, a binder named "natural cement" was used in the United States that was produced by burning a natural rock, which was argillaceous limestone, with a composition almost ideal for cement production. These cements competed for some time with portland cement imported from Europe. The natural cement was weaker, but its price was lower (Klemm 1989).

The development of portland cement in the 19th and 20th centuries was classified by Blezard (1998) into three stages: "Proto-Portland," "Meso-Portland," and "Normal-Portland." The difference between them is in the improved proportioning of the raw materials and in the burning process, reaching an adequate clinkering temperature. Thus, the Proto-Portland cement was essentially a somewhat improved hydraulic lime, not much different from the others of its generation, at the first half of the 19th century; the Meso-Portland cement, with better clinkering, consisted largely of dicalcium silicate and only a little tricalcium silicate; and the Normal-Portland had a significant content of tricalcium silicate and little free lime.

The advancement from the Meso-Portland to Normal-Portland stage was the result of a better choice of the raw mix and also a much better control of the burning process, in particular in the range of the clinkering temperatures, where the calcium silicates are being formed. The development of the rotary kiln to replace the shaft kiln had a considerable impact on the quality of the product and the efficiency of the production process, which became continuous rather than the batch type operation in the shaft kiln (Klemm 1989; Blezard 1998; British Cement Association 1999).

The development in concrete technology might be quantified in terms of the strength of the portland cement, evaluated by the standard test of 1:3 cement:sand mortars cured continuously in water (Fig. 4). The improved quality reflects the mineralogical composition of cements, with a higher C_3S to C_2S ratio, and a better control of the grinding of the clinker.



Fig. 4. Development over time of quality of portland cement as characterized by strength of 1:3 mortar cubes (adapted from Blezard 1998)

Evolution of Scientific Foundations

The foundations for the chemistry of cement were laid by Henry Le Chatelier from France in his doctoral thesis of 1887 (Le Chatelier 1887). He established that the main mineralogical phase in portland cement responsible for its cementing properties had the formula $3\text{CaO} \cdot \text{SiO}_2$ (C₃S using the then current cement chemistry notation). Le Chatelier based his investigation on microscopic petrographic observations that revealed that C₃S was one of four phases. Using chemical analysis, he established guidelines for the composition of raw material required for producing good cements, expressed in terms of ratios named "moduli":

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} < 3 \tag{1}$$

$$\frac{\text{CaO+MgO}}{\text{SiO}_2 - (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)} > 3$$
(2)

He suggested that optimal composition is obtained when ratio (1) is about 2.5 to 2.7 and ratio (2) is 3.5 to 4.0.

The four-phase composition was confirmed by Torrebohm, who named them alite, belite, celite, and felite. Alite was shown to be essentially C_3S , and belite was largely β - C_2S . In 1915, G. A. Rankin and F. E. Wright (Klemm 1989) presented a fundamental study of the ternary system CaO-SiO₂-Al₂O₃ within which portland cement is placed. They provided the cement chemists' notations of C for CaO, S for SiO₂, A for Al₂O₃, F for Fe₂O₃, and \overline{S} for SO₃ (Klemm 1989).

Studies of the mineralogical composition of the cement that served as a foundation for control of the production process were accompanied by investigations of the hydration reactions, to establish the mechanisms of setting and hardening. The crystalline concept was suggested by Le Chatelier in 1881, while W. Michaelis in 1893 resorted to a concept of formation of colloidal-gelatinous material (Lea and Desch 1956). Controversy was struck at that time and continued into the early part of the 20th century regarding which of the two hypotheses better describes the hydration products. A controversy of similar intensity was sparked years later in the 1960s and 1970s regarding the internal structure of the hydrated C-S-H and the significance of surface area measurement with respect to characterization of its structure: H_2O adsorption (Powers and Brownyard 1948, Powers 1960) versus N_2 adsorption (Feldman and Sereda 1968).

Another important characteristic of portland cement chemistry, highlighted already at the end of the 19th century and the beginning of the 20th century, was regulation of setting time by the use of gypsum. From 1876 to 1878, Dyckerhoff of Germany studied the effect of up to 2% additions of gypsum and reported set retardation from 20 to 840 min. The reactions with gypsum were studied by Candolt, and Le Chatelier commented in 1905 on the formation of $Al_2O_3 \cdot 3CaO \cdot 3(CaO \cdot SO_3) \cdot 30H_2O$ (known as ettringite), which may cause expansion deterioration in seawater.

Early 20th Century Technological Developments

The development of portland cement was followed by advancement of technologies for efficient use of this new binder (British Cement Association 1999). A reinforcing system based on the use of twisted steel rods was patented by Earnest L. Ransom in 1884, and the first reinforced concrete skyscraper, the Ingalls Building, was constructed in 1904. In 1927 Eugene Freyssinet developed the prestressing concept, and in 1933 Eduardo Torroja designed the first thin-shelled roof at Algeciras (Torroja (1958)) and Pier Luigi Nervi developed a thin shell construction for airplane hangars. The Hoover Dam, the first massive concrete dam, was built in the United States in 1936.

Architectural concepts to use exposed concrete, particularly precast elements, were demonstrated first in 1923 in France in the Cathedrale Notre-Dame du Haut in Le Raincy. Technologies for surface finishing of precast elements were developed during the 1930s. The precast concrete industry took a sudden rise after World War II, in view of the massive need for quick housing. This development was the result of an integrative effort dealing with the materials and production technology, curing practices, and mechanization of construction sites by such equipment as cranes.

High-Temperature Chemistry and Cement Production

The technology of production of high-grade cement is based on high-temperature chemistry. The high-temperature reactions for clinker formation can be divided into five steps (Taylor 1997; Jackson 1998; Macphee and Lachowski 1998):

- 1. Decomposition of clay materials (\sim 500 to 800°C);
- 2. Decomposition of calcite, calcining (\sim 700 to 900°C);
- Reactions of calcite (or lime formed from it), quartz, and decomposed clays to form C₂S (~1000° to 1300°C);
- 4. Clinkering reactions at 1,300 to 1,450°C to form C_3S . A melt of aluminate and ferrite is formed that acts as a flux to facilitate the formation of C_3S through the reaction of C_2S and lime (CaO); and
- 5. Processes occurring during cooling where liquid crystallizes, forming the aluminate and ferrite phases.

Bogue developed a calculation for estimating the phase composition of portland cement clinker assuming a composition of C_3S for alite, C_2S for belite, C_3A for aluminates, and C_4AF for ferrites.

It should be noted that the portland cement particles, which are obtained by grinding the clinker in the presence of gypsum, are not separated into the individual phases, but rather one particle may contain several phases (Scrivener 1989).

The high-temperature chemistry studies resulted in the establishment of the ternary phase diagram $CaO-Al_2O_3-SiO_2$, which serves as the basic guideline for characterizing the hightemperature reactions and stable-phase compositions. The raw materials for producing such compositions are limestone, which is the major source of CaO, and suitable clays and shales containing 55 to 60% SiO₂, 15 to 25% Al₂O₃, and 5 to 10% Fe₂O₃, with mineralogical composition consisting of clay minerals, quartz, and sometimes iron oxide.

Much attention was given to the optimization of the clinkering process and the grinding thereafter with gypsum. The considerations of the clinkering process were the composition of the cooled clinker, the burnability of the mix (i.e., the ease with which free lime can be reduced to an acceptable value in the kiln), and the role of minor components, energy consumption, and environmental effects. In recent years, much of the change in the production processes of portland cement has been driven by energy and environmental constraints and requirements (European Commission 1999). Modern clinker is produced in a dry process using suspension preheaters and precalciners with shorter rotary kilns. The fuels commonly used are pulverized coal, oil, natural gas, and lignite. There is an increasing tendency to use wastes as partial replacement for the fuels and raw feed (Odler and Skalny 1995).

The overall composition and burning process are affected to a large extent by the ratio between the four major oxides in the raw feed (CaO, SiO₂, Al₂O₃, and Fe₂O₃). This is demonstrated in conventional calculation of the composition using the Bogue equation and the guidelines for optimal choice of the three moduli: LSF (lime saturation factor)— $CaO/(2.80SiO_2)$ $+1.18Al_2O_3+0.65Fe_2O_3$; SR (silica ratio)—SiO₂/(Al₂O₃ + Fe₂O₃); and AR (alumina ratio)—Al₂O₃/Fe₂O₃. Increase in SR lowers the content of the fluxing liquid and thus reduces burnability. The AR modulus controls the ratio between the aluminate and ferrite phases, which may have considerable influence on the properties of hydrated cements.

Special attention has been given in recent years to the influence of minor components. The role of some of them has changed due to environmental and health considerations. A special case is that of the alkalis, sodium and potassium (both the content and the ratio between the two). The sources for alkalis are usually in the fuel, mainly coal and shale. A cycle of gas flow is established in the kiln in which gas is flowing in a direction opposite to the movement of solids, in order to save energy by the use of the hot gas to heat the raw material. As a result, alkalis in the gas react with sulfate to form alkali-sulfates, which may condense and be removed from the gas phase to be combined in a variety of ways with the silicate melts. As a result of such processes, the contents of alkalis in cement can become higher. This may have a variety of influences, some positive and some negative, on the performance of portland cement (Taylor 1997).

Materials Science of Cement and Concrete

The scientific foundations for the behavior of hydrating portland cement and the resulting concrete end product were set first on the basis of the chemistry of hydration reactions. These were followed by studies and characterization of the microstructure and internal bonding using techniques such as electron microscopy, magnetic resonance, atomic force microscopy, adsorption isotherms, and mercury porosimetry.

The understanding of the relations between internal structure and performance in the fresh and mature state serves as a basis for developing advanced systems and solving a variety of technological limitations in existing systems. Numerous books and confer-



Fig. 5. Portland cement hydration reactions: kinetics of hydration and nature of products formed (adapted from Odler 1998)

ences have been published addressing these issues, e.g., Soroka (1979); Skalny (1989, 1991, 1992); Skalny and Mindess (1995, 1998); Taylor (1997); Hewlett (1998); and Ramachandran (2001).

Chemistry of Cement

Early studies of hydration reactions revealed the differences in the kinetics and nature of hydration reactions and products of the various pure individual minerals. Although the fundamentals established were found applicable to many portland cement systems, some significant differences had to be considered due to a variety of influences (Odler 2000; Taylor 1997), such as the following:

- Mineral phases in portland cement are not "pure," but are doped with various foreign ions;
- Alkalis and gypsum present in portland cement affect modes and rates of hydration reactions; and

• Minerals in portland cement are not in form of separate grains. These differences exert considerable influence on the various processes involved in the hydration reactions, due to several factors:

- Nature of dissolution of mineral phases in contact with water,
- Nucleation and growth of hydration products, and
- Rate of diffusion of dissolved ions through hydrated products engulfing unreacted cement grains.

Thus a relevant study of cement hydration requires evaluation of the cement system itself. The nature of the hydration reactions in terms of the rates of reactions of the individual minerals and the hydration products formed are shown in Fig. 5. The process can be divided into several stages: preinduction period (first few minutes, where some dissolution of the minerals occurs and all the alkali-sulfate dissolves, contributing K⁺, Na⁺, and SO₄²⁻ ions to the solution); dormant period (few hours); acceleration stage (3 to 12 h, characterized by nucleation of hydration products); and postacceleration period, when the reactions become diffusion controlled. Details of the mechanisms involved are reported in several publications [e.g., Taylor (1997); Odler (1998)] and are beyond the scope of this review.

An important element in the processes at this stage is the composition of the liquid phase, which is highlighted here in view of the significance of the composition of the aqueous solution on other characteristics, particularly the durability of the mature system. The alkali-sulfates are highly soluble and enter the liquid phase immediately, as K^+ , Na^+ , and SO_4^{2-} ions. The Ca^{2+} ions dissolve into the liquid at a somewhat slower rate, to become saturated with respect to $Ca(OH)_2$ after a few minutes. The OH^- ion concentration in the liquid phase is controlled by dissolution of $Ca(OH)_2$ in the hydration of C_3S and by the dissolution of alkalis present in the clinker materials. Thus the OH^- concentration is greater than expected on the basis of $Ca(OH)_2$ dissolution only, and therefore the pH of the pore solution eventually attains values greater than about 12.5, which is characteristic of a saturated $Ca(OH)_2$ solution. Values as high as 13.5 have been reported, depending largely on the soluble alkali contents.

Composition and Microstructure of Hydrated Cement

It is well known that the major phases of the hydration products are C-S-H, CH, and a variety of sulfoaluminate hydrates, such as ettringite ($C_3A \cdot 3C\overline{S} \cdot 31H$) and monosulfate ($C_3A \cdot C\overline{S} \cdot 12H$). Although there is a rough agreement on their overall composition and structure, the detailed composition and microstructural characteristics are still debated and explored. This is largely because some of the phases, in particular the C-S-H, are largely amorphous and show variability in their structure, which may depend on a variety of factors related to the cement composition, water/ cement ratio, and curing conditions [e.g., Taylor (1997); Odler (1998), Richardson (1999)]. Also, it should be borne in mind that the cement paste, even after many years, is still a "live" system: residues of unhydrated grains always exist, and the hydrated phases are not in equilibrium, i.e., some of the pahses are in a metastable state and therefore are prone to changes under a variety of environmental conditions, such as carbonation.

Several models of the structure of hydrated cement pastes have been developed over the years, based on a variety of concepts, some of them complementary and some in contradiction to each other. Three of the more "traditional" models are presented in Fig. 6. The Powers model is based on a monumental series of studies carried out at the Portland Cement Association (PCA) in the United States during the 1940s, 1950s, and 1960s (Powers and Brownyard 1948; Powers 1968). Applying the physical chemistry concepts available at that time, the PCA group developed many of the fundamental concepts of the structure of the pores and the C-S-H phase, which are still valid: its high surface area and colloidal nature, with the implication of these characteristics to strength generation and volume changes. The concept of two types of pores-capillary and gel pores-can provide a working hypothesis for understanding engineering characteristics of the material. Yet studies with more advanced tools indicate that the pore-size distribution is more gradual in nature, and a large range of pore sizes-over several orders of magnitude-need to be considered (Diamond 1999), (Table 1).

Considerable controversy developed regarding the microstructure of the C-S-H, as reflected to some extent in the models presented in Fig. 6. In part, the differing views were related to the concept of interlayer water [metacrystals in Ishai's (1968) model]: whether they are part of the C-S-H or separate gel pores. Their role was assumed to be greater in the Feldman-Sereda model, with respect to explaining volume changes induced in drying and wetting conditions. The differing views were also reflected in interpretations of surface area measurements of the hydrated material; they are typically about 150 m²/g obtained by BET measurement using water adsorption, about 15 m²/g for BET measurement obtained by N₂ absorption, and about 15 m²/g





Fig. 6. Three traditional models of structure of hydrated portland cement paste: (a) Powers (1960); (b) Feldman-Sereda (1968); (c) Ishai (1968)

calculated from the pore-size distribution obtained by mercury intrusion porosimetry. The technique of low-angle X-ray scattering, which allows surface area measurement at different moisture states, revealed areas of about 800 m²/g for saturated samples (Winslow and Diamond 1974), which are reduced at lower relative humidity. The differences in surface area measurements reflect the accessibility of different spaces to the various adsorbing or intruding materials.

A common element in all the models is the implication that the basic unit is some kind of a C-S-H sheet, and that these units are organized in a variety of modes and varying spaces (gradient of spaces). This is clearly described in the model of Ishai (1968). The nature of interactions involved in removal or adsorption of

Table 1. Characteristic Size Range of Porosities in Hydrated Cement

 Paste

Type of pore	Size of pore (µm)
Interparticle spacing between C-S-H sheets	0.001-0.004
Capillary pores	0.01-1.6
Entrained air bubbles	70-1,200
Entrapped air voids	1,200-4,000

Table 2. Typical Characteristic-Average Compositional Parameters

 in Hydrated Portland Cement Paste

Characteristic compositional parameters	C-S-H	СН	AFm
C/S ratio	1.67	25	25
C/(A+F) ratio	9.1	25	1.8
C/\overline{S} ratio	33	250	4.2

water depends on the space: very low physical interactions for bigger spaces, and stronger ones, approaching those of structural interlayers, for smaller ones.

These structural characteristics have considerable implications for understanding, modeling, and predicting the behavior of the cementitious systems in changing moisture conditions.

Results of modern research on the microstructure and microcomposition of hydrated cements suggest that many of the features of the structure should be characterized in terms of average parameters and gradients. Microchemical analysis using various methods of testing shows variabilities in composition in space that can be interpreted in terms of three main compositional regions:

- Regions high in Ca and Si, low in Al and Fe—characteristic of spots high in C-S-H;
- 2. Regions very high in Ca, low in Si, Al, and Fecharacteristic of spots high in CH; and
- Regions high in Ca, Al, and Fe, low in Si—characteristic of spots high in monosulfate (AFm) and ettringite (AFt).

Average compositions of these phases are provided in Table 2, showing that none of them can be considered "pure." However, one should address with caution such average values, since they represent in fact a much more complex structure (Richardson 1999). For example, distinctions should be made between the inner and the outer C-S-H and the C-S-H formed in the presence of pozzolans. The ratio of Ca/Si (C/S ratio) is often used to characterize the C-S-H, but the average value may range from 1.5 to 2.0, with spot values spreading over a wider range. Lower C/S ratio is characteristic of C-S-H formed in the presence of pozzolans.

When considering the structure of the C-S-H, due attention should also be given to the nature of the Si-O bonding in the SiO_4 hydrated units. At first the structure is that of hydrated monomeric units (SiO₄), and the progress of hydration results not only in the formation of more hydrates, but also in the formation of dimeric units and sometimes even larger units. This is essentially a process in which some polymerization may occur, i.e., silicate polymerization, when silica tetrahedra become linked together in -Si-O-Si-bonds. Various techniques have been used to assess the degree of polymerization, and they indicate that polymerization may occur as hydration progresses (Young and Sun 2001). In a mature paste, polymerization may be driven by conditions such as carbonation and drying. A process of this kind has been suggested as one of the causes of irreversible shrinkage under carbonation and drying conditions. It may be simply perceived as bonds that are formed as the C-S-H foils approach each other on drying, when the interlayer water is removed.

Composition and Microstructure of Concrete

The structure of concrete has often been considered in simplistic terms as a portland cement paste with diluting inclusions of aggregates. This implies that the microstructure of the paste matrix



Fig. 7. Gradients of porosities at ITZ zone measured by backscattered electron imaging (after Scrivener et al. 1988)

in the concrete is identical to that of portland cement paste. However, this is an oversimplified approach, as several levels of heterogeneity may be induced in the concrete, revealed first by French researchers studying a composite system of cement paste cast against aggregate surface (Farran 1956) and later in studies of the concrete itself [e.g., Ollivier et al. (1995); Diamond (1999)], that do not occur in the paste. One such level is associated with the rheological characteristic of the concrete, affecting the distribution of the cement and filler particles in the mass, as well as effects such as bleeding and a second level of heterogeneity that may be due to aggregate-paste chemical interactions.

The processing of the concrete in its fluid state is intended to provide a uniform dispersion of all of the constituents. However, ideal dispersion is difficult to achieve. There is an inherent "wall effect" that leads to a gradient in the dispersion of the fine particles (cement and fillers) in the vicinity of the aggregate surface: the coarser cement and filler particles cannot pack readily near the aggregate surface. Since the cement particle size distribution is typically in the range of 1 to 100 μ m, a zone of about 10 to 50 μ m is formed around the aggregate in which the effective water/ cement ratio is higher (i.e., less cement in this region, with the cement particles being of the smaller size range) (Goldman and Bentur 1994; Ollivier et al. 1995; Alexander et al. 1999; Bentz and Garboczi 1999).

Obviously, the hydrated structure in this zone will tend to be more porous, although the rate of hydration will be higher since the zone consists of smaller particles. The greater porosity will also result in a greater tendency for the deposition of large CH crystals. Gradients of microstructure that develop in this zone, called the interfacial transition zone (ITZ), are shown in Fig. 7. The introduction of fine fillers, such as silica fume, with particles smaller than that of cement (~0.1 μ m) results in densification of this zone (Fig. 7).

The more porous nature of the ITZ is considered a factor affecting strength and transport properties. The extent of its detrimental influence is still in debate. Probably its influence on strength and modulus of elasticity is moderate or small ($\sim 20\%$), and its influence on transport properties could either be direct (the result of a more porous path near the aggregates) or indirect by creating a weaker zone that is more prone to cracking (Bentur 1998a).

An additional influence on concrete microstructure—caused by the properties of the fresh concrete—is bleeding, which creates a different microstructure beneath aggregate and steel bars, in addition to zones of varying porosity throughout the concrete mass. These microstructural characteristics are affected by the rheological nature of the concrete.

Additional influence due to chemical reactions between the aggregate and the cementing paste matrix are rather limited. The exception is the deleterious alkali-aggregate reaction, whereby aggregates containing amorphous silica phases react more readily with the alkaline matrix.

Modeling of Concrete Behavior

Modern materials science concepts have been used to develop models to describe the behavior of concrete, addressing a variety of issues such as mechanical performance and transport characteristics. The development of these models is based on a large number of fundamental studies resolving many characteristics, such as (1) cement hydration and development of microstructure in pastes and concretes; (2) transport characteristics considering the microstructure and processes, such as diffusion, permeation, electromigration, and convection by capillary suction; (3) timedependent volume changes and their dependence on microstructure, considering a variety of physical processes, such as surface tension, capillary stresses, and hindered adsorption; and (4) mechanical behavior based on such concepts as composite materials and fracture mechanics.

Microstructural Modeling

Computer modeling of cement hydration and microstructure enables us to simulate the microstructure obtained in electron microscope analysis and has the potential of becoming a tool for optimizing the composition of the material by means such as control of particle size of cement and fillers, [e.g, Bentz et al. (1995); Van Breugel (1996); Bentz (1997); Bentz and Garboczi (1999)]. The advent of computer modeling is linked with the improved understanding of the processes by which microstructure evolves, as is also the increase in computational power. Computer modeling allows us to consider features differing by several orders of magnitude in size. Such models have been used to quantify the microstructure and phase composition and their variability in the concrete, showing in particular effects such as the ITZ, which is characterized by initial higher porosity. The computer models can be used to predict the effect of combinations of various mineral fillers on the transport properties, considering the variability in microstructure.

Modeling of Transport Properties

Models to predict transport properties have been developed based on the basic laws describing transport of substances through porous media, superimposed on the special microstructural characteristics and composition of pastes and concretes. A variety of transport processes that depend on the transported substance and driving force for the transport were resolved by analytical methods. These were quantified in terms of tests developed to characterize relevant parameters such as diffusion and permeability coefficients [e.g., Kropp and Hilsdorf (1995)]. The processes modeled were diffusion of ions (usually chloride ions, the driving force being concentration differences); electromigration (similar to diffusion but having the electric field as the driving force-this is less common in practice but useful for accelerated tests to determine diffusion coefficients); permeation of gases and liquids (the driving force being pressure difference); and convection mass flow (the flow of a substance transported in the fluid in which it is contained) (Bentz et al. 1995, 1998; Marchand et al. 1998; Nilsson and Ollivier 1996). The convection occurs in the case of

permeation of fluids and is of acute significance in convection, which is the result of capillary suction of water into dry concrete pores in contact with water.

The modeling of the transport phenomena frequently considers combined flow mechanisms of diffusion and convection, diffusion and permeation, and diffusion and electromigration. In modeling of this kind, mass balance equations are used to predict the processes, and due consideration is given to some complicating processes such as chemical binding of some of the migration substances, which is time-dependent-process, and physical binding, which is the result of adsorption on the colloidal high-surfacearea particles of hydrated cement (Marchand et al. 1998). On the basis of these concepts, tests to evaluate transport characteristics were developed that tend to be used to set performance criteria for concrete durability (Kropp and Hilsdorf 1995).

Modeling of Mechanical Properties

Mechanical modeling of cementitious systems has a particularly long history. The earlier concepts were based on developing relations between strength and porosity based on prevailing concepts in porous materials in general, e.g., ceramics (Rice 1984), and in cement systems in particular (Beaudoin et al. 1994; Roy 1988; Brown et al. 1991). This concept is behind the early relations developed between strength and water/cement ratio by Feret in 1896 [Eq. (3)] and Abrams in 1919 [Eq. (4)]:

$$f_c = K \left(\frac{c}{c+w+a}\right)^2 \tag{3}$$

$$f_c = K_1 / K_2^{(w/c)} \tag{4}$$

where K, K_1 , K_2 = constants; c = cement content; w = water content; and a = air content.

This empirical approach is adequate for many engineering calculations and is applied even today. However, it is not sufficient to develop advanced systems in which the role of aggregates, particulate fillers, and fibers is becoming increasingly important. For this purpose, concepts of composite materials (assessing the bonding between different phases) and fracture mechanics have been applied. Models describing these systems on the meso and micro level have been advanced [e.g., Van Mier (1997); Van Mier and Vervurt (1999)].

On the meso level, the cement paste is considered a continuous and uniform phase that interacts with inclusions such as aggregates and fibers. The matrix-inclusion interaction is characterized in terms of a bonding function that in the most simplistic form is modeled by the single parameter of bond strength. A more realistic approach requires addressing the nature of bonding in terms of distribution of properties as well as the rigidity of the ITZ, reflecting its special structure.

Micromechanical models have been used to predict the rigidity of concretes considering the properties of the aggregates and the nature of bonding, as well as to predict the strength of cementitious composites. However, when the overall response of the material is to be considered, to characterize whether its behavior is ductile or brittle, fracture mechanics concepts had to be introduced, combined with characterization of interfacial properties (Shah and Ouyang 1992). Finite-element analysis with inputs of characteristic properties of paste matrix, aggregates, and interfaces can predict the overall behavior of the system. Such modeling is of particular interest in high-strength concrete systems, in which aggregates play a major role in the mechanics of the system and cannot be considered simply as a diluting component in a paste matrix.



Fig. 8. Fracture process zone in front of advancing crack

Micromechanical models have also become common tools in predicting the properties of fiber-cement composites, such as strength and toughness (Li et al. 1995). The concepts applied within these models include fiber-matrix interactions and fracture processes [e.g., Bentur and Mindess (1990); Balaguru and Shah (1992); Bentur et al. (1995)].

With such models it is possible to predict the properties required to achieve high-strength and pseudo-plastic composites. In consideration of the fracture behavior of cementitious materials, the concepts of linear and nonlinear fracture mechanics have been applied (Shah et al. 1995). The nonlinear concept is modeled in terms of a fracture process zone in front of the advancing crack, which consumes energy by a variety of mechanisms induced under the stress field in front of the crack (Fig. 8).

Modeling of Time-Dependent Deformation

Time-dependent volume changes is an area where much effort has been expended for decades to model and develop rules in codes and standards. This pertains to shrinkage during drying and creep under load in combination with drying. Many of the earlier models were empirical ones describing the effect of cement content, water/cement ratio, aggregate content, size of component, environmental conditions, and level of loading.

With a better understanding of the microstructure of pastes and concretes, models based on fundamental physical and chemical processes were developed taking into account a variety of interaction of water molecules with the hydrated material (Hansen and Young 1991). The concepts used for modeling include capillary stresses and disjoining pressures at higher levels of relative humidity and surface tension and interlayer water movements at lower relative humidity [e.g., Bazant (1995)]. Irreversible volume changes were considered in terms of collapse of pore structure and chemical interactions, in particular silicate polymerization (Hansen and Young 1999).

Fresh Concrete: Rheology and Admixtures

The properties of fresh concrete have usually been addressed from a technological point of view to proportion a mix that can be readily transported, placed, and consolidated. The use of traditional water-reducing admixtures has generally been considered in this context.

The advent of high-performance concrete materials is to a large extent based on developing mixes of drastically improved



Fig. 9. Schematic presentation of cement particles: (a) in waterflocculated state; (b) in dispersed state; and (c) dispersed in combination with microfillers

flow properties by controlling particle size distribution in combination with chemicals engineered for the purpose of controlling the interparticle attractions in the fresh material (i.e., high-range water-reducing admixtures). For this purpose a much more comprehensive understanding of the flow properties—and their characterization in terms of tests that are more meaningful than the slump test—are required.

The early foundations for such treatment were laid down at the Portland Cement Association, where the principles of rheology were applied systematically to pastes and concretes (Powers 1968). In the past two decades the area was advanced considerably due to the needs outlined above [e.g., Beaupre and Mindess (1998); Struble et al. (1998)]. Rheological measurements were interpreted in terms of the various modes of suspension of particles in water, in flocculated or dispersed states [Figs. 9(a-b)]. The results of rheological measurements of cementitious suspensions, characterizing stress-strain rate behavior of cement pastes and concretes, can be approximated and modeled as a Bingham fluid, with a yield stress and apparent viscosity (Fig. 10). This behavior can be interpreted in terms of a pseudo-yield stress, which causes the breakdown of the flocculated network, and the plastic viscosity thereafter, reflecting the behavior of a highly concentrated dispersed suspension. A more-detailed characterization can reveal additional aspects related to the thixotropic behavior and irreversible breakdown of the structure at increasing strain rates.

Standard rheological testing techniques based on testing the response of a thin layer (of a few millimeters) of fluid to a strain rate effect, producing a stress, can be applied more readily to cement paste of sufficient fluidity. Such tests can be clearly interpreted in terms of stress and strain rates. However, such instru-



Fig. 10. Stress-strain rate curve of fresh cementitious systems that can be modeled by Bingham-type behavior (adapted from Struble et al. 1998)



Fig. 11. Buildup of surface charge (zeta potential) with increase of superplasticizers that adsorb on cement grains (adapted from Mollah et al. 2000)

mentation is not valid for concrete where aggregate particles are present, and special rheometers had to be developed for this purpose (Wallevik and Gjorv 1990; de Larrard and Chang 1996; Wallevik 1998).

Addition of water to the mix improves the fluidity without breaking the flocculated structure of the cement particles. However, in the presence of larger amounts of water the particles comprising the concrete mix tend to segregate more, once agitation is stopped, and bleeding occurs. Careful grading of the mix to increase its cohesiveness may compensate for some of the extra segregation and bleeding. Thus, water content and the content and composition of the fine aggregate fraction in the mix were traditionally optimized to obtain a required flow with minimum segregation.

The constraints on improvement in flow properties while minimizing segregation are largely overcome in modern concrete technology by the use of high-range water-reducing chemical admixtures (superplasticizers). These admixtures were first developed and applied in Japan (Mighty admixture) and Germany (Melment admixture), and they represented a breakthrough in concrete technology that opened the door to the new generation of concretes such as high-strength/high-performance and self-compacting concretes. These admixtures are synthetic high-molecular-weight water-soluble polymers [e.g., Sakai and Daimon (1995)]. That are effective in dispersing the flocculated cement grains. Solubility is achieved by the presence of adequate hydroxyl, sulfonate, or carboxylate groups attached to the main organic unit, which is usually anionic.

These polymers adsorb on the surface of the grains and facilitate dispersion by three mechanisms: (1) buildup of a negative charge on the surface (i.e., increase of zeta potential) sufficiently large to cause repulsion (-20 to -40 mV) (Fig. 11); (2) increase in solid-liquid affinity; and (3) steric hindrance when oriented adsorption of nonionic polymers weakens the attraction between solid particles (Fig. 12) Haneharo and Yamada 1999; Mollah et al. 2000. These admixtures do not cause set retardation and air



Fig. 12. Schematic description of adsorbed graft polymer superplasticizer causing steric hindrance (adapted from Haneharo and Yamada 1999)



Fig. 13. Influence of traditional and modern high-range water reducers on flow of concrete (adapted from Edmeades and Hewlett 1998)

entrainment, as may occur with conventional water reducers, and therefore they can be added at much higher dosages of about 2% by weight of cement. The difference in the performance of traditional water reducers and modern high-range water reducers is demonstrated in Fig. 13. Development of more-efficient highrange water reducers by better control and optimization of their molecular structure is currently at the forefront of concrete technology.

Another advanced concept of improving workability in low water/binder ratio mixes, which is based on uniform dispersion of cement grains with very fine fillers between them, is shown in Fig. 9(c). Here, the microfiller particles serve to improve flow properties by acting as small rollers between the bigger and rougher cement grains. In a system of this kind, excellent flow can be obtained at a very low water content, thus achieving a mix with hardly any segregation at a low water/binder ratio. The filler is considered part of the binder, alongside the portland cement. This is the fundamental concept underlying the new generation of high-strength and self-compacting concretes using silica fume. The characterization of such concretes by rheological measurements is shown schematically in Fig. 14.



Fig. 14. Schematic description of characteristic rheological behavior of normal strength concretes (NSC), high-strength concretes (HSC), and self-compacting concretes (SCC) (adapted from Wallevik 1998)



Fig. 15. Hydraulic activity of various forms of belite-rich cements estimated from strength development of 0.60 w/c ratio pastes (adapted from Odler 2000). Main belite phases are alpha (cooling rate of 50,000°C/min), alpha' (cooling rate of 3,000°C/min), beta* (cooling rate of 50,000°C/min), and beta (cooling rate of 2°C/min)

Sustainability and Cementitious Materials

The awareness of the ecological impact of technology and the need to address it in our modern society is becoming a factor of increasing importance in the field of cement and concrete. The influence here is at several different levels: (1) producing binders that consume less energy and emit less greenhouse gases, in particular CO_2 ; (2) incorporating industrial by-products and recycled materials in the cementitious binder as well as in the concretes; and (3) producing structures that would function more efficiently over time, in terms of their durability performance.

Binders

Two main ecological issues are currently of concern in portland cement production: energy consumption, and release of CO_2 during the decalcination stage of clinker production. In modern kilns with preheaters and precalciners using the dry process, the energy required is about 3,000 kJ/kg of cement. About two-thirds of this energy is consumed in the decalcination and clinkering reactions, and one-third in energy losses. This energy range is significantly lower than typical values of a few decades ago, which exceeded 5,000 kJ/kg of cement. The theoretical energy required is dependent on the LSF, being in the range of 1,570 to 1,800 kJ/kg for LSF in the range of 80 to 100% (Lawrence 1998). There is a rough correlation between the CO_2 emission and energy consumption, since decalcination is an energy intensive step.

Several strategies are currently being considered or applied to reduce energy and CO_2 emission:

- Improving current technology to produce a cement of similar composition with less energy. This however is not expected to lead to drastic reduction in CO₂ emission (European Commission 1999).
- Improving the reactivity of the clinker to enable the use of leaner mixes and reducing the clinkering temperature by developing efficient fluxes. It should be borne in mind that reduction in the clinkering temperature by about 100°C will provide only modest energy savings of about 5%.
- Producing cements in which the major reactive phase is belite (C₂S), thus reducing the CaO content and CO₂ emissions. Strategies to improve the reactivity of C₂S need to be developed for this approach to be viable (Ishida and Mitsuda 1998; Odler 2000). Rapid quenching or incorporation of minor components (e.g., alkalis, chromates) can lead to the formation of the α or α' polymorph of belite, which is more reactive (Fig. 15). It should be noted that the potential savings by this strat-

Table 3. Range of Composition of Common Mineral Additives (adapted from Odler 2000)

Oxide	Granulated Blast Furnace Slag	Fly Ash (Low Lime)	Fly Ash (High Lime)	Silica Fume
SiO ₂	27-40	34-60	25-40	85-98
Al_2O_3	5-33	17-30	8-17	0-3
Fe ₂ O ₃	<1	2-25	5 - 10	0 - 8
CaO	30-50	1 - 10	10-38	<1
MgO	1 - 21	1-3	1-3	0-3
SO3	—	1-3	1-5	
$Na_2O + K_2O$	<1	<1	0-3	1-5
С	—	<5	<5	0-4

egy are significant but not drastic, in the range of 20%.

- Cements based on combinations of sulfoaluminates and calcium silicates. In these compositions the clinkering temperature can be reduced significantly, and the hydraulic properties are generated not only by reactive C_2S but also by various types of sulfoaluminates. Cements produced in this way can also be adjusted to achieve early strength and expansion for self-stressing (Odler 2000).
- Activation of slags by alkalis, an approach that has been used in Eastern Europe.
- Blends of gypsum with calcium silicate phases (Bentur et al. 1994).
- Blended cements consisting of portland cement and a variety of natural pozzolans and supplementary materials such as fly ash. Currently, and for at least the next decade, this is probably the most-effective practical means to deal with environmental considerations, to reduce energy and CO_2 emission, and to use industrial by-products, (Brandstetr et al. 1997). This is dealt with in greater detail in the next section on composite cements.

Composite Cements

Environmental considerations and economic incentives have resulted in considerable use of a variety of minerals—either natural or industrial by-products—as supplements for portland cement. They are added as a component of the cement or can be incorporated directly into the concrete mix. Their content can be quite high, replacing in extreme cases up to 70% of the portland cement. Typical ranges of composition of the most common mineral additives are given in Table 3. The interest in the use of such mineral additives resulted in more detailed specifications in the United States and Europe for blended cements. The range of compositions as specified by the U.S. and European standards are given in Table 4. These minerals additives can be classified in terms of the nature of their reactivity:

- Latent hydraulic minerals that have some self-cementing properties, where a small amount of activator such as portland cement is needed. They consist of glassy (amorphous) calcium aluminosilicates, with the most notable example being granulated blast furnace slag. Metakaolin, which is made of a clay heated to ~700°C, is another example that is receiving attention as a component for producing high-quality concretes.
- Pozzolanic minerals that have no self-cementing properties and require activation by calcium hydroxide. They are made of an amorphous material consisting mainly of SiO₂ and Al₂O₃ with a relatively low content of CaO. Fly ash and silica fume are examples of industrial by-products that are classified in this group.
- Nonreactive minerals that may affect the grindability of the clinker and modify the rheological characteristics and some properties of the mature concrete. Limestone filler, which is added at levels of less than 10%, is included in this category.

There are also trends to develop composite cements consisting of portland cement and more than one mineral additive.

It should be noted that composite cements may be adjusted to have properties superior to those of portland cement, and this has become one of the driving forces for their increased use. Notable examples are improved resistance to sulfate attack and alkaliaggregate reactions for blended cements containing fly ash.

Recycling

Recycling is receiving growing attention in the construction industry in general, and in cement and concrete technology in particular. The major area where recycling is of significant impact is

Take in Diended and Composite Centents weedrank to Chor Standard 15 111 Cove and Datopean Speetheadons Division	Table 4.	Blended and	Composite (Cements	according to	U.S.	Standard ASTM	C595 and	d European	Specifications 1	EN 197
---	----------	-------------	-------------	---------	--------------	------	---------------	----------	------------	------------------	--------

	Name	Portland cement content	Blended minerals
	Portland blast furnace slag	30-75%	Granulated blast furnace slag
	Slag-modified portland cement	>75%	Granulated blast furnace slag
ASTM C595	Portland pozzolan cement	60-85%	Pozzolan
	Pozzolan modified portland cement	>85%	Pozzolan
	Slag cement	<30%	Granulated blast furnace slag
	CEM I portland cement	95-100	Minor additional constituents
EN 197	CEM II ^a	65–94	Blast furnace slag, silica fume, pozzolans (natural or calcined), fly ash, burnt shale, limestone
	CEM III ^b blast furnace cement	5-64	Blast furnace slag
	CEM IV ^c pozzolanic cement	45-89	Silica fume, pozzolans, fly ash
	CEM V ^d composite cement	20-64	Blast furnace slag, pozzolans, fly ash

^aIncludes subclassification depending on type of blended mineral.

^bIncludes subclassification depending on content of slag: 36-65, 66-80, 81-95%.

^cIncludes subclassification depending on content of pozzolans (silica fume+pozzolans+fly ash): 11-35, 36-55%

^dIncludes subclassification depending on content of blended minerals (blast furnace slag+pozzolans+fly ash): 36–60, 62–80%.



Fig. 16. Modes of recycling concrete wastes and their contents in Japan in 1992 (after Uchikawa 2000)

obviously in the use of industrial by-products such as fly ash and blast furnace slag as components in blended and composite cements and as direct additions to the concrete.

A second developing area of recycling is that of the concrete itself, where two direct sources can be identified: concrete wastes discharged in the manufacturing process, and dismantling of old concrete structures (Tomasawa and Noguchi 1996; Chandra 1997; Hendriks et al. 1998; Hendriks 2000; Uchikawa 2000). A schematic presentation of the wastes and their use in Japan is presented in Fig. 16. At this stage, technologies have been developed to use the recycled concretes as a source of aggregate, but this is quite limited in view of the technological difficulties and cost limitations (Dhir et al. 1998).

Special attention is given to the recycling of water in concrete plants, and this is now covered by standards, such as ASTM C94 and PrEN 1008 (Sandrolini and Franzoni 2001).

Long-Term Performance

Issues of long-term performance of concrete and reinforced concrete are receiving greater attention than ever before, due to a variety of causes:

- The ecological and economic constraints result in greater use of marginal aggregates that are more prone to alkaliaggregate attack. This issue is further aggravated by higher contents of alkalis due to environmental restrictions on cement production, leading to the incorporation of a greater content of alkalis in the cement.
- 2. Concrete structural design was driven for many years primarily by considerations of optimization of the structural stability. This led also to the development of more strengthefficient cements, with which higher strength is achieved at the earlier age of 28 days by increasing the alite content and grinding fineness. The result is the use of leaner mixes and loss of reserve for hydration of the cements at later ages. Thus, the more "economic" structures and more "efficient" cements resulted in many instances in design where long-

term performance was unintentionally compromised. In reinforced structures, this is related to such parameters as concrete cover depth and water/cement ratio.

- Societal needs in cold countries resulted in greater use of CaCl₂ for deicing of concrete transportation structures (e.g., highways, bridges), leading to accelerated rates of steel corrosion in concrete.
- Workmanship quality has declined in many instances, resulting in poor finishing of concrete.

This state of affairs resulted in intensive research followed by code developments to address long-term performance as an important component in the design of concrete materials and structures (ACI 1992; Kropp and Hilsdorf 1995; Pigeon and Pleau 1995; Bentur et al. 1997; Hobbs 1998; Schiessel 1998).

A major emphasis has been given to the transport properties of concrete, quantifying mechanisms of diffusion of ions, permeation of fluids, and capillary absorption. On this basis models to predict service life have been developed, most notably for steel corrosion in concrete, as demonstrated in Fig. 17. The models for corrosion of steel in concrete are based on a comprehensive understanding of the electrochemical nature of steel corrosion. Concrete properties required for durability performance and design



Fig. 17. Schematic description of stages and mechanisms involved in corrosion of steel in concrete and estimation of life cycle

Type and level of risk			Maximum w/c	Minimum ^a strength class	Minimum cement content	Minimum air content
No risk	X0		_			
Carbonation-induced corrosion	XC1	Dry/permanently wet	0.65	C20/25	260	—
	XC2	Wet/rarely dry	0.60	C25/30	280	
	XC3	Moderate humidity	0.55	C30/37	280	_
	XC4	Cyclic wet/dry	0.50	C30/37	300	—
Corrosion induced by chlorides	XD1	Moderate humidity	0.55	C30/37	300	_
other than sea water	XD2	Wet/rarely dry	0.55	C30/37	300	
	XD3	Cyclic wet/dry	0.45	C35/45	320	_
Corrosion induced by chlorides	XS1	Airborne salt, no direct contact	0.50	C30/37	300	_
from sea water	XS2	Permanently submerged	0.45	C35/45	320	_
	XS3	Tidal splash and spray zone	0.45	C35/45	340	—
Freeze-thaw attack	XF1	Moderate water saturation, no de-icing salts	0.55	C30/37	300	_
	XF2	Moderate water saturation, with de-icing salts	0.55	C25/30	300	4.0
	XF3	High water saturation, no de-icing salts	0.50	C30/37	320	4.0
	XF4	High water saturation, with de-icing salts	0.45	C30/37	340	4.0
Chemical attack	XA1	Slightly aggressive chemical	0.55	C30/37	300	_
	XA2	Moderately aggressive chemical	0.50	C30/37	320 ^b	_
	XA3	Highly aggressive chemical	0.45	C35/45	360 ^b	_

 Table 5. Classification of Exposure Conditions and Recommended Limiting Values for Concrete Composition and Properties according to EN 206

^aCharacteristic strength grade, cylinder/cube.

^bSulfate resistant cement.

can be found in the literature and have been used to develop codes that are prescriptive in nature. The more modern codes, such as the European one, provide guidelines based on the nature of the aggressive mechanism (Table 5).

Advanced means to provide extensive service life in severe conditions have been developed and are used in practice, such as (1) use of fly ash and other pozzolans to improve chemical resistance; (2) use of low water/binder ratio concretes with extreme resistance to the transport of aggressive species; (3) development of specialty admixtures to deal with specific durability problems, such as inhibitors to stabilize the depassivation film over the steel bars embedded in concrete; and (4) sealing of the concrete by treatments with polymeric and inorganic materials.

In the drive to develop sophisticated means to deal with durability issues, there is sometimes a tendency to overlook the impact of the more conventional influences and of "good practice" in relation to concrete "cover" and concrete "skin," as defined and shown schematically in Fig. 18(a) (Schonlin and Hilsdorf 1987). In the structure itself, deficient curing has a markedly adverse effect on the permeability of the exposed surface of the concrete, while the "core" of the concrete, ~20 mm away from the surface, will remain relatively wet for prolonged periods [Fig. 18(b)]. This highlights the need to address separately the "cover" concrete, which responds to curing quite differently from the "core" concrete. Practices of achieving durable performance cannot rely only on mix design to achieve impermeable concrete cover are required [Fig. 18(c)].

Tools of life cycle cost analysis are being developed to provide a rational approach for the design for durability. The code requirements such as EN 206 are based to a large extent on a life cycle of 50 years. The life cycle cost analysis should provide the de-



Fig. 18. Schematic description of (a) concepts of concrete cover and concrete skin; (b) its moisture state; and (c) influence of curing on permeability gradients

signer with tools to extend beyond the codes and explore the advantage and economy of more stringent requirements than those stated in the codes.

Four major durability issues have been of particular concern and thus have been studied extensively: steel corrosion in concrete (Bentur et al. 1997), freeze-thaw deterioration [e.g., Pigeon and Pleau (1995)], sulfate attack [e.g., Marchand and Skalny (1999)], and alkali-aggregate attack [e.g., Helmuth and Stark (1992)].

The use of high-performance concretes and concretes with a variety of mineral admixtures to meet the durability needs for most of these issues has been advanced considerably. Special additional means and technologies have been developed to deal with steel corrosion and resistance to cold climate.

The mechanisms of corrosion of steel in concrete have been studied extensively. The role of passivation of the steel in the high-pH environment was established in conjunction with the electrochemical nature of the process in the concrete matrix. Models have been developed to account for the conditions and rates of depassivation and propagation (Fig. 17) and quantify the life cycle and its dependence on concrete cover composition and thickness as well as environmental conditions (chlorides, CO₂, temperature, and humidity conditions). This fundamental knowhow serves as a basis for durability design and development of standards and codes, as well as the advent of sophisticated means to combat steel corrosion in concrete [e.g., Bentur et al. (1991)] such as corrosion-inhibiting admixtures (e.g., calcium nitrite), treatments of the steel surface (e.g., epoxy coating, galvanizing), electrochemical means (e.g., cathodic protection), and special high-performance concretes.

The mechanisms of deterioration of concretes in cold climate, in particular with respect to freeze-thaw effects, have been resolved and quantified in terms of models that serve to predict life cycle and develop means to eliminate the damage associated with such freezing effects as internal microcracking and surface scaling [e.g., Pigeon and Pleau (1995)]. In this context, development of air-entraining admixtures and the accompanying air void spacing factor concept can be considered a breakthrough with an enormous impact on the successful construction of concrete structures in cold zones. Current codes, design practices, and accelerated testing techniques are based on an in-depth understanding of the physical mechanisms associated with freezing of water in the special structure of the cement matrix.

Advanced Cementitious Systems

In recent decades, cementitious systems of advanced performance that can compete with steel and sometimes with ceramics have been developed, and some are even used. A notable example is the use of high-strength concretes in high-rise buildings as the structural material rather than steel. The trends in these systems and the methodologies involved will certainly be guiding us in the next decade and beyond.

The underlying concept in many of the advanced systems is that the basic binder, portland cement, is a commodity and economical material, and advanced performance should be achieved by using it almost as is. This reflects the limitations in producing specialty cements and making them economically available, since economy of scale is an overriding factor in the construction industry. This state of affairs is clearly demonstrated in the decline in availability of special cements such as sulfate resistant (ASTM Type V) and low heat (ASTM Type IV) and the means taken to



Fig. 19. Concept of strength-water/binder relationship and development of concrete strength over time

achieve sulfate resistance and low heat by using normal portland cement (ASTM Type-I) in combination with mineral admixtures.

In view of this state of affairs, the major thrust in development of superior cementitious systems is based on the combination of portland cement with other components tailored specifically for this purpose. This category would include specialty chemical admixtures, fillers to achieve optimal grading, and incorporation of fibers and polymers in cement composites. Often some of these approaches are applied simultaneously to achieve synergistic effects.

High-Strength/High-Performance Systems

The concept of achieving high strength and improved durability by making the concrete highly impermeable has been known for decades and is shown schematically in Fig. 19. This is the w/cconcept laid down by Feret and Abrams years ago. To obtain such concretes of low water/cement ratio, there was a need to address the rheology of the fresh concrete to enable the production of flowing concrete having a low water content with rheological properties that would be adaptable to conventional technologies of production (mixing, pumping, vibrating, and so on).

The key to the solution that enabled the breakthrough into the era of high-strength/high-performance, low water/binder ratio concretes was the combination of effective high-range water reducers and dense packing of the binder, as achieved by incorporation of silica fume [Fig. 9(c)]. Concretes with strength grades of 100 to 150 MPa can be achieved with extremely low diffusivity, orders of magnitude smaller than normal concretes, using normal mixing procedures. They are competing with steel as the structural material in high-rise buildings and in offshore structures where a combination of strength and enhanced durability in a cold marine environment is essential (Nawy 1996; Aitcin 1998; Breitenbucher 1998). The tallest buildings in the world and the deepest offshore structures were built with such concretes.

The conventional high-strength/high-performance concretes are characterized by a water/binder ratio that usually does not go below 0.30. At a lower water/binder ratio, the aggregates become the weakest link in terms of strength, and therefore specialty aggregates such as bauxite need to be used to mobilize the extra strength of the very low water/binder ratio matrix. This is the concept underlying ultra-high-strength systems known as DSP



Fig. 20. Concepts for calculation of flexural strength of fiberreinforced concretes: (a) actual stress distribution of elastic-plastic behavior; and (b) equivalent elastic stress distribution

systems (densified cement/ultrafine particle-based material), where the grading of the cement and microfillers is better controlled (usually with higher contents of silica fume) (Bache 1981).

The issue of grading has thus received a new attention and more fundamental treatment, as well as sophisticated design procedures, which include also the coarser aggregates (Dewar 1999; de Larrard 1999).

The emergence of high-strength concretes of low water/binder ratio matrix resulted in renewed interest in the sensitivity to early age cracking, which is more acute in such concretes. This is associated with combined effects of autogenous shrinkage of the low water/binder ratio matrix and heat liberation induced by the higher binder content characteristic of such concretes. These influences have been studied extensively to predict and model their influence as well as develop innovative means to eliminate them, such as internal curing by lightweight aggregates (e.g., Persson and Fagerlund 1999; Baroghel-Bouny and Aitcin 2000; Kovler and Bentur 2001).

These high-strength concretes possess special workability characteristics associated with their optimal grading, which shows up as improved flow that is not accompanied by segregation. These special characteristics led to the development of selfcompacting concrete in which the slump in a conventional test is over 200 mm (Skarendahl 2001).

Fiber-Reinforced Concretes

Fiber-reinforcement of cementitious materials has its roots in ancient history when straw was used for reinforcement. In modern times the first extensive application of fiber-cement composite was in the asbestos-cement industry, which is now in decline due to health risks associated with asbestos production and use.

In recent decades, fundamental studies have led to the development of specialty fibers that are compatible with the concrete matrix. This compatibility includes composites that are more durable in the highly alkaline cement matrix (such as alkali-resistant glass fibers), fibers that can be more readily mixed uniformly in the concrete (special hydrophilic treatment), and special geometries that allow for enhanced bond by generating anchoring mechanisms (Bentur and Mindess 1990; Balaguru and Shah 1992; Bentur 1998b).

Low contents (0.1% volume) of low-modulus polymeric fibers are used commercially for control of plastic shrinkage cracking (Bentur and Mindess 1990; Balaguru and Shah 1992). Higher contents of steel fibers (0.5 to 1.5% by volume) are used for reinforcement of hardened concrete to replace conventional steel mesh in applications such as slabs on grade and shotcrete (ACI 1999). In mining shotcrete applications, new synthetic fibers have largely replaced steel, at a fiber content of 7 to 9% by volume. The influence of the fibers at this content range is on the postcracking load-bearing capacity, inducing a pseudo-plastic behavior. The flexural resistance of such composites can be calculated based on the concept shown in Fig. 20, and comparative design of fiber-reinforced and steel mesh-reinforced members can be advanced based on this concept.

One of the attractive advantages of the fiber reinforcement concept is the simplification of the construction process by eliminating the need to place a steel mesh. This has led fiber-reinforced concrete to be the dominant technology in shotcreting, replacing mesh-reinforced shotcrete. The fibers used and the mix design are such that conventional concrete production technology and equipment can be used with the fiber-concrete mixes (ACI 1999).

Attention is currently being given to development of the use of high-performance fiber-reinforced cements based on advanced materials and fibers as well as design methods based on micro-mechanical concepts [e.g., Naaman and Reinhardt (1995); Li et al. (1995)]. Special attention is given to synthetic fibers characterized by a geometry of very small diameter filaments (~10 to 40 μ m and less) grouped in a bundled form. The extremely high surface area provides reinforcing efficiency due to inherent high bond, but at the same time they induce difficulties in mixing. These fibers are classified as microfibers (size similar to that of cement grains) in contrast to steel fibers, which are usually of a macro size of 0.1 mm diameter or more. Polymeric macrofibers with complex geometrical shape, similar to steel fibers, are currently being introduced to compete with steel for the reinforcement of hardened concrete.

The current main application of fibers is largely for the purpose of crack control, either in the fresh or hardened state. The control is for cracks induced by environmental loads (humidity and temperature changes) and low-level structural loads, that exist in pavements and concrete linings. Thus, fibers are effective in improving the serviceability of such structures.

Cement-Polymer Composites

Considerable research and development efforts have been directed toward advancing cement-polymer composites using two main concepts: polymer impregnation of the concrete pores, and incorporation of polymer latex dispersions to produce interpenetrating networks of polymer film and hydrated cement (Ohama and Ramachandran 1995).

Impregnation has been considered mainly for production of concrete components of extreme durability performance. The technique can be applied for surface impregnation only (ACI 1997). However, in view of the complexity of the technology (drying of pores, efficient impregnation of monomer, and in situ polymerization) it has not been applied extensively, and the interest in it has somewhat subsided.

The use of cement-polymer latex has gained greater applicability, especially for a variety of mortars intended for coatings, resurfacing, and a variety of repair and adhesive formulations (ACI 1995; 1997). The formation of a polymer film within the mortar improves bond, ductility, flexural strength, and impermeability; it is thus suitable for specialty mortar formulations. A range of polymer latex compositions has been developed that are compatible with the cementitious matrix, giving special attention to the durability of the polymer film in the highly alkaline matrix and elimination of entrainment of air in the fresh mix. The recent trend is for the polymer to be in a powder form, thus enabling the



Fig. 21. Relations between tensile and compressive strength of conventional concretes and newly developed "high-tech" systems VHSC (very-high-strength concretes), DSP&RPC, and NIM&MDF

use of prebagged mixes formulated for different types of applications. This is the basis for many sophisticated products, with some containing in addition to the polymers other additives such as fibers (for coatings and repair) and lightweight aggregates (mortar rendering for thermal insulation).

Cementitious Materials of High Tensile Strength

Cementitious materials, like any typical brittle ceramic, are characterized by a low tensile strength, about one-tenth of the compressive value. This is also true for the high-strength-low water/ binder compositions. This characteristic has a direct impact on construction technology and design, requiring concrete to be used with reinforcing steel. The potential advantages to be gained by drastically changing the ratio between tensile and compressive strength are enormous, and a variety of approaches have been advanced to achieve this purpose (Young 1985).

The simplest approach is to reinforce the cementitious matrix with a relatively large content of high-modulus fibers such as steel: reinforcement at a level of $\sim 1.5\%$ is sufficient to change the behavior from elastic-brittle to elastic-plastic; 10% volume reinforcement will increase tensile strength significantly, severalfold, resulting in a strain-hardening composite. Since such a content cannot be added by simple mixing, special production techniques have been developed such as slurry infiltration into a bed of fibers laid in a mold (SIFCON). Flexural strength values of 50 MPa have been reported (Lankard 1985; Naaman and Homrich 1989). However, the tedious production process and high cost of 10% fibers limit the use of this material to special applications.

A completely different technology was developed in the past two decades, leading to a class of materials known as macrodefect-free (MDF) and new inorganic materials (NIM). They are made of a water soluble polymer [usually PVA (polyvinyl alcohol), poly (acrylamide), or methyl cellulose] and a cement that is either calcium aluminate cement or portland cement (Young 1991). The material requires special processing involving highshear mixing and pressure, resulting in a dough that can be extruded or shaped in similar ways. Compressive and flexural strength values of 300 and 150 MPa, respectively, were reported. Earlier theories attributed these properties to the formation of a material with reduced flaw sizes. Later studies attributed its characteristics to the polymer phase, with the cement component hardly reacting, but serving as a source of Ca ions to cross link the polymers and as a high-quality chemically bonded filler. The material made with calcium aluminate cement is stronger but is sensitive to moisture, which leads to strength reduction and swelling. The complexity of production and the high cost prohibit extensive use of this material in conventional civil engineering applications.

A recent development is an approach based essentially on the combination of a low water/binder matrix of well-graded portland cement and fillers with short fibers, at a content of about 6% by volume. This concept was first advanced by Bache (1981), using a DSP system (cement+silicafume+superplasticizers) with 6% of short steel fibers. The concept was further improved in France, combining in the graded fine material a fraction of graded quartz with particle sizes smaller than 600 µm. The term reactive powder concrete (RPC) was used for this material (Cheyerzy et al. 1995; Richard and Cheyerzy 1995; Bonneau et al. 1997). A modified concept was suggested by Rossi (1997) based on a strategy of using different types of fibers (short and long) with this densified matrix. This material was named HPMFRCC-high-performance multimodal fiber-reinforced cement composite. The water/binder ratio in these materials is in the range of 0.10 to 0.20, with flexural and compressive strengths being 30 to 60 and 170 to 230 MPa, respectively. The components in these systems are less exotic than in the MDF/NIM materials, and the workability is such that they can be produced by conventional technological means. Obviously the material's cost is high (\sim \$700/m³), and it lends itself for application of thin layer components. A recent study by Collepardi et al. (1997) suggests that there is a potential for combining coarse aggregates with RPC matrix while still maintaining many of the superior properties. See Fig. 21 for a comparison of these systems.

The incorporation of special fine aggregate in these systems, such as bauxite and metallic powder, can result in a hardened material with compressive strength as high as 800 MPa. This class of emerging materials is at the cutting edge of concrete technology, and they have been labeled by Aitcin (2000) as high-tech concretes.

Construction with Concrete and Concrete Technology

Much of the review in this paper is centered around concrete as a material and the binder composition. It should be emphasized that the marked advances in the materials aspects are followed by and inspire technological innovations of construction methods and design. Some of these aspects are briefly highlighted here.

The reciprocal relations between the materials and construction technologies are most vividly demonstrated in the case of offshore structures, primarily those intended for oil exploration in the deep seas. The structural and durability needs for offshore structures and the inherent potential advantages of concrete for these purposes were the driving force behind the development of high-strength concrete with improved workability (Nawy 1996).

To facilitate efficient construction, mechanization and automation techniques have been advanced. The improved understanding and control of concrete rheology in the fresh state is frequently a key element in such developments. Slipforming, shotcreting, and roller compaction are examples of techniques allowing rapid and continuous construction in mechanized ways. However, for such methods to be satisfactory there is a need for a special and careful control of concrete rheology. Methods of this kind lend themselves to automation. Robotization, which may be the way of the future, can be more readily adapted for construction with technologies of this kind (Nawy 1997).

A high level of industrialization of the concrete mix production, transportation, and placing has been achieved and is currently the conventional state of the art, using ready-mixed plants, concrete delivery trucks, and on-site pumping. Here too the combination of equipment and control of concrete rheology is a substantial element. Special technologies have been developed for automated finishing, such as screeders and trowlers, which can be readily mechanized and automated.

Technologies for production of concrete members with special properties, in particular high strength and impermeability, were developed to a limited extent. They include preplaced aggregate concrete and vacuum processing. These are of less interest at present because the developments of high-strength-low water/ binder ratio mixes allows the achievement of many of these characteristics using conventional production and placing techniques. Special technologies are applied for underwater concreting, combining methods of operation and control of fresh concrete properties. Antiwashout agents are important elements.

When considering technologies and methods of construction, one should keep in mind that with current concrete properties (and in the foreseeable immediate future), the construction material needed is essentially reinforced concrete. The innovations in prestressing and posttensioning (bonded and unbonded) systems are key achievements. They include the development of new design and application procedures to achieve performance, such as larger spans, technologies for rehabilitation and strengthening of buildings, development of improved tensioning and anchoring technologies, and advanced methods and materials to improve long-term performance (CEB 1992; CEB-FIP 1995; Nawy 2000).

Future Trends

It is very difficult to predict the future, yet some trends can be established, and, perhaps more important, some ideas can be put forward to suggest how we can influence the future. In discussing such trends, a variety of points of view should be addressed:

- Changes and trends that might be predicted by extrapolation of recent developments in cement and concrete technology, as outlined in the sections on sustainability and advanced cementitious systems.
- General trends of development related to economy and society, such as
- Expected increase in world population and urbanization, mainly in developing countries;
- · Growing needs for pollution and waste management; and
- Technological innovation of a generic nature such as information technology and biotechnology. Some of these trends may have direct or indirect effects on cement and concrete technology.

Reference to some of these considerations and their implications to the future of cementitious materials have been the subject of several recent publications, which the present section will draw upon (Mather 1994; Mehta 1994; Neville 1994; ACI 2001). In the following discussion, a classification is made between near-future trends for the next 5 to 10 years and long-term trends beyond that time.

Near-Future Trends

The pressure of ecological constraints and environmental regulations is bound to increase in the coming years. This will lead to continuation of the trend for greater use of supplementary cementitious materials that are in many instances industrial by-products, and seems to be a more viable alternative in the near future than producing special low-energy cements. A complementary alternative that may develop is low-temperature activation of locally available aluminosilicates to be used in combination with portland cement. This trend may change the concept of the cement industry, which may turn from a "portland cement clinker industry" to a "hydraulic binder industry" (Aitcin 2000). The cement will become only one component in a range of fine powders produced and handled by this industry, to be blended and marketed as a variety of products to meet different needs. The fine powders may be industrial by-products as well as such artificial supplementary materials as metakaolin and calcined clay. The end products may serve for production of "normal" concrete as well as speciality "high-tech" binders with controlled composition and particle-size distribution. This versatility might result in binders with a lower content of portland cement as well as portland cement clinker of lower alite (C_3S) and grinding fineness that will be more compatible with the mineral admixtures and high-range water reducers.

The increasing demand to consider durability as a performance criterion as important as strength and structural stability will result in greater use of concretes of low water/binder ratio, which can readily meet both criteria at the same time and may be more efficient than the use of "strong" cements. Cements for low water/binder ratio mixes will have to be adjusted in composition to achieve adequate rheological behavior, in particular compatibility with high-range water-reducing admixtures rather than high-strength (early age and beyond). For this purpose and for the production of high-tech binder, it may be sufficient to relax the requirements for high C_3S content and grinding fines and provide more attention to optimizing the content of sulfate and alkalis (Aitcin 2000).

In order to deal with the need for sustainable construction with cementitious material, a more comprehensive approach will have to be advanced (Hoff 1996; Rostam 1996; Sakai 1996). Concrete technologists, structural designers, and experts in construction management and economics will have to work together more closely. Looking at sustainability from each of the individual points of view, represented by each of these three disciplines individually, is not going to be effective and may even create conflicts. An example pointing toward integration of approaches is the recent establishment of activities to develop life-cycle cost methodologies to address strategies to deal with steel corrosion in concrete. The advent of superior concrete and admixtures to deal with this issue, which has been the thrust in the admixture and concrete industry in the last two decades, will not result in their application unless their advantage in terms of life-cycle cost is established. This is true for prototype evaluation of innovative technologies as well as the use of advanced materials in specific projects.

Aitcin (2000) reflected on this issue by predicting that the trend for BOT (build, own, operate, and transfer) projects may lead to greater use of sophisticated concrete compositions, such as RPC, where the high price of such materials (\sim \$700/m³ for RPC) may not be a deterrent, and if the total cost and life-cycle cost are considered, it may even lead to savings. An example of this kind was cited by Aitcin (2000), demonstrating a cost saving of about 8% for bridge construction with RPC.

Advancing new materials and concepts will require the development of innovative testing techniques. Special attention will have to be given to site tests based on a variety of principles (electrical, electromagnetic, wave propagation, and so on) to assess the internal structure of the concrete. Based on such data, predictions of the transport properties and long-term durability could be made. This is a necessity if alternatives to testing and specification of concrete based on strength only are to be advanced. Such tests and specifications, which are performance related, could pave the way for new and versatile cementitious sys-

tems and combinations that will be tailored for a variety of end uses. The ASTM standard for cements, ASTM C1157, which is a performance standard, is an example.

Long-Term Trends

The impact of environmental considerations has already affected this industry and is bound to continue in a variety of ways by increasing the use of industrial by-products and recycling. However, if drastic changes are to be achieved, one should consider the option of revolutionizing the way in which we use cementitious materials to build structures. This implies developing materials and modes of construction that will drastically reduce the quantities of materials without affecting the performance of the structure. The aim should be for a reduction of the quantities consumed per unit of structure by an order of magnitude. This might be achieved with the development of a new generation of cementitious materials, which will be accompanied by an integrative approach, as outlined below.

Ultra-high-performance cementitious materials with superior tensile strength and ductility can be developed based on the current portland cement composition. Yet the bottleneck for application of these ultra-high-performance materials will be the establishment of innovative construction technologies and design procedures to take advantage of their enhanced properties and consider limitations such as materials cost and processing. The approach that will need to be taken should include structural characteristics as well as constructability, which is becoming an increasingly important issue in view of the rising cost of labor and the scarce availability of skilled professionals on site. This may require the development of concretes with markedly improved rheological properties and self-curing characteristics, as well as new innovative lightweight systems based on cementitious composites with high tensile strength and ductility.

Information technology has its impact on design and production control. However, it should be extended and combined with sensors to develop interactive materials, following ideas and concepts being developed and implemented in other engineering disciplines. Smart buildings are already around, and they may be complemented by smart cementitious materials.

A trend that is currently gaining momentum is the mathematical modeling of the material. This will be enhanced to compile together comprehensive models that will address simultaneously the whole structure on different scales, starting from the material microstructure to the overall behavior under mechanical and environmental loads [e.g., the HYMOSTRUC model—Van Breugel (1995, 1996); (Van Breugel and Lokhorst 2001); CEMY 3D model—Bentz (1997, 1999); Bentz et al. (1995, 1998); DuCON Model—Maekawa et al. (1999)]. The impact from the materials end will be based on the quantitative concepts of hydration and physics of the cementitious systems and their interactions with the mechanics of the system, as expressed in terms of micromechanical concepts and modeling [e.g., Ulm and Coussy (1998)].

Summary and Conclusions

Cementitious materials have been used for thousands of years in a variety of compositions and for a wide range of applications. The level of sophistication in ancient times was quite remarkable and can be attributed to ingenuity based on experience and the learning-by-doing process.

In modern times the development and use of cementitious materials is to a large extent driven by scientific concepts mobilized to push the engineering frontiers. Materials science concepts are routinely applied to develop sophisticated compositions and formulations that can potentially provide performance approaching that of metals and ceramics. A comprehensive approach is consistently being advanced to deal systematically with the cementitious materials and structures in an integrated mode, taking into consideration a variety of aspects such as safety, long-term performance, life-cycle cost. With an integrated approach of this kind, cementitious materials seem to have a competitive advantage for remaining the main construction material well into the new century.

Acknowledgment

The assistance of Ms. Yael Armane in compiling the literature and the bibliographical survey is gratefully appreciated.

References

Aitcin, P.-C. (1998). *High performance concrete*. E & FN Spon, London. Aitcin, P.-C. (2000). " Cements of yesterday and today, concrete of to-

- morrow." Cem. Concr. Res., 30, 1349–1359.
- Alexander, M. G., Arliguie, G., Ballivy, G., Bentur, A., and Marchand, J. (1999). "Engineering and transport properties of the interfacial transition zone in cementitious composites," Report 20, RILEM, Essen, Germany.
- American Concrete Institute (ACI). (1992). "Guide to durable concrete." ACI 201.2R-92, Detroit.
- American Concrete Institute (ACI). (1995). "State of the art report on polymer modified concrete." *Report 584, 3R-95, ACI Manual of Concrete Practice*, Part 5, 1999, Detroit.
- American Concrete Institute (ACI). (1997) ."Guide for the use of polymers in concrete," *Report 548, 1R-97, ACI Manual of Concrete Practice*, Part 5, 1999, Detroit.
- American Concrete Institute (ACI). (1999). "Fiber reinforced shotcrete." Report 506, 1R-98, ACI Manual of Concrete Practice, 1999, Detroit.

American Concrete Institute (2001). "Vision 2030: A vision for the U.S. concrete industry," Concr. Int., 23, 25–34.

- Bache, H. H. (1981). "Densified cement/ultra-fine particle-based materials," 2nd International Conference on Superplasticizers in Concrete, Ottawa.
- Balaguru, P. N., and Shah, S. P. (1992). Fiber reinforced cement composites. McGraw-Hill, New York.
- Baroghel-Bouny, V., and Aitcin, P.-C. (2000). "Shrinkage of concrete: Shrinkage 2000," *Proceedings, PRO 17*, RILEM, Essen, Germany.
- Bazant, Z. P. (1995). "Creep and damage in concrete." 355–390, Materials Science and Concrete—IV, J. Skalny and S. Mindess, eds., American Ceramic Society.
- Beaudoin, J. J., Feldman, R. F., and Tumidajski, P. J. (1994). "Pore structure of hardened portland cement pastes and its influence on properties." Adv. Cem. Res., 8, 163–166.
- Beaupre, D., and Mindess, S. (1998). "Rheology and fresh concrete: Principles, measurement and applications." *Materials science of concrete*—V, American Ceramic Society, J. Skalny and S. Mindess, eds., 149–190.
- Bentur, A. (1998a) "ITZ structure and its influence on engineering and transport properties: Concluding remarks to the conference." A. Katz, A. Bentur, M. Alexander, and G. Arliguie, eds., *The interfacial transition zone in cementitious composites*, E & FN Spon, London, 335– 338.
- Bentur, A. (1998b). "Long-term performance of fiber-reinforced cementitious composites." *Materials science of concrete—V*, American Ceramic Society, 513–536.
- Bentur, A., Diamond S., and Berke, N. S. (1997). *Steel corrosion in concrete*. E & FN Spon, London.

- Bentur, A., Kovler, K., and Goldman, A. (1994). "Gypsum of improved performance using blends with portland cement and silica fume." *Adv. Cem. Res.*, 6, 109–116.
- Bentur, A., and Mindess, S. (1990). Fibre reinforced cementitious composites. Elsevier Applied Science, U.K.
- Bentur, A., et al. (1995). "Fiber-matrix interfaces." in *High performance fiber reinforced composites*, E & FN Spon, London, A. E. Naaman and H. W. Reinhardt, eds. 149–192.
- Bentz, D. P. (1997). "Three-dimensional computer simulation of cement hydration and micro-structure development." J. Am. Ceram. Soc., 80, 3–21.
- Bentz, D. P. (1999). "Modeling cement microstructure: Pixels, particles and property prediction." *Mater. Struct.*, 32, 187–195.
- Bentz, D. P., and Garboczi, E. J. (1999). "Computer modeling of interfacial zone: Microstructure and properties." *Engineering and transport properties of the interfacial zone in cementitious composites*, RILEM, Essen, Germany. M. G. Alexander et al., 349–385.
- Bentz, D. P., Garboczi, E. J., and Lagerren, E. S. (1998). "Multi-scale microstructural modeling of concrete diffusivity: Identification of significant variables." J. Cem., Concr., Aggregates (ASTM), 20, 129– 139.
- Bentz, D. P., Schlangen, E., and Garboczi, E. J. (1995). "Computer simulation of interfacial zone microstructure and its effect on properties of cement based composites." Materials science of concrete—V, American Ceramic Society, J. Skalny and S. Mindess, 155–200.
- Blezard, G. (1998). "The history of calcareous cement." *Lea's chemistry* of cement and conceret, P. C. Hewlett, ed., Arnold, London, 1–18.
- Bonneau, M., Lachemi, M., Dallaire, E., Dugat, J., and Aitchin, P.-C. (1997). "Mechanical properties and durability of two industrial reactive powder concretes." ACI Mater. J., 94, 286–290.
- Brandstetr, J., Havlica, J., and Odler, I. (1997). "Properties and use of solid residue from fluidized bed coal combustion," *Waste materials* used in concrete manufacturing, Noyes, S. Chandra, ed., 1–47.
- Breitenbucher, R. (1998). "Development of applications of highperformance concrete." *Mater. Struct.*, 31, 209–215.
- British Cement Association (1999). Concrete through the ages: From 7000 BC to AD 2000.
- Brown, P. W., Shi, D., and Skalny, J. (1991). "Porosity/permeability relationships." *Materials science of concrete—I*, J. Skalny, ed., American Ceramic Society, 83–110.
- (CEB). (1992). Durable concrete structures: Design guide. Thomas Telford, London.
- (CEB-FIP). (1995). "High performance concrete" CEB, Switzerland.
- Chandra, S., ed. (1997). Waste materials used in concrete manufacturing. Noyes.
- Cheyerzy, M., Maret, V., and Frouin, L. (1995). "Microstructural analysis of RPC (reactive powder concrete)." *Cem. Concr. Res.*, 25, 1491– 1500.
- Collepardi, S., Coppola, L., Troli, R., and Collepardi, M. (1997). "Mechanical properties of modified reactive powder concrete." *Superplasticizers and other chemical admixtures in concrete*, ACI SP-173, V. M. Malhotra, ed., *Admixtures in concrete*, ACI SP-173, American Concrete Institutes, Detroit, 2–21.
- de Larrard, F. (1999). Concrete mixture proportioning. E & FN Spon, London.
- de Larrard, F., and Chang, H. (1996). "The rheology of fresh highperformance concrete." *Cem. Concr. Res.*, 26, 283–294.
- Dewar, J. D. (1999). Computer modeling of concrete mixtures. E & FN Spon, London.
- Dhir, R. K., Henderson, N. A., and Limbachiya, M. C., eds. (1998). "Sustainable construction: Use of recycled concrete aggregate." *Proc., Int. Conf.*, Thomas Telford, London.
- Diamond, S. (1999). "Aspects of concrete porosity revisited." Cem. Concr. Res., 29, 1181–1188.
- Edmeades, R. M., and Hewlett, P. C. (1998). "Cement admixtures." P. C. Hewlett, ed., *Lea's Chemistry of cement and concrete*, Arnold, London, 837–901.
- European Commission (1999). Integrated pollution prevention control: Reference document on best available techniques in the cement and

lime manufacturing industries. Institute for Prospective Technological Studies, Joint Research Center,

- Farran, J. (1956). "Contribution mineralogique a l'etude de l'adherence entre les constituants hydrates des ciments et les materiaux enrobes." *Rev. Mat. Constr.*, 490–491, 155–72.
- Feldman, R. F., and Sereda, P. J. (1968). "A model for hydrated portland cement paste as deduced from sorption length change and mechanical properties." *Mater. Struct.*, 1, 509–520.
- Goldman, A., and Bentur, A. (1994). "Properties of cementitious systems containing silica fume or non-reactive microfillers." Adv. Cem. Based Mater., 1, 209–215.
- Haneharo, S., and Yamada, K. (1999). "Interaction between cement and chemical admixture from the point of cement hydration, adsorption behavior of admixture and paste rheology." *Cem. Concr. Res.*, 29, 1159–1166.
- Hansen, W., and Young, J. F. (1991). "Creep mechanisms in concrete." *Materials science of concrete—I*, J. Skalny, ed., American Ceramic Society, 185–200.
- Helmuth, R., and Stark, D. (1992). "Alkali-silica reactivity mechanisms." *Materials science of concrete—II*, J. Skalny, ed., American Ceramic Society, 131–208.
- Hendriks, C. (2000). *Durable and sustainable construction materials*. Aeneas, The Netherlands.
- Hendriks, C., Pieterson, H. S., and Fraay, A. F. A. (1998). "Recycling of building and demolition waste—An integrated approach." *Sustainable construction: Use of recycled concrete aggregate*, R. K. Dhir et al., eds. 419–431.
- Hewlett, P. C., ed. (1998). Lea's chemistry of cement and concrete. Arnold, U.K.
- Hobbs, D. W., ed. (1998). Minimum requirements for durable concrete. British Cement Association, U.K.
- Hoff, G. C. (1996). "Toward rational design of concrete structures— Integration of structural design and durability design." *Integrated design and environmental issues in concrete technology*, K. Sakai, ed., E & FN Spon, London, 15–30.
- Idorn, M. G. (1997). Concrete progress from antiquity to the third millennium. Thomas Telford, London.
- Ishai, O. (1968). "The time-dependent deformation behavior of cement paste, mortar and concrete." *Proc. Conf. The Structure of Concrete* and Its Behavior under Load, Cement and Concrete Association, London. 345–364.
- Ishida, H., and Mitsuda, T. (1998). "Science and technology of highly reactive β-dicalcium silicate: Preparation, hydration and gels." *Materials science of concrete*—V, J. Skalny and S. Mindess, eds., American Ceramic Society, 1–44.
- Jackson, P. J. (1998). "Portland cement: Classification and manufacture." *Lea's chemistry of cement and concrete*, P. C. Hewlett, eds., Arnolds, 25–94.
- Klemm, W. A. (1989). "Cementitious materials: Historical notes." Materials science of cement and concrete, J. Skalny, ed., 1–26.
- Kovler, A., and Bentur, A. (2001). "Early age cracking in cementitious systems." Proc. RILEM Int. Conf., RILEM, Essen, Germany.
- Kropp, J., and Hilsdorf, H. K., ed. (1995). "Performance criteria for concrete durability." *RILEM Rep.* 12:E & FN Spon, London.
- Lankard, D. R. (1985). "Slurry infiltrated fiber concrete (SIFCON): Properties and applications." "Very high strength cement based materials," *Mat. Res. Soc. Proc.* 42, J. F. Young, Materials Research Society, 277–286.
- Lawrence, C. D. (1998). "The production of low energy cements." *Lea's chemistry of cement and concrete*, P. C. Hewlett, ed., Arnold, London, 421–470.
- Lea, F. M., and Desch, C. H. (1956). Chemistry of cement. Edward Arnold, London.
- Le Chatelier, (1987). Experimental researches on the constitution of hydraulic mortars. English translation—1905, McGraw-Hill, New York.
- Li, V. C., et al. (1995). "Micromechanical models of mechanical response of HPFRCC." *High performance fiber reinforced cement composites 2*, A. E. Naaman and H. W. Reinhardt, eds. E & FN Spon, London, 43–100.

- Macphee, D. E., and Lachowski, E. E. (1998). "Cement components and their phase relations." *Lea's chemistry of cement and concrete*, P. C. Hewlett, ed., Arnold, London, 95–130.
- Maekawa, K., Chaube, R., and Kishi, T. (1999). *Modeling of concrete performance*. E & FN Spon, London.
- Malinowski, R. (1979). "Concrete and mortars in ancient aqueducts." Concr. Int., 1, 66–79.
- Malinowski, R., and Garfinkel, Y. (1991). "Prehistory of concrete." Concr. Int., 13, 62–68.
- Marchand, J., Gerard, B., and Delagrave, A. (1998). "Ion transport mechanisms in cement-based materials." *Materials science of cement* and concrete, J. Skalny and S. Mindess eds., American Ceramic Society, 307–400.
- Marchand, J., and Skalny, J. P. (1999). *Sulfate attack mechanisms*. American Ceramic Society,
- Mather, B. (1994). "Concrete—Year 2000 revisited." in *Concrete Technology: Past, Present and Future*, P. K. Mehta, ed., ACI SP-144, American Concrete Institute, 31–40.
- Mehta, P. K. (1994). "Concrete technology at the crossroads—Problems and opportunities." *Concrete technology: Past, present and future*, P. K. Mehta, ed., *ACI SP-144*, American Concrete Institute, 1–30.
- Mollah, M. Y. A., Adams, W. J., Schennach, R., and Cocke, D. L. (2000). "A review of cement—Superplasticizer interactions and their models." Adv. Cem. Res., 12, 153–161.
- Naaman, A. E., and Homrich, J. R. (1989). "Tensile stress-strain properties of SIFCON." J. Am. Concr. Inst., 86, 244–251.
- Naaman, A. E., and Reinhardt, H. W. (1995). High performance fiber reinforced cement composites 2 (HPFRCC 2). E & FN Spon, London.
- Nawy, E. G. (1996). Fundamentals of high strength high performance concrete. Longman Group, U.K.
- Nawy, E. G., ed. (1997). *Concrete construction engineering handbook*. CRC Press, Boca Raton, Fla.
- Nawy, E. G. (2000). *Prestressed concrete: A fundamental approach*. Prentice-Hall, Upper Saddle River, N.J.
- Neville, A. (1994). "Concrete in the year 2000." Advances in concrete technology, V. M. Malhotra, ed., CANMET, Canada. 1–18.
- Nilsson, L.-O. and Ollivier, J.-P. (1999). "Fundamentals of transport properties of cement-based materials and general methods to study transport properties." M. G. Alexander et al., *Engineering and transport properties of the interfacial zone in cementitious composites*, RILEM, Essen, Germany, 131–148.
- Odler, I. (1998). "Hydration, setting and hardening of Portland cement." *Lea's chemistry of cement and concrete*, P. Hewlett, ed., Arnold, London, 241–148.
- Odler, I. (2000). Special inorganic cements. E & FN Spon, London.
- Odler, I., and Skalny, J. (1992). "Potential for the use of fossil fuel combustion by the construction industry." *Materials science of concrete—II*, J. Skalny, ed., American Concrete Society, 319–336.
- Ohama, Y., and Ramachandran, V. S. (1995). "Polymer modified mortar and concrete." *Concrete admixtures handbook*, V. S. Ramachandran ed. Noyes, Park Ridge, N.J., 558–656.
- Ollivier, J. P., Maso, J. C., and Bourdette, B. (1995). "Interfacial transition zone in concrete." *Adv. Cem. Based Mater.*, 2, 20–38.
- Persson, B., and Fagerlund, G., eds., (1999). "Self-desiccation and its importance in concrete technology." *Proc. Int. Seminar*, Lund, Sweden.
- Pigeon, M., and Pleau, R. (1995). Durability of concrete in cold climates. E & FN Spon, London.
- Powers, T. C. (1960). "Physical properties of cement pastes." 577–613. Proc. Symp. Chemistry of Cement, Vol. II, Washington.
- Powers, T. C. (1968), The properties of fresh concrete. Wiley, New York.
- Powers, T. C., and Brownyard, T. L. (1948). "Studies of physical properties of hardened portland cement paste." *Research Department Bulletin No.* 22, Portland Cement Association, Chicago.
- Ramachandran, V. S. (2001). Handbook of analytical techniques in concrete science and technology. Noyes, Park Ridge, N.J.
- Rice, R. W. (1984). "Pores as fracture origins in ceramics." J. Mater. Sci., 19, 895–914.

- Richard, P., and Cheyerzy, M. (1995). "Composition of reactive powder concrete." Cem. Concr. Res., 25, 1501–1511.
- Richardson, I. G. (1999). "The nature of C-S-H in hardened cements." *Cem. Concr. Res.*, 29, 1131–1148.
- Ronen, A., Bentur, A., and Soroka, I. (1991). "A plastered floor from the neolithic village Yiftahel (Israel)." *Paleorient*, 17, 149–155.
- Rossi, R. (1997). "High performance multimodal fiber reinforced cement composites (HPMFRCC): The LCPC experience." J. Am. Concr. Inst., 94, 478–483.
- Rostam, S. (1996). "Service life design for the next century." *Integrated design and environmental issues in concrete technology*, K. Sakai, ed., E & FN Spon, London, 51–67.
- Roy, D. M. (1988). "Relationships between permeability, porosity, diffusion and microstructure of cement pastes, mortar and concrete at different temperatures." *Proc. Symp. on Pore Structure and Permeability* of Cementitious Materials, Materials Research Society, 179–189.
- Sakai, E., and Daimon, M. (1995). "Mechanisms of superplastification." *Materials Science of Concrete—IV*, J. Skalny and S. Mindess, eds. American Ceramic Society, 91–112.
- Sakai, K., ed. (1996). Integrated design and environmental issues in concrete technology. E & FN Spon, London.
- Sandrolini, F., and Franzoni, E. (2001). "Waste wash water recycling in ready-mixed concrete plants." *Cem. Concr. Res.*, 31, 485–489.
- Schiessl, P. (1998). "Durability design strategies for concrete structures under severe conditions." *Concrete under severe conditions*, O. E. Gjorv, K. Sakai, and N. Banthia, eds., E & FN Spon, London, 17–26.
- Schonlin, K., and Hilsdorff, H. (1987). "Evaluation of the effectiveness of concrete in structures." Concrete durability, J. M. Scanlon ed. ACI SP-100, American Concrete Institute, Detroit, 207–226.
- Scrivener, K. L. (1989). "The microstructure of concrete." Materials science of concrete—I, J. Skalny, ed., American Ceramic Society, 127– 162.
- Scrivener, K. L., Bentur, A., and Pratt, P. L. (1988). "Quantitative characterization of the transition zone in high strength concrete." Adv. Cem. Res., 1, 230–237.
- Shah, S. P., et al. (1995). "Toughness characterization and toughening mechanisms." *High performance fiber reinforced cement composites* 2(HPFRC-2), A. E. Naaman and H. W. Reinhardt, eds. E & FN Spon, London, 193–228.
- Shah, S. P., and Ouyang, C. (1992). "Measurement and modeling of fracture processes in concrete," *Materials science in concrete—III*, J. Skalny ed. American Ceramic Society, , 243–270.
- Skalny, J., ed. (1989). Materials science of concrete—I. American Ceramic Society.
- Skalny, J., ed. (1991). Materials science of concrete—II. American Ceramic Society,
- Skalny, J., ed. (1992). Materials science of concrete—III. American Ceramic Society,
- Skalny, J., and Mindess S., eds. (1995). Materials science of concrete— IV. American Ceramic Society.
- Skalny, J., and Mindess, S., eds. (1998). Materials Science of Concrete—V. American Ceramic Society.
- Skarendahl, A. (2001). "Self-compacting concrete: State of the art report." *RILEM Rep. 23, RILEM*, Essen, Germany.
- Snell, L. M., and Snell, B. G. (2000). "The early roots of cement." Concr. Int., 22, 83–84.
- Soroka, I. (1979). Portland cement paste and concrete. MacMillan, New York.
- Struble, L., Xihuang, Ji, and Salenas, G. (1998). "Control of concrete rheology." *Materials science of concrete: The Sidney Diamond symposium*, M. Cohen, S. Mindess, and J. Skalny, eds., American Ceramic Society, 231–245.
- Taylor, H. F. W. (1997). Cement chemistry. 2nd Ed., Thomas Telford, London.
- Tomosawa, F., and Noguchi, T. (1996). "Towards completely recyclable concrete." *Integrated design and environmental issues in concrete technology*, K. Sakai, ed., E & FN Spon, London, 263–272.
- Torroja, E. (1958). The structures of Eduardo Torroja. F. W. Dodge Corporation,

- Uchikawa, H. (2000). "Approaches to the ecologically benign system in cement and concrete industry," J. Mater. Civ. Eng., 12(1), 320-329.
- Ulm, F. J., and Coussy, O. (1998). "Coupling in early-age concrete: From material modeling to structural design." Int. J. Solids Struct., 35, 4295–4311.
- Van Breugel, K. (1995). "Numerical simulation of hydration and microstructural development in hardening cement-based materials. II: Applications." *Cem. Concr. Res.*, 25, 522–530.
- Van Breugel, K. (1996). "Models for prediction of microstructural development in cement-based materials." *Proc. Workshop*, July 1994, NATO ASI series E: Applied Sciences, 304, 91–106.
- Van Breugel, L., and Lokhorst, S. J. (2001). "The role of microstructure development in creep and relaxation of hardening concrete." 245–257 A. Kovler and A. Bentur, "Early age cracking in cementations systems."
- Van Mier, J. G. M. (1997). Fracture processes of concrete—Assessment of material parameters for fracture models. CRC Press, Boca Raton, Fla.
- Van Mier, J. G. M., and Vervurt, A. (1999). "Test methods and modeling for determining the mechanical properties of the ITZ in concrete." "Engineering and transport properties of the interfacial transition

zone in cementitious composites." *Report 20*, M. G. Alexander et al., RILEM, Essen, Germany, 19–52.

- Vitruvius, P. (13 BC). *De Architectura Libra Decem, (Ten Books on Architecture*), English translation by F. Granger, London (1931).
- Wallevik, O. (1998). Rheological measurements on fresh cement paste, mortar and concrete by use of a coaxial cylinder viscometer. Icelandic Building Research Institute, Iceland.
- Wallevik, O., and Gjorv, O. E. (1990). "Development of a coaxial cylinder viscometer for fresh concrete." *Proc. RILEM Colloquium, Properties of Fresh Concrete*, Chapman and Hall, U.K., 213–224.
- Winslow, D., and Diamond, S. (1974). "Specific surface area of hardened portland cement as determined by SAXS." J. Am. Ceram. Soc., 57, 193–197.
- Young, J. F., ed. (1985). "Very high strength cement based materials." Mater. Res. Soc. Symp. Proc. 42, Materials Research Society,
- Young, J. F. (1991). "Macro-defect-free cement: A review," pp. 101–121 in *Mater. Res. Soc. Symp. Proc.*, 179, Materials Research Society,
- Young, J. F., and Sun, G. (2001). Silicate polymerization analysis. Handbook of analytical techniques in concrete science and technology, V. S. Ramachandran, ed. Noyes, Park Ridge, N.J. 629–657.