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NATIONAL RESEARCH COUNCIL

Nonconventional Concrete Technologies

Renewal of the Highway Infrastructure

Committee on Nonconventional Concrete Technologies for Renewal of the Highway Infrastructure National Materials Advisory Board Commission on Engineering and Technical Systems National Research Council

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PREFACE

Preface

In response to the enactment by the U.S. Congress of the Intermodal Surface Transportation Efficiency Act (ISTEA), the Federal Highway Administration (FHWA) requested that the National Research Council (NRC) conduct a study on nonconventional concrete technology for renewal of the highway infrastructure. ISTEA directed the FHWA to initiate a comprehensive, long-range infrastructure research and development (R&D) program. Since current research in the field has tended to concentrate on modifications or refinements of traditional concrete technologies, the Office of Advanced Research of the FHWA requested the NRC undertake this study in order to access the broad expertise in materials science of the National Materials Advisory Board (NMAB) to help identify truly innovative materials and procedures that may not have been previously considered.

The NMAB convened the nine-member Committee on Nonconventional Concrete Technologies for Renewal of the Highway Infrastructure to conduct this study. The objectives of the study were to look beyond near-term developments in concrete technology to identify innovative materials and procedures that have the potential to accelerate the highway construction process, improve the durability of highway pavement and bridges, and enhance their serviceability and longevity under adverse conditions. To ensure that new perspectives on possible future R&D directions were included and that the widest spectrum of fields within materials science was accessed, five distinguished scientists with little previous experience in infrastructural materials R&D were named to the committee. Their expertise ranges from ceramics and biomimetics to metallurgy and geopolymer science. The other four committee members have extensive expertise in conventional concrete technology, structural engineering, or architectural design, and provided an informed perspective on the constraints,

problems, and priorities of infrastructural materials R&D as well as background information on current R&D programs.

The committee defined the idea of designing "nonconventional concrete" as taking current knowledge and experience about concrete technology-its service requirements and its limitations-and going "back to the drawing board." The committee believed that by incorporating current ideas and understanding of both advanced structural and natural materials with possible materials-science systems approaches, it would be possible to identify nonconventional technologies with distinct advantages over conventional concrete. The committee did not consider possible nonconventional remediation or repair techniques, since this would have increased the scope of the study tremendously. The committee also did not consider the question of potential increases in initial cost for implementing nonconventional techniques. The committee believed that cost arguments would have detracted from the central objective of the report and would have been beyond the resources and expertise of the committee, since the cost of innovative materials and processes must be viewed within the construct of the total life-cycle of the structure and not simply from the perspective of the lowest cost for original construction.

To access the many disciplines incorporated in materials science and engineering, and compile the ideas and data required for this study, the committee organized a two-day workshop. In addition to the committee, the workshop was attended by twenty individuals with expertise in solid state physics, electrochemistry, metallurgy, ceramics, biological systems, geological systems, microstructural modeling, microwave processing, polymer science, structural engineering, civil engineering, and concrete research and practice. The emphasis of the workshop was on postulating innovative areas of long-term research that have high-payoff potential. The attendance roster for the workshop is presented in Appendix A.

The results of the workshop and the expertise of the committee were then used as the basis for the composition of this report. The report is divided into five chapters. Chapter 1 provides a short tutorial on conventional concrete from both a materials-science perspective and a systems approach perspective. The chapter also discusses the advantages and disadvantages of the current technology and presents the characteristics of an "ideal" concrete. Chapter 2 focuses on the potential methods for manipulating the microstructure and chemistry of the concrete system to improve the processing and properties of the material. Chapter 3 discusses potential nonconventional reinforcement

systems for concrete. Chapter 4 examines concrete processing technologies. Chapter 5 integrates the information presented in the previous chapters to demonstrate the interrelationships among the different components of concrete technology and the importance of the materials-science systems approach to concrete research.

Comments or suggestions that readers of this report wish to make can be sent via Internet electronic mail to nmab@nas.edu or by fax to the NMAB at 202/334-3718.

Carolyn Hansson, Chair

Committee on Nonconventional Concrete Technologies for Renewal of the Highway Infrastructure

Acknowledgments

This study was exciting because it challenged experts in a variety of fields to cross intellectual boundaries and think innovatively about concrete technology. The experts agreed to undertake this challenge for no reason other than their own intellectual curiosity and their desire to aid the development of new infrastructural materials and techniques. The committee is grateful for all the help it received and expresses its thanks to everyone who participated. Without the patience and support provided by many individuals and organizations, this report could never have been completed.

In particular, the committee thanks Herbert A. Franklin of Bechtel Corporation. His support as technical advisor to the committee was invaluable. He provided great insight and made significant contributions to the report. Harold Jabloner of Hercules, Incorporated, and Youjiang Wang of the Georgia Institute of Technology should also receive special thanks for their participation and insight while working with the committee.

The committee is grateful for the dedication of Richard A. Livingston of the Federal Highway Administration for his vision and assistance to the committee. Jeff W. Rish of Wright Laboratories also provided valuable insight.

This study relied heavily on the information collected from a range of materials-science experts at an international workshop that the committee organized. The committee is grateful to all of the participants, who provided the balance of expertise, insight, and originality needed to develop and scrutinize ideas about potentially new and innovative nonconventional concrete technologies. A complete list of workshop participants can be found in Appendix A.

The committee also thanks the staff of the National Materials Advisory Board, particularly Robert M. Ehrenreich, senior program manager, and Pat Williams, senior project assistant. The committee also thanks Bonnie Scarborough, Charles Hach, and Jack Hughes.

Finally, the chair of the committee expresses her appreciation of the study members for their dedication and patience during the course of this study. This report could never have been completed without their diligence and goodwill. However, she would like to specifically note that Robert M. Ehrenreich did a superb job in shepherding the committee through the process of transforming nine independent and willful minds from nine diverse disciplines into a working, focused unit. On a personal note, she is particularly thankful to him and Norbert S. Baer for their support during the course of the study.

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Executive Summary

Conventional Portland cement concrete is a conglomerate of hydraulic (Portland) cement, sand, stone, and water. It was developed approximately 150 years ago to imitate natural stone while providing less labor-intensive methods of shaping building materials (i.e., casting rather than hewing and carving). In materials science and engineering (MSE) terms, conventional concrete is a particulate-strengthened, ceramic-matrix composite material. The sand and stone are the dispersed particles in a multiphase matrix of cement paste. Reinforced concrete can then be considered a "fiber-reinforced" composite, with the rebar acting as the "fiber." One fundamental difference, however, between conventional concrete and other engineering composites is that the composition and properties of the cement paste do not remain constant after processing but vary with time, temperature, and relative humidity. Another issue is the porosity. At normal relative humidities, the pores in concrete are filled with a highly alkaline solution (with pH between approximately 12.5 and 13.8) that can be regarded as a separate phase of the microstructure and plays a major role in determining the strength of the concrete and the durability of the structure.

The dimensions of the different structural features in concrete span 10 orders of magnitude, from nanometer-sized pores and gel "particles"; to rebar reinforcement that can be tens of meters in length; to paste, sand, and stone particles of all sizes in between. Although the performance of concrete is influenced by the properties (e.g., density and porosity) of its sand and stone components, these properties are fixed by nature. Therefore, it is the cement paste in conventional concrete that is the most important MSE-systems component because

its structure and composition can be controlled to modify the properties of the overall material.

Conventional concrete has many advantages over other structural materials: (1) it is the lowest-cost structural material by an order of magnitude; (2) it can be produced from materials found in abundance all over the world, meaning that transportation costs are low; (3) it is a relatively low consumer of power during its production; (4) it is extremely versatile, with essentially the same material being used in both high and low technology constructions; (5) it is more chemically inert than other structural materials; (6) it is resistant to water; (7) it readily lends itself to reinforcement; and (8) it provides good protection for steel (used as reinforcement) because of its high alkalinity.

Unfortunately, conventional concrete also has limitations: (1) its network of capillary pores and microcracks can allow aggressive species (e.g., chlorides) to enter and cause corrosion of steel reinforcement, which in turn causes the concrete to crack and spall; (2) it is degraded by repeated freezing and thawing because of its free-water content; (3) its hydration reaction produces a decrease in volume that results in shrinkage cracking; (4) its setting and strength development processes are difficult to control, making placement, compaction, and curing critical stages in ensuring a durable final product; and (5) it is brittle and must be reinforced to improve mechanical strength and toughness.

As each of these problems has been identified, conventional concrete research and development (R&D) has advanced a new additive to solve it. Although the various chemical and mineral additives solve a specific problem, they may also react with each other to enhance or diminish the value of each, cause new problems, or create a mixture so complex that it is difficult to control and reproduce. It is recognized that significant near-term research is being pursued within the cement and concrete research community.

The objectives of the NRC study that produced this report were to look beyond near-term developments in concrete technology to identify R&D opportunities in innovative, nonconventional materials and processes that have the potential to accelerate the construction process, improve the durability of highway pavement and bridges, and enhance the serviceability and longevity of new construction under adverse conditions. Meeting even one of these three objectives could save billions of dollars in construction and maintenance costs. The U.S. Department of Transportation estimates that the cost of maintaining 1993 highway conditions is \$49.7 billion per year and the cost of improving them is \$65.1 billion per year. For bridges, the cost to maintain 1994 conditions is estimated at \$5.1 billion per year and the cost of improving them at \$8.9 billion per year.

The main thrust of this report is that concrete, as a material as well as the structure created from it, must be viewed not as the simple conglomerate of constituent materials assembled through a sequence of unit processes but as a single integrated system.¹ The committee recognizes that the systems approach inherently requires an interdisciplinary framework. In turn, such a framework requires effective program management to enable and assure resonance of multiple viewpoints (i.e., from the specialized research levels at one end to the applications level at the other). Enhanced performance and reduced life-cycle costs can only be realized from this perspective. The synergies between constituent materials and unit processes must be understood quantitatively and manipulated to improve performance at reduced life-cycle cost. To realize a systems approach to concrete design, the materials and processes must be understood at a level of detail far in excess of the current state of the art.

The following sections of this Executive Summary present conclusions and recommendations developed from a systems-approach perspective that can aid in the development of nonconventional concrete technologies with superior properties. It should be noted that the committee neither attempted to prioritize the conclusions and recommendations presented in this report nor considered the potential increases in initial cost for implementing nonconventional techniques. The committee believed that such considerations would have detracted from the main objective of the report and that the research community would best be served by the presentation of the widest range of innovative ideas without the overlaying of potential cost constraints.

POTENTIAL MATRIX MATERIALS AND THEIR SYNTHESIS

The major conclusion and recommendation of the committee regarding potential matrix materials and their synthesis is that a sustained R&D effort is required to obtain a thorough understanding of the development and behavior of the cement matrix and its

¹Thus, the innovative aspect introduced by the committee is the examination of the effects of these materials on concrete within a systems approach.

microstructure on the atomic and molecular level. The committee believes that such an understanding is the primary path toward the development of more reliable methods to control the micro-, meso-, and macro-morphology of concrete and to produce a nonconventional concrete superior to conventional concrete. This knowledge would require establishing detailed, nonempirical relationships between the microstructures produced by processing methods and the resulting properties and performance of the concrete.

The committee also formulated the following conclusions and recommendations on nonconventional concrete matrix materials and their synthesis:

- The processing of conventional Portland cement can be considered as a reaction of a basic oxide (e.g., CaO) with an acidic monomer (e.g., SiO_2) to form a polymer. Although there are numerous other methods for synthesizing a cementitious material by this approach, very few are sufficiently low-cost or widely enough available for use in roads and bridges. The committee concludes that novel cement materials must be based on one or a combination of the following three strategies: (1) use the next least expensive basic oxides other than CaO to produce the initial acidic monomer (e.g., Na₂O); (2) use the basic calcium oxide and silica in conventional Portland cement in conjunction with recycled or by-product materials that already contain a substantial amount of acidic monomer (e.g., glass, blast-furnace slag, fly ash, silica fume) to reclaim the energy previously invested in producing these materials or to produce different reactions and products; or (3) use basic calcium oxide and silica in conventional Portland cement but refine and control the reaction sequence.
- Theory and experiment have shown that all inorganic gels fall into the same universality class, the fundamental physics of which is independent of the length scale of the internal structure of the gel. The study of large-scale percolation effects involving the interaction of aggregate and the theory of gelation and critical phenomena suggest possible mechanisms of rheology control. The committee recommends that research be pursued on the use of surfactants, surface charge controllers, pH controllers, nucleating agents, and superplasticizers for the manipulation or elimination of gelation and the introduction of new, more stable phases.
- Certain synthetic polymers, cellulose derivatives, and clays absorb large amounts of water. The use of such materials as organic

polymers, wood, paper waste, and swelling clays may have a beneficial effect on the rheology and workability of the concrete and possibly increase its strength at the critical point of the sol-gel transition but with the possible (and potentially detrimental) consequence of requiring a larger proportion of water. The committee recommends that research be conducted on the application of these materials to maintaining more constant hydration reaction conditions.

- Few techniques are currently available to control the temperature of the gel network formation reaction. The temperature of the pour at different stages of the setting process could potentially be maintained at desired levels by the use of sequential endothermic and exothermic side-reactions. The committee recommends that research be pursued on the development of sequential endothermic and exothermic side-reactions to improve the thermal control of the gel network formation reaction.
- The reactive inorganic additives (supplemental cementitious materials [SCMs]; e.g., fly ash, silica fume, and blast-furnace slag) that are being increasingly added to concrete, need to be viewed as integral components of the cement mix rather than as mineral additives. An understanding of the behavior of additives that are aluminum-rich as opposed to those that are aluminum-poor is critical. The committee believes that characterization of the chemistry of SCMs and exploration of their interactions with other matrix components with the goal of exploiting these interactions and consistently improving concrete properties are particularly important areas for further research. The committee also recommends that research be conducted on the possible surface activation by pretreatment of these additives to improve desirable chemical reactivity and physical properties.
- The committee believes that another particularly promising area of research is the possibility of extending the life of steel reinforcement by changing the matrix of the concrete either to maintain reducing conditions at the interface (e.g., the use of oxygen scavengers, such as sulfides, organics, and other agents) or to prevent significant amounts of water from coming in contact with the rebar. Smart matrix passivation exploiting the selective migration of ionic species caused by functional chemical gradients should be explored as an alternative approach to rebar protection.
- The addition of nuclei to conventional Portland cement paste at key points in its synthesis might permit the incubation time of

setting to be controlled, the spatial and temporal homogeneity of the material to be improved, or even the gel phase to be crystallized into more chemically durable phases. The committee recommends that research be undertaken to increase understanding of the linkages among synthesis and processing, structure and composition, properties, and performance in concrete in order to develop such new technologies as crystalline or macromolecular nucleating agents and growth modifiers. Lessons learned from successful synthetic (e.g., metals, ceramics, polymers, and their composites), biological, and geological materials should also be applied to concrete R&D to permit the possible tailoring of microstructures to control properties for specific long-term performance.

REINFORCEMENT AND LAYERED STRUCTURES

The committee recommends that concrete reinforcement R&D focus on an integrated concrete system of component materials, reinforcements, and multiple reinforcing phases. A potential design for a nonconventional concrete system would be a layered structure. Layered concrete structures can be designed for particular functions by stacking and combining material layers with different chemical, structural, or mechanical properties. The internal layers could include:

- visco-elastic materials, to dampen structural vibrations
- shape memory alloys, which can exhibit high damping capacity and might improve earthquake resistance in large constructions (Van Humbeeck et al., 1996)
- foams, porous materials, or three-dimensional woven structures to absorb the energy and stress waves produced by continuous pressure (the materials could also be infiltrated by a liquid medium to provide further dissipation and absorption of energy)
- fiber reinforcements, to bridge, deflect, and arrest crack growth

The committee concludes that such a design approach would have to be based on models of the properties of the constituent materials and the interfaces between these materials, such as:

• thermodynamic and kinetic behavior, including phase transformations and rates of chemical reactions

- · interfacial interactions within the microstructure
- · effects of local damage on structural integrity and durability
- · energy and momentum transfer and dissipation
- · energy absorption capacities and resiliency during service loadings

The committee also believes that a particularly promising area of research that should be pursued concerns the extension of reinforcement lifetime in lowpH, nonconventional concrete technologies by: (1) the application of coatings to protect the rebar, such as sacrificial reducing agents to prevent oxygen from reaching the steel rebar; or (2) the replacement of the carbon-steel rebar with a nondegrading continuous reinforcement, similar to stainless steel or composite materials.

PROCESSING

The committee concluded that processing and net-shape forming capabilities of a nonconventional concrete must at least emulate or exceed the capabilities of conventional concrete. The following issues must be taken into consideration when examining a potential nonconventional concrete process: (1) processing requirements that correspond to new material developments; (2) processing and constructability constraints that influence the success of a construction material; (3) scale-up possibilities to attain acceptable performance and required amounts from novel process plants for expected construction scenarios; (4) robustness and simplicity of the process controls that are needed in a production facility to produce the performance variables and strengths desired; and (5) parameters that influence the placing, finishing, and curing requirements of new concrete material (e.g., flow and workability, resistance to mix separation under a variety of conditions, tolerance of environmental conditions, and the need for and interaction with a range of typical reinforcing materials).

The committee formulated the following conclusions and recommendations concerning the development of nonconventional processing technologies:

• The production processes for nonconventional concrete will involve the selection, preparation, mixing, and delivery of source materials, including the use of cement binders, the mixing or

blending of raw materials in controlled amounts, the delivery of blends either as slurries or dry mixes, and the placement of the mixes, usually as slurries, into forms or machines for final net-shaping. The committee concludes that nonconventional concrete technologies will require higher levels of process control than are currently available and strongly recommends that R&D be undertaken in every aspect of the production process to permit better placement and to optimize the performance and properties of potential nonconventional concretes. The major areas of improved process control include cement feedstock production, cement hydration, concrete mixing, and fiber mixing.

- The committee concludes that quality assurance procedures will be critical during the delivery of a nonconventional concrete from the processing facility and its placement in a precasting yard or construction site. Realistic and routine tests must be available to provide specific information about the material, especially when current experience is superseded by the use of new materials. The committee recommends that R&D should focus on the development of test methodologies that: (1) are seamless throughout the entire process; (2) improve the availability and reliability of the data collected during the production and construction process for use by all parties; (3) ensure the delivery and use of the proper raw concrete or concrete elements; and (4) allow the implementation of model-based design for the concrete system within an MSE-systems approach. Suitable tests are largely unavailable at the present time.
- Concrete is usually placed far from its initial batch mixing location. The committee believes that particularly important is the development of test methods and sensors that will better describe the dynamics of the setting process in continuous fashion from initial batch mixing to transportation to the construction site, pouring and compaction in workforms, and final finishing and curing operations. Although current tests may assure a certain level of quality at placement, the number of variables and parameters tested are so numerous and difficult to quantify that it takes experience and insight to determine why a test failed and how to rectify the deficiency. The committee recommends research into nonconventional continuous processes with the potential of yielding a more consistent product than possible with batch processes. Continuous mixing,

especially on-site, would appear to offer a more consistent product. Real-time monitoring of rheological and chemical properties with the goal of process monitoring and chemical modification is needed to achieve continuous control over the properties of the delivered concrete.

SYSTEMS APPROACH

The committee recommends that future concrete-systems R&D be considered within the context of "model-based design." Model-based design is predicated on the fundamental understanding, at all length scales, of materials and their behavior from the processing of the raw materials to the preparation of the concrete to the setting process to the understanding of its behavior during inservice life. A materials understanding at all length scales means that the behavior of the material is understood quantitatively from the atomic level to the microscopic level to the materials and their processing to be continuously controlled. Model-based design, often called "Smart Processing," relies extensively on a sensor-rich environment to allow computer-controlled adjustments to materials and processing parameters.

The committee concludes that the most fundamental need for realizing a systems approach to concrete and the design of concrete-based structures is more extensive basic knowledge of materials and processes. The physics and chemistry of the gelation process needs to be understood both qualitatively and quantitatively, as do the interactions between cement and aggregate and between cement and reinforcement. The global and local constitutive properties (e.g., mechanical behavior) of the cement, aggregate, reinforcements, and their interfaces also need to be determined. Further work on solution thermodynamics of the relevant hydrate systems and kinetic modeling is also warranted. Without this basic understanding, any significant advance in the science of concrete and its applications will not be forthcoming. Model-based design within the construct of a systems approach will not happen until the fundamental knowledge base is significantly expanded.

The committee recommends that the final product should also be monitored through discrete embedded and/or external sensors. This would allow the formulation of an explicit quantitative understanding of degradation processes that could then be fed back into the model-based design methodology. It would also permit cost-effective, localized repairs before damage accumulation takes the material or structure out of service. The goal is to minimize maintenance costs and maximize in-service time by eliminating routine preventative maintenance.

The committee concludes that the final overarching requirement to implement a model-based design methodology is to view these materials and the derived structures within a total life-cycle cost context. Although the use of sensors and on-line computational tools to adjust materials and processes and to monitor in-service performance is expensive, the use of this approach will greatly increase the life of the material and structure, and thereby potentially reduce total life-cycle costs. For this approach to succeed, the costs of the structure must be viewed from the standpoint of total life-cycle costs and not simply from the perspective of the lowest cost for original construction.

Introduction and Background

This chapter provides an overview of conventional concrete technology from a materials science and engineering (MSE) systems perspective specifically its structure and composition, synthesis and processing, properties, and performance. The advantages and disadvantages of conventional Portlandcement concrete are summarized, and the characteristics of an ideal concrete are discussed.

The focus of the MSE systems approach is the manipulation of the ways that materials are synthesized and processed to control their microstructures at various length scales to achieve certain bulk properties and system performance. The strong interrelationship among synthesis/processing, structure/ composition, properties, and performance is depicted in Figure 1–1 and was the main conclusion of the 1989 NRC report *Materials Science and Engineering for the 1990s*.

The sensitivity of the properties of materials to microstructural changes can be demonstrated by numerous examples with widely varying chemistries (NRC, 1989, 1991). Even in single crystal form, structural nonuniformities like lattice defects (e.g., dopant elements, dislocation, twins, stacking faults, and second-phase precipitates) affect the physical properties of materials (e.g., conductivity, hardness, magnetic susceptibility, and strength). Most materials are used in polycrystalline forms, however, since there are myriad possibilities of modifying their extrinsic physical and chemical properties through the modification of their structures. These modifications may span the entire material structure, from the nanometer to the micrometer to the macro scale.

The MSE systems approach also applies to concrete. The same strong correlation among synthesis/processing, structure/composition,

properties, and performance exists for concrete structures as for any other engineered material.

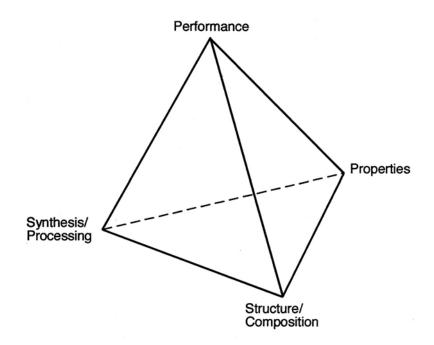


FIGURE 1–1 The interrelationship of the four elements of materials science and engineering: synthesis/processing, structure/composition, properties, and performance. Source: NRC, 1989.

STRUCTURE AND COMPOSITION OF CONVENTIONAL PORTLAND CONCRETE

Conventional concrete is a conglomerate of hydraulic (Portland) cement, sand, stone, and water. It was developed approximately 150 years ago to imitate natural stone while providing less labor-intensive methods of shaping the material (i.e., casting rather than hewing and carving). As such, it was initially expected to resist only compressive loads. As highway systems developed and expanded after World War II, however, concrete started to find new uses in roads and bridges, where it was subjected to tensile-bending stresses as well. A comparison of the mechanical properties of concrete with those of other materials is presented in Figure 1-2.

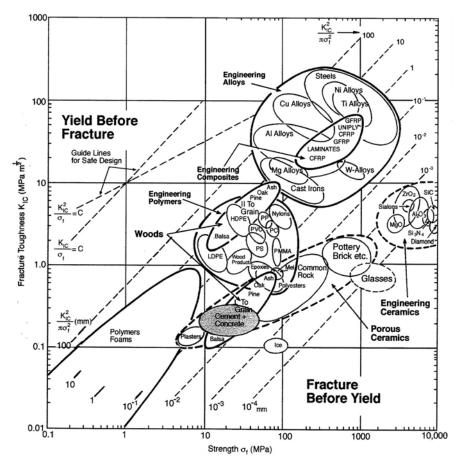
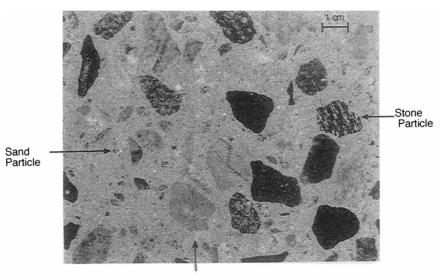


FIGURE 1–2 Fracture toughness versus strength for concrete and other structural materials. Source: Ashby, 1992.

In MSE terms, conventional concrete is a particulate-strengthened, ceramic-matrix-composite material (Figure 1–3). The sand and stone are the dispersed particles in a multiphase matrix of cement paste. Reinforced concrete can then be considered a "fiber-reinforced" composite, with the reinforcing steel bar (rebar) acting as the "fiber." One fundamental difference, however, between conventional concrete and other engineering composites is that the composition; and hence the properties, of the cement paste do not remain constant after processing but vary with time, temperature, and relative humidity. A second difference is concrete's porosity. The pores of concrete are filled with a highly alkaline solution with a pH of between approximately 12.5

and 13.8 at normal relative humidity. This solution can be regarded as a separate phase of the microstructure and plays a major role in determining the strength and durability of concrete.



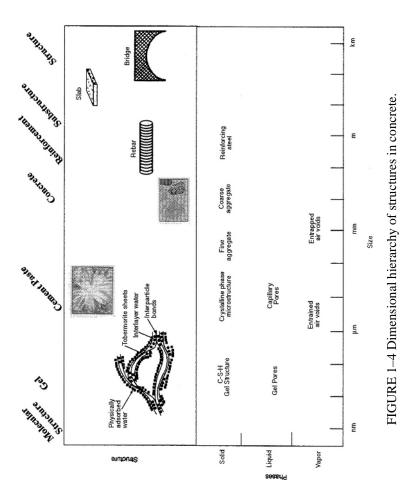
Cement Paste Matrix

FIGURE 1–3 Macrophotograph of plain polished section of concrete showing sand and stone particles in a cement paste matrix. Source: Hansson, 1995.

The dimensions of the different structural features in concrete span 10 orders of magnitude (Figure 1–4), from nanometer-sized pores and gel "particles" to rebar that can be tens of meters in length, and to paste, sand, and stone particles of all sizes in between. Although the performance of concrete is affected by the properties (e.g., density and porosity) of its sand and stone components, these properties are determined by nature. Suitable aggregate must be selected from available sources. Therefore, it is the cement paste in conventional concrete that is the most important MSE systems component because it can potentially be tailored to fit the job.

Cement Paste

Calcined Portland cement consists of several anhydrous oxides, primarily tricalcium silicate (C_3S) and dicalcium silicate (C_2S), with



smaller amounts of tricalcium aluminate (C_3A) and calcium aluminoferrite (C_4AF). Cement also contains small amounts of impurities, such as magnesium, sodium, potassium, and sulfur compounds. The specified composition ranges for Type I Normal Portland cement are given in Table 1–1.

Conventional cement is produced by mixing and grinding proportionate amounts of the raw materials (i.e., limestone or chalk [predominantly calcium carbonate] and clay or shale [predominantly aluminum silicates]) to give a Ca:Si ratio of approximately 3:1. The mixing and grinding were traditionally carried out in a water slurry, but modern cement plants usually use a more energy-efficient dry process that eliminates the need for water evaporation. The constituents are generally represented as a ternary system of CaO+SiO₂+Al₂O₃, with some substitution of iron for aluminum. The ternary phase diagram exhibits a peritectic reaction between Ca₈SiO₅, Ca₂SiO₄, Ca₃Al₂O₆, and liquid at 1455°C (Osborn and Muan, 1964). The addition of Fe₂O₃ to the system results in the formation of a lower melting peritectic eutectic, with the compound 4CaO·Al₂O₃·Fe₂O₃ in equilibrium with the above four phases at 1338 °C (Lea and Parker, 1964). The constituents undergo a partial reactive melting and liquid-phase sintering during subsequent heating to between 1500° C and 1600°C in a rotary kiln. This process results in the formation of "clinker," which consists of hard, shiny globules of C₃S and C₂S that are held together by the peritectic mixture of mostly C₃A and C₄AF. There are two environmental problems associated with this rocess. First, a considerable amount of energy is required to produce the clinker-approximately 1400 and 800 cal/g for the wet and dry processes, respectively. Second, the decomposition of $CaCO_3$ during the process results in

TABLE 1-1 Major Constituents and Composition Ranges of Type I Normal Portland Cement (ACI, Section 225R, 1995)

Composition	Abbreviation	Wt. percent
3CaO·SiO ₂	C ₃ S	42 to 65
$2CaO \cdot SiO_2$	C_2S	10 to 30
$3CaO \cdot Al_2O_3$	C ₃ A	0 to 17
4CaO·l ₂ O ₃ ·Fe ₂ O ₃	C_4AF	6 to 18
Mg, Na, K, and S oxides		Balance
	$\begin{array}{c} 3\text{CaO}\cdot\text{SiO}_2\\ 2\text{CaO}\cdot\text{SiO}_2\\ 3\text{CaO}\cdot\text{Al}_2\text{O}_3\\ 4\text{CaO}\cdot\text{l}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3 \end{array}$	$\begin{array}{ccc} 3\text{CaO}\cdot\text{SiO}_2 & \text{C}_3\text{S} \\ 2\text{CaO}\cdot\text{SiO}_2 & \text{C}_2\text{S} \\ 3\text{CaO}\cdot\text{Al}_2\text{O}_3 & \text{C}_3\text{A} \\ 4\text{CaO}\cdot\text{l}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3 & \text{C}_4\text{AF} \end{array}$

significant CO₂ emissions.¹ The cooled clinker is then ground to the required fineness to produce commercial cement. Other materials are added during this final grinding stage, particularly gypsum (CaSO₄·2H₂O), which controls set time.

When mixed with water, the cement powder hydrates to form cement paste, which is an interconnected or interlocking network of solid and semisolid phases that gives concrete its strength and stability. The rate at which the constituents of clinker react with water varies, as shown schematically in Figure 1–5. The logarithmic time-scale on this diagram should be noted. The reactions start within seconds of the cement being mixed with water but may not reach completion for many years.

Figure 1–5 is a representative diagram and does not take temperature into account. The reactions are exothermic, and the temperature of the concrete is therefore not constant throughout the hydration processes but initially rises and then gradually falls. In massive structures, the temperature can rise in excess of 60°C. If the temperature were constant, this figure could be regarded as an isothermal section of a time-temperature-transformation (TTT) diagram. Unlike the processing of steel, however, there is generally little control of the processing of concrete. Although some newer methods for controlling the curing process are being introduced, particularly for high-performance concrete (e.g., the use of nitrogen or embedded cooling pipes in the structure to cool the aggregates or concrete), temperature control is primarily limited to the use of hot water for mixing in cold weather and the addition of ice to the mixing water in hot weather.

It is often postulated that the initial reaction is "through-solution" in that the reactant solids dissolve in the water, react, and then precipitate as the hydrated product. The reaction is subsequently topochemical (Mehta, 1986), giving rise to the initially rapid and progressively slower hydration process. The topochemical reaction involves the formation of a solid product directly on the surface of the reactant, which then demands either the diffusion of the solid reactant outward to the surface of the forming product or the diffusion of water inwards to the clinker/hydrate interface. Observations of hollow shells of reactant products containing unhydrated clinker, known as "Hadley grains" (Figure 1–6), are cited as evidence for the topochemical reaction.

¹ The CaCO₃ is more thermodynamically stable than the hydrated cement products, which reacts with the CO₂ in the atmosphere to convert again into carbonates.

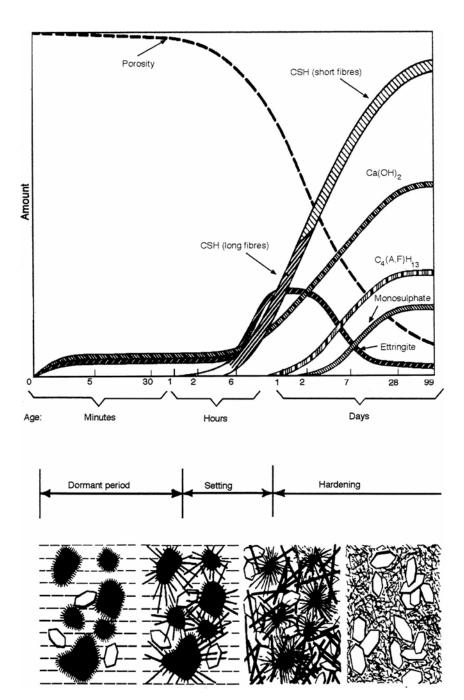


FIGURE 1–5 Phases of cement paste as a function of time after mixing the dry cement clinker with water. Source: Soroka drawing from Locher and Richartz personal communication as printed in Soroka, 1979.

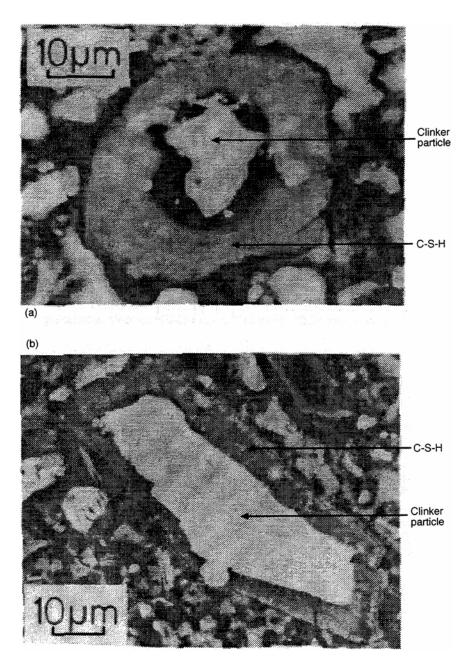


FIGURE 1–6 Partially hydrated clinker particle surrounded by hydrated calcium-silicate-hydrate gel (C-S-H): (a) image of 7-day old conventional Portland cement paste; (b) image of 60-day old conventional Portland cement paste. Source: Scrivener, 1984.

The aluminate phases C_3A and C_4AF are the first components of the clinker to hydrate, and they react with the gypsum (CSH_2) to initially form $C_6AS_3H_{32}$ (ettringite). This is a metastable product, however, which then further reacts to form a monosulfate, C_4ASH_{12} . The calcium sulfoaluminates constitute about 15 to 20 percent of the volume of the paste but do not play a major role in the structure-property relations (Mehta, 1986).

The principal constituent of the paste is calcium-silicate-hydrate (C-S-H), which is 50 to 60 percent by volume of the solids and is formed by the hydration of C_3S and C_2S . C-S-H is largely responsible for the strength and cementing properties of the paste. Calcium hydroxide (CH), a product of the calcium silicate hydration reactions, comprises 20 to 25 percent of the solid volume but does not significantly contribute to the strength of the paste. Moreover, CH is a major reason for the poor acid-resistance of concrete because it has a higher acid-solubility than does C-S-H. On the other hand, CH buffers the pore solution pH to approximately 12.5, a level at which reinforcing steel is readily passivated.

Cement has the fluidity of a slurry when first mixed with water and can easily flow into a formwork. However, as the sulfoaluminates form interlocking crystals and the C-S-H begins to form, the resulting network of solids causes the cement to set (i.e., to transform from a slurry into a stiff mass).² The material has no strength at this stage of hydration and consequently is very friable. As stated above, the length of time required for initial setting is determined by the amount of gypsum present in the clinker. The onset of strength gain ("hardening") occurs only on the formation of C-S-H, which starts some hours after mixing (Figure 1–5).

The water/cement (w/c) ratio is the most important parameter in determining the properties of hardened concrete. A w/c ratio of approximately 0.23 is theoretically needed for complete hydration of the cement components but is not actually sufficient. C-S-H is usually classified in concrete R&D terminology as a "gel" and defined as having "particles" that are extremely small (of micrometer dimensions) and poorly crystalline. Within the gel itself, there are water-filled spaces referred to as "interlayer spaces" or "gel pores." The whole mass is thought to be held together by either van der Waals forces or, more probably, hydrogen bonds. The total volume of water in the gel pores

²In the terminology of the physical chemist, this setting is defined as a "gel."

corresponds to a mass fraction of approximately 0.19, giving a theoretical total w/c ratio requirement for complete hydration of 0.42. It is important to note that this meaning of the word "gel" is different than that used by physical chemists and discussed above.

In practice, however, a w/c of 0.42 is only sufficient if a "water-reducing" chemical admixture is used, because additional water is required to create a workable mix. Thus, w/c ratios of at least 0.50, and often considerably higher, were common until recently, when the negative effects of high w/c ratios on the durability of concrete were recognized. The excess water exists in the large spaces between the cement particles and between the cement and the aggregate that do not become completely filled with gel. These spaces form a network of "capillary pores" with cross-sectional dimensions on the order of micrometers.

Because of the small dimensions of the pores (approximately 0.2 to 3.0 (m) and the polar nature of water molecules, the water is chemisorbed on the gel. Thus, the interlayer water behaves quite differently from both the water of hydration (which is bound by primary chemical bonds) and the water in the capillaries (which can flow freely).

The pore water is a concentrated ionic solution that is saturated in Ca(OH) ₂, contains NaOH, KOH, and soluble sulfates, and has a pH in the range of 12.5 to 13.8. The solution is always in intimate contact with the solid phases of the paste and therefore also contains equilibrium concentrations of the species comprising the solids.

Hydrated cement occupies a smaller volume (by approximately 11 percent) than the sum of the volumes of the dry cement and the added water that becomes chemically bound. Taking into account the presence of the gel pores, the total contraction of theoretically fully hydrated cement with a w/c of 0.42 is approximately 8 percent.³ The contraction due to this volume change is known as chemical or autogenous shrinkage and can result in the development of microcracks. This is aggravated at the surface by the loss of water due to evaporation, resulting in so-called plastic shrinkage because it occurs when the mix is still plastic. As a consequence, cracking at the surface may be particularly severe. In normal concretes, the plastic

³It should be noted that this figure pertains solely to the cement matrix. The shrinkage of a concrete structure is less than one percent, since the cement matrix is only a small volume fraction of the entire concrete mass.

shrinkage is counteracted by bleeding (i.e., the accumulation of water at the surface due to the settling of the solids in the mix).

Macro- and Microstructure

The macro- and microstructures of conventional Portland cement concrete are extremely complex. They are investigated at a variety of scales, from the macro-level of visual inspection to determine the degree of cracking, to analytical methods that include (1) optical microscopy of polished plain sections to determine such data as the distribution of air voids or the amount of bleeding (Figure 1–3); (2) thin-section petrography with polarized light or fluorescent dye impregnation to determine the type of aggregate used, the w/c ratio, or the porosity distribution (Figure 1–7); (3) scanning electron microscopy of plain

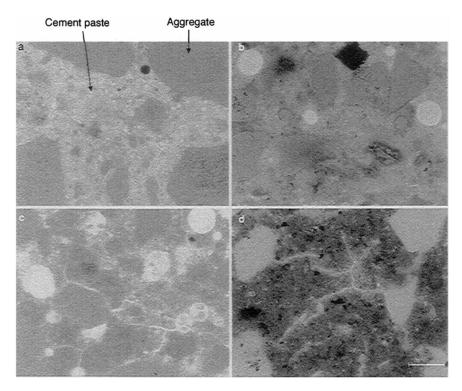


FIGURE 1–7 Fluorescence photograph where shading is an indication of the cement paste porosity (i.e., the lighter the shading of the photograph, the higher the water:cement ratio). The figures show densities corresponding to water:cement ratios of (a) approximately 0.60, (b) approximately 0.50, (c) 0.40 to 0.45, and (d) under 0.40. The scale bar is 120 μ m. Source: Jensen et al., 1985.

polished sections using back-scattered electron imaging techniques to obtain such information as the distribution of phases in the cement paste or the degree of hydration (Figure 1–6); and (4) scanning electron microscopy using secondary electron imaging of free surfaces (Figure 1–8) or fracture surfaces to ascertain the morphology of the phases and understand the hydration processes. At the fine end of the scale, the fractal dimensions and gel porosity of the paste are studied by more sophisticated methods, such as small-angle x-ray or neutron scattering, nuclear magnetic resonance, transmission electron microscopy, and dielectric or impedance measurement. Knowledge of the microstructure of concrete is still fairly limited, however, and requires further research, especially if a MSE systems perspective is ever to be implemented.

Chemical and Mineral Admixtures

In practice, conventional concrete rarely contains only Portland cement, sand, stones, and water. Most concretes also contain one or

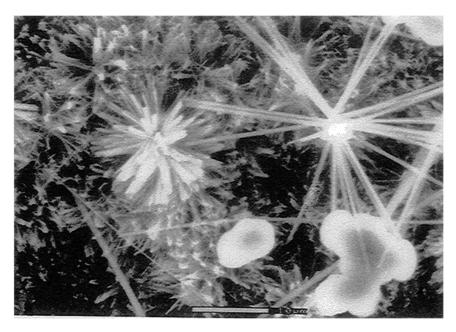


FIGURE 1–8 Secondary electron image taken in an environmental SEM showing long needle-like ettringite crystals and short "chrysanthemum-like" arrays of calcium-silicate-hydrate gel (C-S-H). Source: Hansson, 1995.

more of the following chemical admixtures, which further increase the complexity of the macro- and microstructure.

- Water reducing agents and high-range water reducing agents (also known as plasticizers and superplasticizers) are basically surfactants and allow a workable mix to be produced at low w/c ratios. A low w/c ratio results in incomplete hydration, and the unhydrated clinker particles then act as additional aggregate. The long-term effect of a large fraction of unhydrated clinker on properties—as in new high-performance concretes with a w/c of approximately 0.25—is not yet known. It has been suggested that the volume changes associated with further hydration on exposure to moisture could cause internal cracking. On the other hand, this concern can be counteracted by the anticipation that the unhydrated clinker will allow the autogenous healing of the microcracks formed in the period between setting and hardening. Techniques to enhance this process should be investigated.
- Accelerators are used to increase the rate of hydration, particularly in cold climates. The most effective accelerator is CaCl₂, but chlorides cause corrosion of the steel reinforcement. The use of CaCl₂ is therefore severely limited and controlled. There has been considerable research in recent years to develop nonchloride accelerators that are effective without detrimental secondary effects. Another secondary effect of accelerators is that acceleration of the hydration reaction tends to result in a coarser porosity or a more open microstructure than in nonaccelerated concrete.
- *Retarders* are used in warm climates or in situations where the oncrete must be transported over long distances to ensure that the concrete does not set before being placed and compacted.
- *Air-entraining agents* are used to incorporate a distribution of fine airvoids in the cement-paste phase to provide spaces for the water to expand on freezing, thereby reducing the possibility of internal stress and cracking. The size and distribution of the voids must be such that the distance between any water molecule and the nearest air void is minimal. These parameters determine concrete's degree of resistance to freeze/thaw cracking.
- *Corrosion inhibitors* are added to the concrete to reduce the susceptibility of the reinforcing steel to chloride-induced corrosion. They function either by blocking the pores and hence the diffusion of chlorides from the environment or by increasing the corrosion resistance of the steel itself.

Supplementary cementing-materials (SCMs) or mineral admixtures (e.g., fly ash, silica fume, blast-furnace slag) are also usually added to concrete as partial replacement of the cement. This concrete can be regarded as a repository for these "waste materials," but SCMs can also improve the strength and durability of the concrete if utilized from an MSE systems perspective (see Chapter 2). Fly ash, for example, improves the rheological properties of freshly mixed concrete and therefore reduces the water required for a given slump (workability). Silica fume (fine [$\leq 1.0 \mu m$] amorphous silica), together with a high-range water reducer, significantly reduces the coarse porosity of the cement and the propensity for cracking due to expansive chemical reaction between the cement and certain types of aggregate, known as alkali aggregate reactions. One difficulty with incorporating SCMs into a concrete system is that, as waste materials, their manufacture is not controlled and their chemistries and physical morphologies may vary. Within an MSE systems perspective, however, SCMs would have to be characterized before use to ensure that the proper levels of uniformity and quality are present to achieve the desired effect.

SYNTHESIS AND PROCESSING OF CONVENTIONAL CONCRETE

"Cast-in-place" concrete can be mixed and placed at the construction site or delivered to the site as ready-mixed concrete for placing. Alternatively, concrete can be "pre-cast" under controlled conditions and delivered to the site as finished structural elements. Currently, more than 60 percent of concrete is cast-in-place. Whatever the production site, the quality and proportions of all component materials must be carefully controlled to produce concrete that fulfills specifications. For example, any moisture uptake in the components during storage must be taken into account in determining the amount of water to be added during mixing. Thereafter, the method and duration of mixing, the placing of the concrete in the formwork, the compaction (often by vibration), and the curing play major roles in the quality and durability of the finished product.

PROPERTIES OF CONVENTIONAL CONCRETE

Concrete has traditionally been specified in terms of its compressive strength at 28 days after placement. The rationale was that the stronger

the concrete, the more able it would be to resist forms of attack. It is only within the last 10 to 15 years that it has become recognized that while compressive strength is essential, it is not sufficient to determine durability, and that the majority of failures of concrete structures have nothing to do with the concrete's compressive strength.

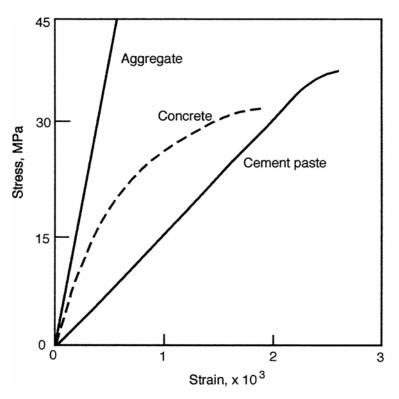


FIGURE 1–9 Typical compressive stress-strain curves for cement paste, concrete, and aggregates. Source: Shah and Winter, 1968.

Although concrete can be regarded as a dispersion-strengthened, ceramicmatrix composite, it is unlike other engineered composites in that its mechanical (and other) properties do not follow the law of mixtures,⁴ as illustrated in Figure 1–9. The reason for this is that the interface between components is the "weak link" in concrete and plays a major role in determining a number of its properties. The paste phase at the aggregates, formwork, or rebar interface is considerably more porous, contains a higher proportion of calcium hydroxide and calcium

⁴Definitions of this and other terms are given in the glossary.

aluminum sulfate hydrates, and has less C-S-H than the rest of the bulk paste. Consequently, this interface provides an easy fracture path and a low-energy route for the diffusion of aggressive species via the pore water, such as chlorides and sulfates. This interface may only be a few tens of micrometers in size in new concrete and becomes negligible after some years. This finding illustrates one of the major problems associated with research on concrete. Most of this research is conducted on young concrete that is cast for this purpose in the laboratory in small quantities and tested for a period of a few years at most. "Labcrete" is generally far more homogeneous than commercially made concrete, which is produced in far larger quantities, is produced in several batches in real structures, and is very heterogeneous because—as every concrete producer knows—it is impossible to reproduce a concrete exactly from one batch to the next, whether in the laboratory, processing plant, or construction site.

PERFORMANCE OF CONVENTIONAL CONCRETE

Although, as stated above, concrete has been almost universally specified on the basis of its compressive strength at 28 days after casting, concrete structures are almost always designed with a sufficiently high safety margin that catastrophic failures due to lack of intrinsic strength (i.e., overload failure) are rare. Failure is usually a gradual deterioration that can be attributed to a lack of "durability," the term used to describe resistance to ambient conditions. Corrosion of the rebar, freeze/thaw damage, salt scaling, alkali aggregate reactions, and sulfate attack can all result in cracking and spalling of the concrete cover.

The performance of concrete is dependent on a number of factors, the predominant ones being its age and the environment to which it is exposed. Because the cement-paste phase continues to harden over the lifetime of a concrete structure, its properties change and generally improve with age (Figure 1–10). Nevertheless, the treatment of the structure in its first few hours can have profound effects on its subsequent durability. Moreover, because of the paste's "liquid phase," cyclic changes in temperature and relative humidity can significantly alter the internal structure of concrete. The most prevalent cause of failure is corrosion of the rebar, despite the fact that the calcium (and sodium and potassium) hydroxide buffers the pore solution. The ability of the cement to protect the steel declines as the alkaline

calcium (and sodium and potassium) hydroxide component reacts with CO_2 to form calcium carbonate, even though the carbonation reaction actually strengthens and hardens the cement "paste."

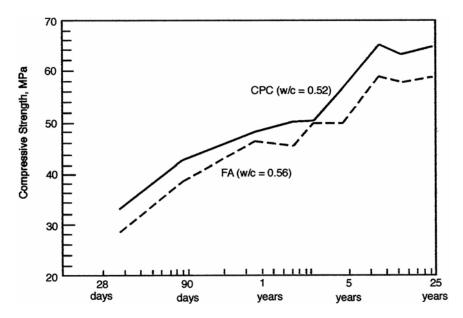


FIGURE 1–10 Compressive strength of conventional Portland cement concrete (CPC) and Portland fly ash cement concrete (FA). Unpublished data from H. Caratin, Ontario Hydro Technologies, 800 Kipling Avenue, KR 252, Toronto, Ontario M87 5S4, Canada.

A more severe problem is chloride-induced corrosion. Chlorides can diffuse through the capillary pore and/or micro-crack network to the rebar, where they cause instability in the passive film on the steel, leading to local film breakdown and corrosion pit formation. The resulting expansive corrosion layer causes cracking in the matrix. Environmental changes are also responsible for other problems: freezing results in expansion of the pore solution and causes internal stressing, while repeated drying and wetting can cause both absorption of undesired species from the environment and leaching of critical components from the concrete. Thus, normal environmental conditions interact with concrete's microstructure to cause the material to deteriorate over time (Figure 1–11, Figure 1–12, Figure 1–13, Figure 1–14, through 1–15).

Concrete structures are failing at an alarmingly increasing rate and at earlier stages of their specified service lives. This can be partly attributed to exposure to increasingly hostile environments (e.g., marine environment, chemical industrial use, and exposure to deicing-salt). Nevertheless, it is becoming increasingly clear that

INTRODUCTION AND BACKGROUND

the predictions of laboratory studies are not being borne out in practice. The extent of the problem is such that finding ways to improve concrete durability has been described as a "multibillion-dollar opportunity" (NRC, 1987). The U.S. Department of Transportation (DOT) estimates that the annual cost to maintain overall 1993 highway conditions is \$49.7 billion and that additional improvements would require an average annual investment of approximately \$65.1 billion. For bridges, the cost to maintain overall 1994 conditions is estimated at \$5.1 billion, and the average annual cost to improve them at \$8.9 billion (DOT, 1995).



FIGURE 1–11 Corrosion of reinforcing steel in the support structure of an elevated highway caused by deicing salts seeping from the deck. The expansion of the corrosion products has caused spalling of the concrete cover. Source: Hansson, 1995.

ASSESSMENT OF CONVENTIONAL CONCRETE TECHNOLOGY

This section summarizes the advantages and disadvantages of conventional concrete technologies.

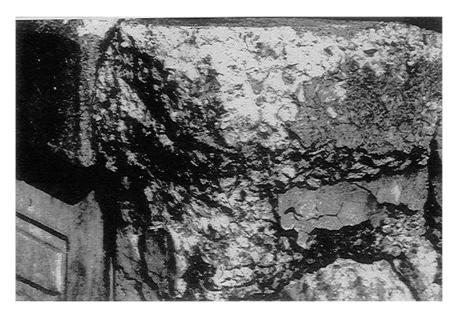


FIGURE 1–12 Spalling of concrete surface caused by repeated freezing and thawing. Courtesy of R.D. Hooton, University of Toronto.

Advantages

The reasons for the widespread use of concrete are manifold:

- Concrete is the lowest-cost structural material by an order of magnitude (roughly 10 cents a kilogram) when compared with other engineered construction materials.
- The raw materials for concrete are available in almost every corner of the world, enabling it to be produced for local markets with minimal transportation cost.
- Concrete is a relatively low consumer of power in its production. The energy contents of unreinforced concrete and steel reinforced concrete are estimated at 450 to 750 and 800 to 3,200 kWh/ton, respectively, whereas the energy content of structural steel is approximately 8,000 kWh/ton.
- Concrete is extremely versatile. It is used in high-tech engineering constructions (e.g., offshore oil platforms, high-rise buildings), low-tech construction (e.g., sidewalk paving), and artworks (e.g., sculpture).
- Concrete is more chemically inert than other structural materials and exhibits excellent resistance to water, making it an

ideal material for such water-control structures as pipelines and dams. Contrary to popular belief, water is not deleterious to plain or reinforced concrete. It is the chemical species dissolved in water (e.g., chlorides, sulfates, and carbon dioxide) that cause deterioration.

- Concrete readily lends itself to reinforcement because it is strong in compression and high in stiffness. Although relatively weak in tension, the tensile strength of concrete can be increased by the use of steel reinforcing bars (rebars).
- Concrete provides good protection for rebar by acting as a physical barrier to the ingress of corrosive species and by supplying chemical protection in the form of a highly alkaline environment. The high level of passivation allows low-quality recycled steel (e.g., black or mild steel) with high levels of impurities to be used.
- Supplementary materials (e.g., fly ash, blast furnace slag, condensed silica fume, rice-husk ash) have been added to concrete in recent years to: (1) reduce raw-material costs, (2) turn waste materials into useful products, and (3) improve the properties of concrete, if added and cured appropriately.

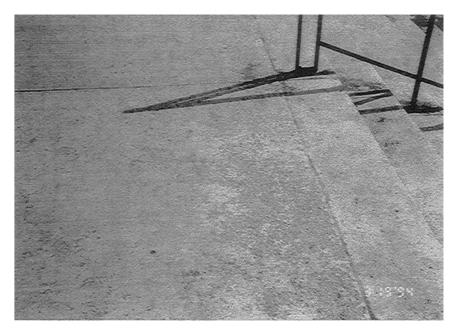


FIGURE 1–13 Salt scaling on concrete steps within six months of being cast caused by the use of deicing salts.



FIGURE 1–14 Cracking in concrete paving caused by an expansive reaction between the aggregate and the alkalis in the cement paste. Source: Hansson, 1995.

Disadvantages

From the microstructural viewpoint, conventional concrete has two main disadvantages. First, the *inherent capillary porosity* of Portland cement allows aggressive species to move into the concrete,

INTRODUCTION AND BACKGROUND

constituents to be leached out, and damage to occur from repeated freezing and thawing of the pore solution. Porosity can be reduced significantly by limiting the w/c ratio, but this results in incomplete hydration, the long-term effects of which are unknown. Second, the reduction in volume during hydration leads to *plastic shrinkage* and microcracking, which can add to the problem of porosity as well as reduce overall strength.

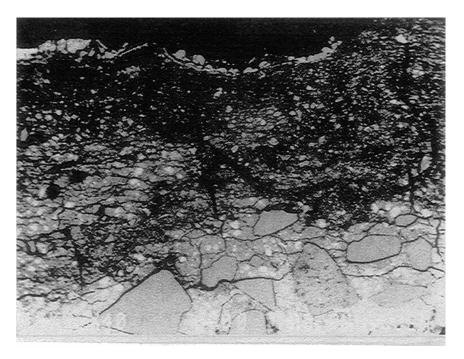


FIGURE 1–15 Backscattered electron SEM image of the surface layers of concrete exposed to 1.5 percent sulfate solution. Source: Crumbie et al., 1989.

From the processing viewpoint, conventional concrete also has two main disadvantages. The first is complexity. The large number of components makes it difficult to replicate mixes exactly and to control homogeneity. The second disadvantage is the temporal separation of the setting and hardening processes. The incubation period before setting is not only desirable but essential to allow for placement and compaction. However, since the setting or stiffening of concrete is largely controlled by the hydration of the aluminate phases and the hardening is produced by the hydration of the more slowly reacting calcium silicate phases, there is a period in which concrete is stiff but unable to bear any load. In this state, it is easily damaged by vibration or unintentional loading. This problem is exacerbated by the use of high-range water reducing agents (superplasticizers), which lengthen the period between setting and the onset of hardening. Many of the problems associated with concrete in practice stem from inadequate curing. It is essential that concrete be prevented from drying out during the early stages of hardening because this leads to inadequate hydration and shrinkage cracking in the surface layers (i.e., in precisely those parts of the structure most susceptible to degradation by salt, ices, sulfates, and so forth).

The chief mechanical weaknesses of conventional concrete are lack of intrinsic toughness and tensile strength. New "high-performance" concretes have compressive strengths far in excess (from two to five times) of conventional concretes, but tensile strengths are not improved in proportion, and the lack of strain capacity can lead to significant amounts of autogenous shrinkage cracks. Moreover, the lack of bleeding in these mixes can lead to severe plastic shrinkage in the absence of appropriate wet curing. Laboratory development of "macro-defect free cements" has shown that lack of toughness and tensile strength can be attributed to the presence of large defects, such as cracks and voids. Elimination of these flaws from normal engineering structures is not practical because of the large scale, however.

The brittle failure of Portland cement concrete structures is prevented by the use of steel reinforcing rods ("rebar") to absorb tensile loads. As mentioned above, however, the steel may corrode if the concrete cover is neutralized by carbonation or if chlorides penetrate it and break down the passive film on the steel. Oxides and hydroxides, the products of the corrosion, occupy a much larger volume than the original metal. Expansion of corrosion products puts the concrete into tension locally, resulting in cracking and spalling. It is often the effects of the production of these corrosion products that limits the life of a structure rather than a reduction in the load-bearing capacity of the rebar itself.

The ability of steel and concrete to work together is also dependent on the bond between the two materials and the joinery details that enable forces to flow through the structures to the ground. The properties of reinforced concrete, whether pre-cast or cast-in-place, are critical to the design of effective joints to divert lateral forces, brittle failure, normal tolerance control, expansion and contraction, and corrosion. These characteristics require a combination of structural design as well as material innovations for optimum performance.

CHARACTERISTICS OF AN IDEAL CONCRETE

Attempts to overcome the disadvantages of conventional concretes have been approached with what might be called a "Band-Aid" philosophy. Solutions to specific problems have been sought without considering the entire structure from an MSE systems perspective. In each case, the solution to a specific problem has been to add another component to the mix, thus increasing its chemical and microstructural complexity. The interaction of all these additives has sometimes created further problems. Consequently, the first priority in the design of the construction material of the future should be to apply an MSE systems approach that takes into account all of the problems to which structures are exposed. This may mean that different material designs will be required for different applications, that the surface layers of a structure may have to be different from the rest of the structure, or that a multilayered structure is needed.

The construction industry has defined some immediate needs for conventional concrete: faster placement with smaller crews, easier forming methods, and faster strength gain to allow earlier stripping of forms. Large projects continue to be planned and executed around the world, and large-scale production would be essential before any nonconventional concrete could find widespread use. Processing performance improvements must also be attainable by the less-sophisticated smaller construction companies, whose huge number of smaller projects demand a wide variety of types of concrete deliveries. New techniques must also be sufficiently flexible to accommodate a wide range of applications in order to limit the number of techniques available and not confound the different users. Processing and netshape forming of a nonconventional concrete material must at least emulate the capabilities of current concrete materials as well as exceed them in as many areas as possible (Table 1–2). The following goals should be given high priority in the design of a "new improved concrete":

• Developing a system in which setting and hardening coincide, as illustrated in Figure 1–16 and Figure 1–17. This would eliminate the current problem of the mix initially being stiff but friable and therefore susceptible to mechanical damage for a considerable period after placement.

	-	
Property	Conventional Concrete	Ideal Concrete
Porosity	Porous	Impermeable as baseline
Weight variations	Heavy	Light as baseline
Workability	Variable with insufficient control	Controlled variability
Chemical resistance	Poor acid resistance but excellent water resistance	Water as well as sulfate and acid resistance
Shrinkage	<1% of total concrete system but causes matrix micro-cracking	Zero as baseline
Frost resistance	Requires air entrainment	Resistant without air entrainment
Fire resistance ^a	Provides good insulation but can be explosive if internal moisture cannot escape	Good insulation and nonexplosive
Wear resistance	Reasonable	High
Consistency of product	Significant inconsistencies between batches	Various levels of strength and rates of strength gain with small coefficients of variation; consistent properties between batches
Field monitoring quality assurance	Slump, density, air-content testing	Continuously controlled mixing, transporting, and placing to achieve targeted performance using advanced sensor technology
Off-line quality assurance	Compressive, flexural tests, air void distribution, water content, cement content	Continuously tested to achieve targeted performance using advanced sensor technology
Source materials	Constituent base materials from widespread regional resources, thus avoiding dependence on geographically limited sources	Same but with increased use of waste materials
Manufacturing flexibility	Choice of locations, including central plant, construction site, remote locations using portable/temporary facilities	Same
Placement methods	Static and moving formwork, extruding machines, mass placement by moving machines, pumping	Same
Placement environments	Variety of environmental conditions, including extremes of temperature and humidity as well as under water	Same
Reinforcement	Metal and rough-surface materials; chemically inert to steel	Good bond to advanced com- posite materials as well as steel
Chemical additives	Too many	Preferably fewer with higher predictability
Labor	Existing labor/skill resources for full-scale processing	Same
"Concrete with low	permeability explodes in fire because	the moisture expands violently o

TABLE 1-2 Notional Comparison of Conventional Concrete with Ideal Concrete

"Concrete with low permeability explodes in fire because the moisture expands violently on evaporation and cannot escape.

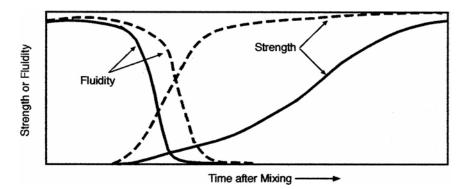


FIGURE 1–16 Decrease in fluidity (setting) and the onset of strength (hardening) as a function of time after mixing. Solid lines indicate the properties of conventional concrete. Dotted lines indicate the desired properties of a nonconventional concrete.

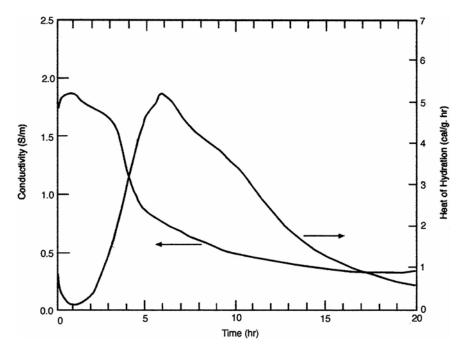


FIGURE 1–17 Electrical conductivity (which is indicative of setting) and heat of hydration (which is indicative of hardening) data for ordinary type I cement pastes. Source: Gorur et al, 1982. Reprinted with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

• Developing a system in which the microstructure—and hence properties —can be manipulated and controlled during processing (as in conventional metallurgy) in order to tailor the properties of the final product to the application.

2

Controlled Synthesis of Potential Matrix Materials and Reactive Additives

This chapter applies the MSE systems methodology to the synthesis of nonconventional concrete matrices. Specifically, this chapter discusses possible means of controlling the synthesis of conventional concrete in order to change its structure, composition, and chemistry to produce nonconventional concrete with superior performance and properties.

The synthesis of conventional Portland cement is basically the reaction of a basic oxide (CaO) with an acidic monomer (SiO_2) to form a polymer. Although there are numerous other methods for synthesizing a cementitious material, very few are sufficiently low-cost or widely available for use in roads and bridges. Novel cement materials therefore must be based on one or a combination of the following strategies: (1) use of the next least expensive basic oxides other than CaO to produce the initial acidic monomer (e.g., Na₂O); (2) use of the basic calcium oxide and silica in conventional Portland cement in conjunction with other materials that contain a substantial amount of acidic monomer to produce different reactions and products; or (3) use of the basic calcium oxide and silica in Portland cement but refining and controlling the reaction. Some possible combinations of these three strategies to produce a nonconventional matrix and potentially resolve some of the shortcomings of conventional concrete matrices are:

• An energy efficient and environmentally benign strategy to produce matrices that incorporate waste materials (e.g., ground glass, blastfurnace slag, fly ash, silica fume) in a manner that permits the energy previously invested in producing these materials to be reclaimed.

- A strategy that refines and controls the reaction to produce a less alkaline matrix that would not readily react with carbon dioxide. Other means of passivating the rebar would have to be found, however, or the matrix would have to be sufficiently impermeable to make passivation of the steel unnecessary. Although attempts to commercialize a new concrete on the basis of this strategy were previously unsuccessful (Henrichsen, 1996), new opportunities may exist that could be exploited.
- A strategy that used sodium oxides to decompose and activate the aluminosilicate materials to form the matrix, thereby reducing the ion exchange problem that occurs between calcium silicate and many sodium compounds. A sodium aluminosilicate gel phase would have to be formed that would resist aqueous attack as well as the calcium silicate phase does.
- A strategy that moderated or controlled the thermal stresses resulting from hydration reactions to reduce the crack density of the matrix and thereby prevent the transport of degradation factors.

Methods for controlling the synthesis of conventional concrete in order to change its structure, composition, and chemistry, and produce nonconventional concretes with superior performance and properties include the addition of agents and reactive inorganic additives to control gelation and rheology, water distribution, concrete shrinkage, temperature fluctuation, and rebar corrosion.

GELATION AND RHEOLOGY CONTROL

Improved methods for controlling the setting process of conventional concrete are essential to producing nonconventional concretes with superior properties and performance.

Theoretical and experimental advances over the past 10 years have shown that virtually all gels fall into the same universality class, which means that the fundamental physics of these gels is independent of the length scale of the gel's internal structure. The concept of universality allows the microscopic behavior of molecules and colloids to be extended to macroscopic systems, such as the sand and stone aggregates. Conventional concrete exhibits rheological behavior similar to gels on both the macroscopic and microscopic scale. The term gel, as used in this section, is a subset of the many materials referred to as gels. In the world of physics, all systems that exhibit the rheological characteristics shown in Figure 1-16 fall into the universality class of gels.

UNIVERSALITY CLASS: A DEFINITION

Universality class is a concept that derives from scaling behavior in the theory of critical phenomena. A percolation threshold is a connectivity critical point at which the distinction between a solid and a liquid vanishes, just as the critical point of water is the point at which the distinction between liquid water and water vapor vanishes. In the case of connectivity, many random structures, such as those of percolation clusters and random walk polymers, exhibit a fractal structure. The mass of an object generally scales as the dimensions raised to some power (e.g., for a sphere, a Euclidean object, the mass scales as the radius to the third power). The mass of a fractal object scales as its dimensions to some power less than that of space in which it is embedded. This fractal relationship means that the structures are described by "dilational symmetry" (i.e., they look the same after doubling or tripling their size). All critical phenomena fall into one or another "universality class," which means that all objects exhibit the same scaling behavior near the critical point, because no matter how big or small, or what an object is made of, all properties that relate to the critical transition will be the same.

These fractal geometry and critical phenomena represent the most important and rigorous mathematical description of random systems that has been developed to date. Slumping is a perfect example. The same principles apply, whether applied to the collapse of a sand pile, the rheology of baking dough, or the slump test of concrete. The length scale in a sandcastle is about the size of a grain of sand and in dough is roughly a particle of flour. A single grain of sand, of course, does not slump as a result of added water, only the pile does. If one were to observe the pile of sand with a magnifying glass, one would not see fractal behavior. Concrete may exhibit fractal behavior over a huge range of length scales because one would see a range of particle sizes with a magnifying glass, in a teaspoonful, a shovelful, and even a truckload of concrete.

The most important consequence of gelation is the sol-gel transition. On the microscopic level, this transition occurs when a random growth process on either a molecular or colloidal scale generates a sol of clusters with a fractal structure. One of the properties of fractal clusters is that their density decreases as their mass increases. In principle, a cluster can become arbitrarily large with an arbitrarily small mass. The sol-gel transition occurs when these fractal clusters get sufficiently large to start to impinge on each other and reach a percolation threshold. The material becomes a solid at this point in the sense that it exhibits elastic, rather than viscous, mechanical properties because the linked fractals are theoretically nondeformable. It is a solid with no strength, however, because there is a relatively small amount of chemical bonding between the solids in the structure. Just after the sol-gel transition, the material is exceedingly fragile. Applied stresses cannot be relieved by viscous flow, and the solid behaves as a brittle material with a very low fracture-toughness. Hence, it cracks easily.

Although this description of the sol-gel transition is based on colloidal gels, the principle of universality and the fact that the mechanical properties of a concrete body are the same as for the colloidal gel mean that a conventional concrete structure will be transformed from a liquid to a very weak, brittle solid at some point. This state in the gelation process (the "set" in concrete terminology, as described in Chapter 1) has two major consequences for the material.

- The material is susceptible to a large amount of damage during placement. As a practical matter, the rheology of the concrete as it is being poured and the gelation and setting during curing are intertwined. Under the large shear stresses associated with pouring and forming, there is no real distinction between a gel that is easily fractured into small pieces and a viscous liquid containing aggregate.
- The material is easily subject to cracking from vibration or unintentional loading in its first few hours that can affect its durability. Although the cracks may be sufficiently small that the aggregate in the concrete can bridge them and prevent significant degradation of the bulk mechanical properties of the structure, the cracks permit the ingress of water, salt, and CO₂, making it more susceptible to chemical degradation.

There are three possible methods to control the synthesis of the concrete matrix to produce a nonconventional concrete that has superior properties and performance:

• *Gelation acceleration.* If gelation could be accelerated after the material has been poured, the opportunity for further damage could be reduced. This acceleration might be achieved by

microwave drying, for example, which has been common in the ceramics industry for some time and more recently been applied to accelerate the setting of cement. Wu et al. (1987) report that 15 to 30 minutes of microwave treatment enhanced the strength and lowered the permeability of the hardened concrete. Hutchison et al. (1991) showed that the induction period for the hydration of cement was reduced by microwave heating. More recently, Johnson (1996) has attempted to quantify such effects.

- Gelation inhibition. If the sol-gel transition of the matrix is delayed, the concrete will remain workable for a longer time with less water, making it less susceptible to cracking during placement. A cement that did not gel like conventional cement would likely have much better and more reproducible properties. It is well known in the laboratory that surfactants retard or suppress gelation. It is no coincidence that the current additives called "high-range water reducers," which can make concrete workable at much lower water-to-cement ratios, are surfactants. Surfactants work by preventing either the formation of fractal clusters or their percolation. In addition to surfactants, there are other possible strategies that could be explored for inhibiting gelation. Sols also gel as a result of changing their surface charge, by changing the pH, by suppressing the effect of repulsive surface charges through the addition of an electrolyte that screens the charge, or through the addition of another sol with an opposite surface charge. One of these approaches could be used to inhibit the gelation of nonconventional concrete.
- Gelation elimination. Although gelation is an important stage in the synthesis of conventional Portland cement, it is by no means obvious that gelation is essential or desirable in a concrete matrix. A potentially rich field of innovative study would be the elimination of gelation and the development of methods in which the matrix would solidify by becoming progressively more viscous, as occurs in glass. Changing the reaction pathway to eliminate gelation may require the use of higher temperatures in the setting process or a significant departure from CaO-SiO₂-Al₂O₃ chemistry.

AGENTS TO CONTROL WATER AND SHRINKAGE

As stated in Chapter 1, hydrated cement has a smaller volume than the sum of the volumes of the dry cement and the water that becomes

chemically bound. This contraction of approximately 8 percent can cause the development of microcracks. The contraction is further aggravated by loss of water through evaporation, causing cracking at the surface of the structure to be even more severe. Potential nonconventional methods for controlling the release of water to maintain more stable conditions during the hydration reaction could help prevent microcracking. Potential methods for water and shrinkage control include the addition of synthetic polymers and cellulose derivatives, wood and paper waste materials, swelling clays, and high-range water reducers. Research into commercial production of shrinkage control agents is currently under way (Henrichsen, 1996; N.S. Berke, personal communication).

Synthetic Polymers and Cellulose Derivatives

Certain synthetic polymers and cellulose derivatives have the ability to absorb large amounts of water and have been used in oilwell cements. Such materials might be of use by releasing water in a controlled manner and thus regulating the temperature cycle and maintaining more constant hydrationreaction conditions, albeit at the expense of increasing the amount of water required for effective processing. They could also prevent water from draining out of forms and have a beneficial effect on the rheology and workability of concrete. Additionally, fibers used for these purposes might increase the strength of the cement during the sol-gel transition and, because they shrink when dry, help to prevent cracking by putting the material in a mildly compressive state. This appears to be an extremely fruitful area for further research. An example of a potentially nonconventional concrete system is given below.

• Considerable research has been conducted on the effects of fiber reinforcement of concrete (Wang, 1996). Virgin polypropylene in the range of 0.5 to 1.0 percent and carpet waste fiber in the range of 1 to 2 percent have been added to concrete to improve performance under tension and enhance crack prevention by reducing the friability of the concrete structure between setting and hardening. Hydrophilic synthetic polymers (e.g., poly[vinyl alcohol] [PVOH], hydroxyethyl cellulose) could also play multiple roles in the setting process by serving as water-control agents, crystal habit modifiers, and sources of organic material for

"fossilization" replacement reactions. PVOH has been shown to play a variety of positive roles in cement and concrete (Wang et al., 1987; Chu et al., 1994; Wang et al., 1994; Robertson, 1995). For steel fiber-reinforced cement bricks, the addition of 1.4 percent PVOH enhanced both bonding strength and frictional resistance. It is postulated that PVOH may coat fiber surfaces, helping to form a dense, fine-grained, ductile, and hydrophilic interfacial layer adjacent to the steel fibers. PVOH also inhibits the nucleation of calcium hydroxide crystals while possibly increasing the nucleation of calcium silicate hydrate. PVOH may also serve a lubricant function, allowing better packing of cement particles around steel fibers. It may also improve the cement–aggregate bond.

Wood and Paper Waste Materials

It may be possible to use sawdust or paper pulp as water-control agents. Shredded newsprint might also help to reduce micro-cracking by acting as a reinforcement—similarly to its role with flour paste in papier maché—and by reducing the friability of concrete between setting and hardening (Lin et al., 1994). These organic materials may also promote a chemically more-reducing environment that could serve to protect the rebar. Recycled paper pulp that is no longer suitable for paper formation is a relatively inexpensive source of organic material.

A potential risk of using organic materials is that they tend to decompose. However, if such materials as wood and waste paper materials can be made to act as source material for "fossilization" replacement reactions, this tendency could actually be beneficial. Fossilized wood results from the reaction of minerals in groundwater with the acidic decay products of cellulose and lignin in the wood. Similarly, sawdust and paper might neutralize, precipitate, and immobilize calcium and silica to create more C-S-H. Since an appreciable amount of free, saturated water occurs in cracks, the mineralization of material in the crack would help to heal it. It may be possible to pretreat sawdust or newsprint to make it more reactive. It may also be possible to post-treat cement with short-fiber pulp from paper recycling.

Swelling Clays

Clays that swell substantially, such as montmorillonite, could also act as water-control agents, possibly modified to hold large amounts

of water in the initial stages of setting and to release water as calcium ions are released into solution, thus deflocculating the clays and shrinking them. This may improve the rheological properties of cement. The clays would then react in the later stages of the setting process to become part of the matrix and ensure a good pre-structure for durability. Although these clays have proven to be unsuitable for conventional concrete, rheological studies have shown that they can counteract self desiccation and increase dispersion of silica fume, for example (Henrichsen, 1995).

High-Range Water Reducers (Superplasticizers)

Water-reducing agents that decrease the usual w/c ratio by 5 to 15 percent are called plasticizers, while those effecting a reduction approaching 30 percent are HRWRs, or superplasticizers. Such agents currently make it possible to produce high-strength concrete, particularly when used in conjunction with silica fume. If the normal w/c ratio is maintained, a "flowing" or self-leveling concrete is produced. The two principal materials used as HRWRs are sodium salts of sulfonated melamine formaldehyde (SMF) condensates and sulfonated naphthalene formaldehyde (SNF) condensates, both of which are anionic linear polymers. Lignosulfonates are also commonly employed. Timing is significant. The greatest effect is achieved if the HRWR is added to the cement a few minutes after mixing (Taylor, 1990).

Recent research, while focusing on the use of HRWRs in conventional concrete, provides an example of how the study of the roles of additives on the molecular level can lead to the production of high-durability concretes and new casting technologies, thus illustrating the benefits of the systems approach. Optical and scanning-electron microscopic examination of rapidly frozen samples suggest that water reduction is achieved by improving the dispersion of the cement grains in water, decreasing or preventing flocculation, and freeing the water normally trapped in the flocs. Factors affecting deflocculation include an increase in the zeta-potential, solid–liquid affinity, and possible steric hindrance (Taylor, 1990). Reviewing the mechanisms of HRWR action, Sakai and Daimon (1995) conclude that dispersion of cement particles is improved by electrical repulsion and steric hindrance effects. They argue that new types of HRWRs will play a significant role in the development of high-strength and high-durability

concretes and in the development of new casting technologies, such as highly flowable concrete.

THERMAL CONTROL AGENTS

The hydration of Portland cement is an exothermic process (Figure 1-17). In large pourings, the heat released can raise temperatures to levels at which unwanted side-reactions occur. Given the large thermal expansion coefficient of water, thermal gradients cause differential expansion during the exothermic setting process and thermal tensile stresses during final cooling, both of which cause stress cracking. Cracking problems are especially severe when the paste is beginning to form a gel network and, as stated above, is effectively a solid but has almost no strength. Cracks are thus easily initiated and do not flow together and heal. The diagram of phase transformation versus time in Figure 1–5 is for a single temperature and does not take into account the above effect. The superposition of temperature on the diagram would be analogous to a TTT diagram for steels.

The water-control agents discussed in the previous section may also help control thermal changes by slowing the rate of hydration and giving more time for the heat generated to dissipate without the development of significant temperature gradients. These water-control agents might also help by maintaining a more constant chemical potential of the water, thus causing the reaction rate and the heat release to be more uniform.

Other potentially innovative methods for controlling the matrix gelation process are by the use of additives that cause endothermic or exothermic sidereactions.

- Components may be introduced that could produce endothermic sidereactions. Pozzolanic or supplementary cementing materials can reduce the total heat of hydration. These side-reactions may absorb heat at the same rate at which it is produced and act as a thermal buffer. They may even be able to reverse and release heat later in the reaction, thus continuing the thermal buffering action.
- An alternative approach to thermal control is to introduce exothermic side-reactions, such as the oxidation of powdered iron. Such side-reactions would maintain the pour at above ambient temperature but would release heat uniformly throughout the

body. These side-reactions could even be designed to react more rapidly at the surface, canceling thermal gradients. Exothermic sidereactions could also be used to make the setting temperature more independent of climate. This reaction would be particularly advantageous in colder weather, resulting in more uniform setting, and possibly could also be used to prevent freezing in cold weather.

REACTIVE INORGANIC ADDITIVES

Many inorganic substances (e.g., fly ash, silica fume, blast-furnace slag) have been incorporated as "additives," or supplemental cementitious materials, in cement mix designs. Some are added as inexpensive extenders, but most are reactive and combine with the Ca(OH)₂ to produce more C-S-H. Although the effects of these additives have been studied by the empirical measurement of the resultant properties of the cement mix, their detailed role in affecting the microstructure is poorly understood. At best, they can actually improve the performance of the concrete (e.g., reduce permeability and refine the microstructure and pore structure) and at their worst do no harm, reduce cost, and utilize what would otherwise be industrial waste.

In a MSE systems approach, these reactive inorganic materials would be considered an integral and important part of the matrix and would be integrated into the chemical design of the cement. Three examples of how these additives would be incorporated within a MSE systems approach are:

 Naturally occurring materials, such as volcanic ash and diatomaceous earth, referred to as "pozzolans," have been used as cement components since Roman times. These materials usually have small particle size and are amorphous. Their beneficial function is to supply additional reactive silica and alumina to the cement paste. The additional silica reacts with the calcium hydroxide component of the cement, producing the more stable C-S-H phase more quickly and facilitating curing. It would also react more slowly than the silica and alumina components of the cement, delaying the sol-to-gel transition. If these materials are also rich in alumina, they can hydrate in an alkaline environment and compensate for excess water.

- Unreacted materials are inherently more durable as vitreous substances than xerogels.¹ By providing acidic oxides, the effective pH of the pore phase would be reduced in a controlled manner rather than by the vagaries of such environmental factors as CO₂ and acid deposition.
- Processes could potentially be developed that would purify and activate these inorganic reactive materials, just as silicate phases are treated with calcium carbonate and "purified" of water and carbonate to create clinker. If close regard were paid to the types of chemical reactions that were desired in the cement, these materials could be activated by an acid treatment (e.g., hot water or steam) that would generate additional reactive acidic silanol groups in their surface layers and remove soluble contaminants, such as sulfates. Other nonconventional reactive components could include colloidal silica and/or alumina or recycled container glass.

As stated in Chapter 1, one difficulty with incorporating SCMs into a concrete system is that, as waste materials, their manufacture is not controlled and their chemistries may vary. Within an MSE systems perspective, SCMs would have to be characterized before use to ensure that the proper levels of uniformity and quality are present to achieve the effects discussed above.

REBAR CORROSION CONTROL AGENTS

The ancillary role that conventional cement plays in passivating the rebar poses some significant challenges for a nonconventional cement. As stated in Chapter 1, the calcium hydroxide component that generates the high-pH conditions and prevents the rebar from corroding also tends to dissolve rather rapidly under natural water conditions. A nonconventional cement matrix that would be more stable than conventional cement would thus require new strategies for rebar passivation. There are four approaches to this problem: (1) employ some other chemical system in the matrix to passivate the rebar;

¹A xerogel is a gel that has dried under near-ambient conditions, in contrast to an aerogel, which is dried under supercritical conditions, or a hydrogel, which is not dried. Whatever their conditions of formation, gels have considerable surface area and porosity that vitreous materials do not.

(2) devise a matrix that prevents external aqueous solutions from coming in contact with the rebar; (3) apply a coating to the rebar placement; or (4) develop a replacement for the rebar that does not degrade in high pH environments.

The first approach would require the development of a matrix with a chemical attribute other than pH to passivate the rebar. Redox reactions could passivate the rebar in a more neutral chemical environment and lead to a far less expansive Fe⁺² oxide coating. Substances such as sulfide ores or blast-furnace slags could create a sufficiently reducing environment to reduce the rate of rebar corrosion. Organic materials (e.g., sawdust, paper pulp, polymers) may also function as reducing agents and limit the rate of rebar corrosion, which is dependent on the availability of oxygen, while helping maintain low pH. Many of these substances have already been discussed as having other roles in the matrix. Clever mechanical and chemical design within an MSE systems approach could exploit this potential synergism. For example, slag can contribute both activated silicates and reducing agents or polymers could be designed to act as both water-control agents and reductants. Of course, only substances that do not themselves produce expansive corrosion products would work. It will also be important to design structures so that these sacrificial agents are not exhausted prematurely or are exhausted at the end of the structure's useful life. A truly nonconventional approach would be to develop a chloride scavenger to prevent the migration of chlorides to the surface of the rebar. Calcium aluminates to some extent act as chloride scavengers.

The second approach would be to develop a nonconventional matrix that would not allow significant amounts of water to come in contact with the rebar. Such a matrix could not have any continuous porosity and could not generate cracks unless they were self-healing. Self-healing could occur if a substance was added that was more soluble in the oxidizing environment of a large open crack than near the rebar. As solutions passed through the crack, the sealing agent would leach out of the matrix and then precipitate in the more reducing environment near the rebar. Conceivably, a "smart " corrosion inhibitor could be developed in which the mobile agent passivated the rebar at the places were it was most exposed to chlorides or, for materials with low pH, to water.

The third and fourth approaches concern changes to the actual reinforcement and thus will be discussed in the next chapter.

EVOLUTION OF STRUCTURE OF CONCRETE

The linkages among the four points of the MSE tetrahedron in Figure 1-1 (i.e., synthesis/processing, structure/composition, properties, and performance) are not understood for conventional cements and concrete but are clearly important. An understanding of these linkages is required if better performing concretes are to be produced. Just as the key to improved metals and ceramics has been the understanding and control of microstructural evolution, so must it be for cements and concrete.

Increased understanding of these linkages might make it possible to develop such new technologies as crystalline or macromolecular nucleating agents. The addition of nuclei to conventional Portland cement at key points in its synthesis might make it possible to control the incubation time of setting, improve the spatial and temporal homogeneity of the material, or crystallize the gel phase into more chemically durable phases. An analogous area of research is biomimetic synthesis.

Biomimetic Synthesis

Biomimetics is the study of biological materials to determine the structure and properties of biocomposites and the organismal strategies in their synthesis in order to apply this knowledge to the formation of novel materials with useful engineering properties. Biological composites are composed of inorganic filler phases that are highly organized and structured inside a macromolecular matrix. Examples include mammalian bones and teeth, mollusk shells, echinoderm skeletal units, and many other biocomposites in which the inorganic phases take the form of structural units with morphological, crystallographic, and geometrical order. The physical and chemical properties of biological composites are orders of magnitude better than any of their synthetic analogs.

The structural control in layered materials is influenced by an organic matrix that acts as a template in the assembly of the inorganic units and the forming of microstructures tailored for specific physical properties. The constituent species of the inorganic phases are fairly simple (e.g., $CaCO_3$), but because the units are highly organized in two- and three-dimensional configurations, the resultant properties are highly isotropic, multifunctional, and specifically designed to

provide the necessary physical properties to the organism that produces it.

Biological hard tissues may provide important lessons for concrete research and development. The constituent phases are simple, easily accessible, and synthesized in ambient aqueous conditions. Thus, novel strategies for the design and synthesis of nonconventional concrete materials could potentially be developed from the study of biological materials. This could include structural design guidelines for multifunctional, functionally gradient, and laminated or three-dimensional micro- and macro-architectures that incorporate smart materials and self-healing concepts. Furthermore, organic macromolecules may be useful as templates in the structure of nonconventional concrete, either as nucleating agents for filler particles and fibers or as growth modifiers to control particle morphology and shape to achieve anisotropic properties.

3

Reinforcement

Concrete is an attractive building material because of its relatively low cost, environmental stability, and high compressive strength. Due to its inherent low tensile strength, however, concrete requires reinforcement in applications where significant tensile stresses will be realized in order to maximize its loadcarrying capability and improve its toughness. Conventional concrete technology utilizes composite theory to optimize the effects of various combinations of matrix materials, graded aggregates, and reinforcement materials (e.g., continuous rebar reinforcement and fiber) on overall performance and properties. This chapter discusses the potential effects of continuous reinforcements, discontinuous-fiber reinforcements, and multiplereinforcing-phase configurations on the properties and performance of nonconventional concrete technologies within an MSE systems context.

Reinforcements may be used in concrete in more than one manner. For example, continuous reinforcements are used in non-prestressed reinforced concrete to improve the load-carrying capability of the structure by providing high tensile strength, while discontinuous reinforcements are added to improve the toughness needed to alter crack paths and cracking mechanisms. A discontinuous consequence of using or non-prestressed continuous reinforcements in concrete is that the concrete must crack before the benefit of the reinforcement can be realized. In addition to compromising the mechanical integrity of the concrete, this cracking can result in exposure of the reinforcement to environmental factors (e.g., water, road salt, etc.) that may corrode the reinforcement phase. In prestressed concrete, however, a continuous reinforcement is placed under tension until the concrete sets, at which

time the reinforcement is secured against the concrete. The tensile stress in the reinforcement develops a counteractive compressive stress in the concrete. The concrete can thus carry loads without cracking until the tensile stress created exceeds the compressive stress produced by the prestressed reinforcement. This configuration utilizes the high compressive strength of concrete more fully. It is evident from these examples that the performance requirements of reinforcements that are prestressed to those that are not. Furthermore, the composition, processing, and properties of the concrete matrix also dictate the requirements of the reinforcement.

PERFORMANCE REQUIREMENTS

Performance requirements are usually defined in terms of the structural elements (concrete plus reinforcement) rather than the property requirements of the individual constituents. Furthermore, the performance requirements of the concrete structural elements vary with application and are frequently dominated by a specification of compressive strength. For example, a residential driveway will typically require a 14 to 21 MPa (2,000 to 3,000 psi) standard concrete without additives. In contrast, a prestressed concrete bridge girder may need 69 MPa (10,000 psi) concrete with special additives for rapid strength gain during processing. High-strength concrete provides reduced creep strain over time and therefore greater prestress retention upon transfer of the jacking forces during production. High-strength concrete also shows improved bond strength with embedded prestressed rebar.

In addition to structural performance requirements, durability and life extension are at the forefront of infrastructure materials concerns. For example, in addition to vertical forces from the bridge support bearings, a bridge abutment may also be subjected to lateral pressures from retained soils and ground water (which may also have a deleterious chemical content), deicing salts, and seasonal temperature and relative humidity fluctuations. These environmental conditions drive the specifications for concrete permeability, reinforcement cover, and possibly reinforcement coatings and alternative reinforcement materials, all of which are aimed at improving the durability of concrete structures.

Translating the property requirements of a concrete structural system into specific reinforcement requirements is a nontrivial exercise. In

general terms, the move towards higher strength concrete in prestressed concrete beams requires the use of higher yield-strength, prestressed continuous reinforcements, and precludes the use of most nonmetallic materials as rebar despite their resistance to corrosion because of their inferior tensile strength and stiffness properties. In fact, higher strength concrete with low permeability may further facilitate the use of metallic rebar by reducing the exposure of such reinforcement to environmental factors. However, in applications where concrete (including high-strength concrete) can crack under service loads, protective coatings or an environmentally resistant reinforcement are needed to improve the durability of the structural system. Improved concrete durability may also require the use of discontinuous reinforcement to provide mechanisms for crack bridging, crack tip blunting, and crack deflection.

CONTINUOUS REINFORCEMENT

The ancillary role that conventional cement plays in passivating the rebar poses some significant challenges in developing a nonconventional concrete. Most of the potential nonconventional matrices discussed in Chapter 2 would require new strategies for rebar stability. Two of the strategies (employing some other chemical system in the matrix to passivate the carbon steel rebar or devising a matrix that would prevent external aqueous solutions from coming in contact with the rebar) were discussed in Chapter 2. This section discusses two alternative approaches for resolving the rebar dilemma: the application of coatings to protect the rebar and the replacement of the carbon steel rebar with a more thermodynamically stable continuous reinforcement.

Coatings for Steel Rebar Reinforcement

If new types of concrete are permeable and/or brittle, and therefore subject to greater microcracking, prestressed and non-prestressed reinforcement materials must possess greater resistance to chloride-induced corrosion than does carbon steel. This implies the use of either a corrosion resistant rebar (e.g., stainless steel) or a corrosion-resistant coating for carbon-steel rebar. The latter must be an impermeable coating that is more resistant to mechanical damage and chemical degradation than those in current use. A matrix with a lower pH would allow the use of metal coatings (e.g., zinc galvanizing), however, since it is the high pH of conventional concrete that dissolves the metal used to protect the steel. Two potential nonconventional coatings for rebar protection are:

- A sacrificial reducing agent, such as newspaper pulp, that would prevent oxygen from reaching the steel rebar. Compressible coatings could also mechanically protect the concrete. In the case of a pulp coating, the expansive corrosion products would have to compress the coating before the matrix was put into tension. However, the problem of bonding (discussed below) would have to be addressed in such a process.
- Polymers that currently cannot readily be recycled as resins may be an economic form of barrier coating. The environmental and performance benefits of polymer disposal in this manner, however, need to be assessed with respect to cost.

A major problem is the efficient transfer of load between the concrete and the reinforcement in both prestressed and non-prestressed concrete elements. Fine finishes do not allow good mechanical interlocking and anchoring. Stainless steel is currently being produced with ribbed surfaces similar to those of carbon steel to ensure good mechanical interlocking and anchoring. Epoxy coatings provide low adhesion between the rebar and the concrete, and reduce anchoring. The anchoring is still generally adequate, however, and any alternative coating would have to provide anchoring that is at least as good as epoxy coated rebar.

Alternative Continuous Reinforcement

An alternative to protecting steel rebar would be the development of a replacement that does not degrade in chloride, neutral, or acid environments. Such a replacement might take the form of either a rigid composite structure, such as a fiber-reinforced plastic composite, or a linear or planar structure, such as a woven-fiber mat. The reinforcement would have to bond sufficiently with the concrete matrix to provide for load transfer, durability, and weatherability regardless of whether it was used as a prestressed or non-prestressed reinforcement. Since tensile stresses are carried by the reinforcement, accurate

placement of a flexible reinforcing structure within the structural element at locations of maximum tensile load would be crucial and may present a significant challenge. For a web-like composite reinforcement structure, the continuity of the concrete would be ensured by the large open spaces of the web. For a dense mat-like composite structure, delamination between the reinforcement and concrete could be a concern. Also, the reinforcement will be exposed to compressive loading as well as shear loads perpendicular to the axis of applied tension, and therefore the structural element must have sufficient compressive strength and stiffness to resist damage from such loading.

Fiber-reinforced plastic composites are characterized by reasonable strength, low density, chemical resistance, and durability, all of which can be tailored to meet performance needs. The resin matrix in a fiber-reinforced plastic composite provides structural continuity, transfers loads among reinforcing fibers, and protects the reinforcement. Important considerations in selecting a resin include chemical, environmental, and thermal stability; mechanical properties; processability; and cost. Many matrix and fiber materials are available, and efforts are underway to assess the cost-effectiveness and life span of these materials. The matrix and fiber materials must be carefully selected and effectively combined within the context of the concrete system to meet performance requirements at reasonable cost.

Two broad categories of polymers that may be used as the matrix phase in fiber-reinforced polymer composites for continuous reinforcement in concrete are thermoplastics and thermosets. Most resins under consideration are thermoset and often belong to one of three common types: epoxy, polyester, or vinyl ester. Each generic type may include numerous variations, depending on the chemistry of the resin and the hardener. A thermoset polymer hardens (cures) due to chemical reaction (cross linking) when the resin is mixed with the hardener and the mixture is heated above certain temperatures. Additives are often used to enhance the properties of resins, such as fire resistance, ultraviolet resistance, temperature resistance, and curing requirements. Since a thermoset composite rebar could not be bent, it must be pre-shaped. Certain textile processes (e.g., braiding, knitting) might be adapted to make jointless reinforcing frames.

Thermoplastics have shown excellent toughness and resistance to most acids, bases, and solvents. Low-cost thermoplastics (e.g., nylon, polypropylene) have been used for making sporting goods and other products. Thermoplastic rebars may be bent into required shapes by thermal forming. As discussed above, however, the bonding of thermoplastics and concrete is expected to be poor, and research on better bonding is necessary (e.g., pultrusion and surface patterning to improve mechanical interlocking and anchoring). In addition, Japanese research indicates that fiber-reinforced plastic composites show excessive deformation under load due to low elastic modulus and high creep (Henrichsen, 1996).

Numerous types of fibers with excellent chemical and environmental resistance (e.g., glass, aramid [Kevlar 49[®]], and carbon fibers) are currently available as the reinforcement phase in composites for various applications. All of the synthetic fibers have lower densities than steel, and some have greater strength. Aramid and carbon fibers also have a much higher specific modulus than steel. However, they are more expensive than steel and are also brittle. E-glass fiber provides high strength and a reasonable modulus and is available at low cost. Although it is not stable in the high pH environment of conventional concrete, E-glass can be used as a reinforcement material in a nonconventional concrete with a low pH matrix. Alternatively, an alkali resistant glass could be used.

For applications requiring a high-modulus reinforcement, there are much more cost-effective options than E-glass. High-strength carbon fiber is the most widely available and provides both high strength and high modulus. It is also moderately priced by composite standards but is much more expensive than carbon steel. High-modulus fiber can provide even higher modulus but is currently unattractive for high-volume applications due to its high cost by concrete standards. Aramid fiber also has good strength and modulus, but its main distinction is its exceptional toughness (Majumdar and Laws, 1991).

DISCONTINUOUS-FIBER REINFORCEMENT

Discontinuous-fiber reinforcement enhances the properties and performance of concrete in two ways: it increases the tensile properties of the material and reduces concrete shrinkage and the associated cracking. By definition, however, discontinuous-fiber reinforcement cannot be used as a prestressed reinforcement phase. In the current state of practice, discontinuous-fiber-reinforced concrete is typically made by adding a small fraction (usually 0.42 percent by volume) of short fibers (typically 5 to 500 mm [0.25 to 2 inches] long) to the concrete during mixing. Common types of fibers that have been used include steel, alkali-resistant glass (Majumdar and Laws, 1991), and

polypropylene (Keer, 1984; Bentur and Mindess, 1990). Fibers range in diameter from < 1 μ m to 500 μ m (0.04 to 20 mils), have tensile strengths on the order of 0.5 to 4 GPa (75 to 580 ksi), and elastic moduli ranging from 5 to 230 GPa (725 to 33,000 ksi; Banthia and Mindess, 1995). Although fiber properties are well defined by the research community, specific parameters are not directly used in the development of improved concrete mix designs for construction projects.

In the fracture process of discontinuous-fiber-reinforced concrete (FRC), fibers bridging the cracks can provide resistance to further crack propagation and expansion before being pulled out or stressed to rupture (Figure 3-1). It has been widely shown that such fiber reinforcement can significantly improve the tensile properties of concrete. Orders of magnitude increases in toughness (energy absorption) over plain concrete have been commonly observed (Keer, 1984; ACI Committee 544, 1986; Wang et al., 1987; Bentur and Mindess, 1990). A significant reduction in the shrinkage and cracking of concrete associated with setting has been observed with discontinuous-fiber reinforcement at fiber-volume fractions as low as 0.1 percent for polypropylene fibers (Fibermesh, 1995). Other benefits include improved fatigue strength, wear resistance, durability, and fire resistance (Moff, 1996). Discontinuousfiber-reinforced concrete is being used in many applications, including buildings, highway overlays, bridges, and airport runways (Keer, 1984; ACI Committee 544, 1986; Bentur and Mindess, 1990). There is also the potential to use discontinuous fibers in place of steel rebar for applications where the goal of reinforcement

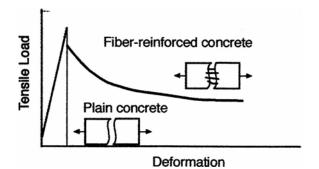


FIGURE 3-1 Tensile load versus deformation for conventional concrete and discontinuous-fiber-reinforced concrete showing the increased resistance to crack propagation and crack opening by the addition of discontinuous fibers. Source: Wang, 1994. is to improve the integrity of the concrete rather than to carry tensile load. One such example would be a pavement slab supported by a relatively stiff foundation. In high load-bearing applications, such as a beam, fibers may be employed together with traditional steel reinforcement for improved reliability (Wang et al., 1994).

For the low volume fraction of high-modulus fibers currently used (i.e., less than 2 percent), the tensile strength of FRC is essentially unaffected. After the peak load produces matrix cracking, however, FRC can carry a significant level of load over a wide range of continued deflection (Figure 3–2). The fibers hold the cracked concrete pieces together, provide a mechanism to blunt crack propagation, and prevent spalling and hole formation. Research is currently being conducted to enhance the understanding of the fundamental mechanisms that control the fracture behavior of discontinuous-fiber-reinforced concrete. Detailed knowledge of these mechanisms may allow the design of discontinuous-fiber-reinforced concrete structures to be optimized.

For some drawn fibers (e.g., polyethylene), the drawing process produces a very smooth surface that does not allow mechanical anchoring. Adequate load transfer thus becomes an issue in situations where the purpose of the reinforcement is to provide tensile strength by consolidating the cracked pieces of concrete. If the purpose of the discontinuous reinforcement is to dissipate energy by crack tip

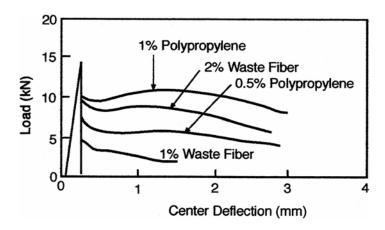


FIGURE 3-2 Load versus center deflection for discontinuous-fiberreinforced concrete showing that fibers can carry significant loads over a range of continued deflection. Source: Wang, 1994.

blunting and deflection mechanisms, however, the weak mechanical interface between the fiber and concrete matrix may be desirable.

Reinforcement of concrete with discontinuous fibers provides several exciting opportunities for future research. To improve the fundamental understanding and performance capabilities of discontinuous-fiber-reinforced concrete, the committee recommends the following research be conducted:

- definition of the specific required properties of discontinuous fiber reinforcements (performance requirements of fiber reinforcements should be derived from the structural performance and durability requirements for concrete)
- determination of the optimum volume fraction, mixing, and placement of discontinuous reinforcement as a function of concrete composition and end application
- augment understanding of the influence of fiber composition, microstructure, aspect ratio, and texture on the mechanical properties of concrete
- optimization of the fiber-matrix interface as a function of structural element application
- development of cost-effective processes to modify the fiber surface in order to achieve the appropriate level of mechanical interlocking between fiber and matrix
- development of a model of the structural behavior of discontinuousfiber-reinforced concrete that can be validated by data obtained from full-scale tests and performance evaluation in the field

MULTIPLE REINFORCING PHASES WITHIN A CONCRETE SYSTEM

A truly innovative nonconventional concrete system would be based on a layered structure. Structural elements could be designed to have particular properties by stacking and combining layers with different chemical, structural, and/or mechanical properties. Ceramic, metallic, or polymeric layers could be used, along with particulates, whiskers, fibers (discontinuous or continuous), aggregates, or continuous reinforcements. For example, the surface layer of a concrete road structure must be tough and wear-resistant to withstand daily wear and tear (e.g., point impacts, continuous vehicle pressure, and abrasion). The internal layers could perform a number of other functions by being made of:

- visco-elastic materials, to dampen structural vibrations
- shape memory alloys, which can exhibit high damping capacity and might improve earthquake resistance in large constructions (Van Humbeeck et al., 1996)¹
- foams, porous materials, or three-dimensional woven structures to absorb the energy and stress waves produced by continuous pressure (the materials could also be infiltrated by a liquid medium to provide further dissipation and absorption of energy)
- · fiber reinforcements, to bridge, deflect, and arrest crack growth

Furthermore, smart materials concepts could be incorporated into the nonconventional concrete system for on-site diagnostics and dynamic real-time measurements and corrections. For example, fiberoptic strain gages could be used to measure dimensional changes and induced stresses, and piezoelectric sensors and actuators could be used to show the effects of internal and external pressure changes.

The design of a layered composite concrete system must be based on knowledge of the properties of the constituent materials, the interfaces between them, and how they respond to the service loads and environments. Promising materials could be selected for preliminary development, testing, and model verification. Modeling concepts should focus on the development of constitutive models of the static and dynamic behavior of the entire composite system on micro, meso, and macro levels. Use of finite element analysis, validated by experiment, can help in the design and determination of the layer thickness and material properties required to optimize the chemical and physical performance of a new type of concrete, particularly toughness, compressive strength, and thermal expansion. Examples of needed model capabilities are:

- thermodynamic and kinetic behavior, including phase transformations and rates of chemical reactions
- interfacial interactions within the microstructure
- · effects of local damage on structural integrity and durability
- · energy and momentum dissipation
- · energy absorption capacities and resiliency during service loading

¹The committee understands that shape memory alloys are temperatureactivated. However, the martensitic phase of such alloys shows a strong amplitude-dependent internal friction, allowing for the material's high damping capacity.

Concrete Processing

This chapter discusses nonconventional methods for the processing and netshape forming of entire concrete systems (i.e., cement, aggregates, and reinforcements) in order to modify structure and composition and enhance properties and performance. The first section deals with process control, which includes orchestration of the procedures needed at the point of production (e.g., mixing techniques and concrete transportation) to obtain the desired product. The second section discusses materials testing and quality assurance, including the need for improved testing procedures to permit better decision making throughout the production process and particularly at the point of placement. The third section investigates placement methods, especially if the concrete contains fibers or intrinsic reinforcements that might reduce the amount of labor needed to place rebar.

The committee concludes that the following issues should be taken into consideration when examining potential nonconventional concrete processes: (1) processing requirements that correspond to new material developments; (2) processing and constructability constraints that influence the success of a construction material; (3) scale-up possibilities to attain acceptable performance and required amounts from novel process plants for expected construction scenarios; (4) robustness and simplicity of the process controls that are needed in a production facility to produce the performance variables and strengths desired; and (5) parameters that influence the placing, finishing, and curing requirements of new concrete material (e.g., flow and workability, resistance to mix separation under a variety of conditions, tolerance of environmental conditions, and the need for and interaction with a range of typical reinforcing materials).

PROCESS CONTROL

The production processes of conventional and nonconventional concrete involve the selection and preparation of source materials, the mixing and blending of raw materials (including cement binders) in controlled amounts, the delivery of blends either as slurries or dry mixes, and the placement of the mixes, usually as slurries, into forms or machines for final net-shaping. Every aspect of the production process must be controlled to optimize performance and properties, and higher levels of process control than are currently available will be required for nonconventional concrete technologies. Four major aspects of processing require improved control: feedstock production, hydration, concrete mixing, and fiber mixing.

Control of Cement Feedstock Production

Even apparently small variations in the dry cement feedstock (e.g., chemistry, particle size) can cause large changes in the resulting concrete. Essential is an understanding of the effects of materials variability on the course of reaction so that the quality control factors can be specified. The initial procedures must be controlled in order to provide a known base for the process activities that follow. In Denmark, for example, the cement industry aims at producing a uniform cement strength at a specified age (e.g., 7 and 28 days). This is accomplished by intensive quality assurance efforts in feedstock production and through close attention to fineness, size distribution, and grinding temperature during the grinding process. The concrete producers apply tight rheological controls of the cement and cement paste to achieve a consistent and conforming end-product (Henrichsen, 1996).

If clays are to be added to the mix, as proposed in Chapter 2, they can be added dry or as slurry. It should be noted that ASTM specifications set limits to the amount of clay that can be beneficially used in concrete. Popovics (1992) discusses some of the potential problems. The heterogeneous reactions of clay with liquids, for example, are difficult to control. The most common method is for the clay to be predispersed in a slurry, as is the case for the micro-silica additions that are used to improve the matrix. Modified clay can also be mixed with a plasticizer. A nonwetting agent could be used to improve the mixing of fine powders. These processes might benefit from the separation of the reactive part of the mixing from the rheological part of the placement.

SLUMP TEST

The slump test measures the consistency or mobility of the slurry and is the main method of determining the workability of concrete before placement. In the slump test, fresh concrete is placed in an inverted openended steel cone that is set vertically on a steel base with the large end of the cone at the bottom. All cone dimensions and filling procedure are carefully detailed and specified in the ASTM C–143 Standard. After filling the cone and striking off the top surface of the concrete, the operator lifts the steel mold off, leaving a cone of concrete that will them slump (settle or flow) to varying degrees, depending on its consistency. The difference in height in inches between the slumped concrete and the steel cone (initial state) is the slump value, which is then used to characterize that mix. A greater slump indicates a more mobile, easier flowing mixture. Many parameters of the mixture affect the slump in a nonlinear manner, however.

Accurately measuring the water content of the aggregates in bulk is a persistent problem in the production of concrete and can cause mix deviations and placement problems. This problem is compounded by the difficulty in accounting for the various shapes found in huge quantities of aggregates in finetuning mix designs and blend behaviors.

The ceramics industry has developed numerous devices for the preparation and mixing of powders, such as twin-vee mixers, attritor mills, and ball mills. One novel approach to cement feedstock production would be to ball mill the powders, using the aggregate itself as the milling medium. Thus, the mixing media would not have to be separated from the powder at the conclusion, and the mixing balls would be free. A disadvantage to dry ball milling in conventional concrete is that the rough aggregate would be rounded somewhat. In a nonconventional concrete, however, this type of milling might lead to better pouring properties and less particle–particle interaction among the chunks of aggregate.

Control of the Hydration Process

As stated in Chapter 2, the sol-gel transition of the conventional cementmatrix has advantages and disadvantages for processing. The advantage is that although there is some change in the consistency of concrete, particularly due to such factors as absorption of water by the aggregate, loss of water by evaporation, etc., the rheology is relatively insensitive to the extent of the hydration reaction until the material is very near the gel point, making the material physically insensitive from the time of mixing to the time of placement. When viewed as a chemical process, however, the sol-gel transition is a disadvantage because the degree of hydration at the time of placement is unknown and uncontrolled. Part of the problem is that the hydration process has several phases: the saturation of the soluble components of the cement powder with water, the development of a hydration layer on the surface of the cement grains as they dissolve, and the development of the gel phase that "precipitates" from the supersaturated region at the water-hydration layer interface. There are several approaches that are incorporated into current practice or at least partly known in the laboratory that could provide the needed amount of control:

- On-site mixing of the concrete would permit closer monitoring and control of the time of the hydration reaction.
- Electrochemical or electrorheological sensors could be used on-site to monitor the extent of reaction so that the material could always be poured at some well-defined point in the reaction process.
- Viscosity modifiers could be added on-site to make the working characteristics of the concrete more uniform and more independent of the extent of hydration.

Uncertainties in the hydration reaction rate could also be reduced by using such nonconventional techniques as:

- Presaturating the process water with certain soluble components before adding it to the cement powder.
- Pretreating the powder itself, perhaps with steam, to ensure more uniform initiation of hydration (caution would be needed to prevent excess hydration).
- Adding small amounts of nucleating agents for the crystalline phases, such as ettringite, to eliminate such uncertainties as the induction period and the critical supersaturation levels for nucleation (prehydrated cement has been used in some laboratory studies as a nucleating agent to accelerate reaction).

• Controlling temperature either physically by insulating the mixing equipment or chemically by adding some type of material that undergoes an exothermic or endothermic reaction (see Chapter 2).

Concrete Mixing Control

The main instrument used at the fabrication plant for the batching of concrete components is the drum mixer. Drum mixers rotate at variable speeds and contain interior vanes to blend the ingredients by shearing and mixing actions. The drums on the trucks that deliver concrete to the construction site also contain these features. Although large-scale fabrication plant and small-scale truck drum mixers have been used for years, much remains unknown about their operation and effectiveness.

Two major matters of concern in mixing are the development of uniform slurries or mixes and the prevention of agglomerations of particles. Little is known about the proper particle size and the breakdown of particle groups for optimum mixing of the cement feedstock or about the changes in the mix-water content that fluidizes the mixture and eventually reacts chemically with the cement. High-range water reducers may be used to disperse the cement particles and prevent flocculation. Smaller cement particles hydrate more uniformly and can improve the resulting concrete, but agglomeration problems may occur if the particle size is too fine. Agglomeration may also occur when cement is used that has been stored too long, although this problem is well known by batchplant technicians and is usually averted by proper quality assurance procedures.

In the polymer and ceramics industries, control of reproducible mixing is one of the most difficult yet important processing variables. It should not be taken for granted in concretes either. Hence, resolution of the difficulties of blending materials would greatly improve the entire control process. Research is required to obtain more detailed knowledge about what occurs during mixing and whether the rolling drum is the best way to mix concrete. Nonconventional concrete may require higher intensity mixing and improved mixing processes to ensure better products.

Continuous processes generally yield more consistent products than batch processes. If both dry and wet mixing could be performed as one continuous process, the results could be continuously monitored and the input stream modified to produce a more consistent product. Such a process would be ideal for the application of statistical process control techniques, especially if it could be done on-site, and would obviate the need to find other uses for off-specification products.

The techniques and experience of other industries that must measure and mix ingredients to get a consistent product in large quantities (e.g., ceramics and paint producers) should be examined to determine their applicability and relevance to the concrete industry. Indeed, some ceramics techniques are already being used in the concrete industry. For example, the high-intensity mixing used for shearing agglomerates in the ceramics industry is currently being used to prepare the concrete for nuclear facility construction in Europe (Henrichsen, 1996). The rheological properties of cement pastes and concretes have been studied extensively in the laboratory, primarily the parameters of viscosity and yield stress. Roy and Asaga (1979), Chappuis (1991), and Yang and Jennings (1993) showed the effect of shear mixing rate and time on the yield stress of cement paste and concrete; the yield stress was markedly decreased by high shear rates.

Control of Fiber Mixing

The placement of discontinuous reinforcing fibers in concrete presents several processing issues. First, special processes are needed to disperse the fibers, especially if fiber content is to exceed one volume-percent. Second, the addition of fibers to the mix causes changes in both the workability and the rate of strength gain, often because other additives are needed to allow the fibers to co-mingle successfully (see Chapter 3). Third, assuring the quality of a mix full of chopped fibers is difficult, and process controls to avoid clumps of fiber sticking together are critical. Hence, the use of reinforcing fibers in the matrix must be given careful consideration in the rheometric procedures for nonconventional concrete technologies.

There are precedents for using a steel mesh and cement for some articles, and the use of chopped fiber in plastic boat building is well known. After shearing of the fiber bundle is done successfully, the chopped fiber is sprayed and combined with resins to create fiberglass hulls. An analogy in the construction industry would be the use of fiber-reinforced gunite that is sprayed onto surfaces for special building applications (Hannaut, 1978). Technology has also been developed for the extrusion or disbursement of fiber in a slurry as it is moved or poured, which is then dewatered by vacuum on a moving belt and formed into thin sheets that can be layered together, much like plywood, to achieve thicknesses up to 30 millimeters (Majumdar and Laws, 1991).

Woven fibers may be preferred in some instances because they can be seen and thus placed accurately before being infiltrated with a cement slurry. There are methods for using three-dimensional textiles, such as geotextiles, that form a continuous-space net for reinforcement. All of these technologies will demand accurate rheometrics to ensure proper placement and to achieve the expected properties and performance.

MATERIALS TESTING AND QUALITY ASSURANCE

Quality assurance is a key activity for any materials use, including concrete. It is important to be able to perform realistic and routine tests to provide specific information about the quality of a material, especially when current experience is superseded by the requirements of a new material. Thus, quality assurance will be critical when considering the delivery of a nonconventional concrete from a process facility to the precasting yard or construction site. The current tests performed on conventional concrete are listed in Appendix C. The critical problems that lend themselves to basic research will require identification, however. Standards organizations will also need to be involved in expediting the protocols for new materials.

The emphasis of quality assurance procedures should be on the use of nonconventional test programs that: (1) are seamless throughout the entire process; (2) improve the availability and reliability of the data collected during the production and construction process for use by all parties; (3) ensure the delivery and use of the proper raw concrete or concrete elements; and (4) allow the implementation of model-based design for the concrete system within an MSE-systems approach.

For example, the predominant method of determining the workability of concrete before placement is the slump test. Workability is the property that determines a concrete slurry's capacity to be placed, consolidated, and finished without segregation of its components. Although the slump test may assure a certain level of quality, the

CONCRETE PROCESSING

variables and parameters that influence the test results are so numerous and difficult to quantify that it takes experience and insight to determine why a material failed a test and how to correct the problem. Water is often added to obtain a better result, which is frequently the worst option available. The complex process dependency included in the slump measurement is a fruitful topic for further research, and the parameters controlling slump, including time between batching and placement, need to be clearly identified and understood. Some research on theology is being conducted in the U.S. and France. For example, Banfill (1993) summarized the relation between slump and yield stress as measured by a more complex rheometer for concrete. The yield stress for concrete is about two orders of magnitude greater than that of cement paste.

Even with further improvement, however, the slump test will not provide sufficient information to allow the formulation of optimum decisions or the implementation of model-based design within an MSE-systems approach. As stated above, process control and test methods should be performed continuously so that (1) variations from desired performance can be promptly identified and rectified, and (2) new products can be designed and manufactured faster and cheaper with higher quality. Research is urgently needed to develop advanced test methods and sensors that better describe the dynamics of concrete's development in a continuous fashion.

Electrochemical and electroacoustical methods could be developed to measure the extent of chemical reaction and the progress of gelation. High-frequency electroacoustic measurements could probe the relatively short mechanical relaxation times and might be able to detect the onset of gelation before it becomes visually apparent. Electrical conductivity and dielectric loss measurements could also be used to monitor the extent of chemical reactions. There are also numerous nonintrusive sensing technologies (e.g., neutron scattering to measure water content and the degree of binding of water [Livingston et al., 1995]) that might be adapted to cement processing.

Furthermore, the electrical and dielectric properties of Portland cement and other cementitious materials are important diagnostic properties during curing and hardening. Gorur et al. (1982) were among the first to use microwave equipment (9 GHz) to monitor the hydration process continuously, and they found a nearly exponential decay in the complex dielectric constant as hydration took place (Figure 1-17). McCarter and Curan (1984) and Perez and Roy (1984)

attempted to interpret cement's electrical behavior in terms of various conduction and polarization mechanisms. Perez-Pena (1986) and Perez-Pena et al. (1989) showed that the function of the electrical conductivity or relative dielectric permittivity determined at low frequencies (approximately 1 KHz) had a complementary relation to the heat produced during hydration. Electrical conductivity diminished as the heat released increased. This finding enabled a convenient nondestructive means of evaluating the hydration and hardening process. It also made it possible to assess the effects of various chemical admixtures and additives on the hydration process. At the other extreme in the hardened materials, the relative permittivity and dielectric loss diminished with increase in frequency and were found to be very low in the MHz region for low w/c pastes, especially in the microwave range up to 200 MHz (Perez-Pena et al. 1986, 1989). Other work has resulted in the use of microwave heating to rapidly determine the water content of concrete (Naik and Ramme, 1987).

Extensive research is currently being conducted in other fields to develop sensors to measure chemical and physical parameters for extreme environments (NRC, 1995a, 1995b; see Appendix B). This work should be examined to determine its applicability and relevance to concrete.

PLACEMENT METHODS

Batch mixing and concrete placement are usually separated by both space and time. There is time between the mixing of the constituents until the plastic concrete is placed in the forms or machines to take on final net-shape. The stiffness of the concrete is increasing during this interval, and the workability of the mix is decreasing. These changes must be taken into account when carrying out the activities (e.g., consolidation and finishing) that take place after the constituents of a concrete are combined. The time period prior to setting might be lengthened (e.g., to allow for long-distance delivery) or shortened (e.g., to accelerate strength gain). Thus, the placement methods are vitally related to the workability of new concrete and its changes with time.

The physical changes in concrete are due to gel formation that causes the plastic concrete to be somewhat thixotropic (Figure 1–17). Colloidal silicate pastes, which exhibit high thixotropy, show big changes in their shear rates, depending on conditions. Thixotropy is

a difficult phenomenon to take into account and needs to be better understood. Thus far, researchers have been unable to obtain uniform results from sol-gel experiments in the laboratory, where control of the experiment is optimum. The ability to probe and continuously determine free- and bound-water concentrations in the microstructure (e.g., neutron scattering or microwave methods; see above) may prove useful for handling workability issues as well as for predicting the final properties of the material.

Better tests are also needed to indicate performance during placement, especially in the area of advanced rheometrics. Comparable tests exist in other areas that might be adaptable to concrete:

- Shear viscosity testing is routinely used in the paint industry.
- Centrifuge methods are used to determine the particle size distribution of insoluble particles for analytical measurements of suspensions.
- Other viscometric measures are available that might be considered for the rheometrics of concrete—for instance, suspensions could be added to modify flowability.

For conventional concrete, the slurry is delivered to the forms or placing machines, where it is poured or pumped around steel reinforcement or prestress tendons that are already in place. All of the aforementioned process controls will have a new measure of complexity if the reinforcement is included in the concrete itself in the form of small fibers. Such reinforcement is already a trend in conventional concrete. In Canada, for example, bridge decks are being reinforced with fiber, thereby eliminating corrosion of the rebar and consequent deterioration of the deck.

A potential nonconventional placement method would be the on-site production of nonconventional concrete by combining individually stable material streams, one of which would be an activator liquid that would initiate the gelation process. Such a method would eliminate the time and distance variations typically found in conventional concrete.

As stated above, there is difficulty in making measurements during the concrete production process that will allow critical control in achieving the desired performance specifications. Once the trial mix has been designed in the laboratory and tested full-scale, the process is regarded as largely fixed and is controlled mainly for obvious deviations. The development and advent of new rheometrics will not

only enhance the delivery, placement, consolidation, and finishing of concrete, it may also promise a new measure of control to meet target properties and performance specifications. Applying more advanced rheometrics raises the new problem of analyzing a host of parameters, however, all of which vary simultaneously. Thus, advanced statistical approaches will probably be required to deal with this new problem (see Chapter 5).

5

Systems Approach to Concrete Technology

Concrete and the structures constructed from concrete have historically been viewed primarily as the linear sum of their individual parts. Analyses of the interrelationships of the constituent materials of concrete were typically empirical and did not consider the complex chemical and physical interactions between the constituents. Similarly, a systems approach has not been rigorously used to investigate the interactions between concrete and the other parts of engineered structures. The committee has concluded that major advances in the development and application of nonconventional concrete technologies require the use of a MSE systems approach. This chapter examines the MSE systems approach and discusses the need for a model-based design methodology within the construct of total life-cycle costs (i.e., not simply from the perspective of the lowest cost for original construction).

The MSE systems approach can be used to enhance the performance of concrete in two ways. First, conventional concrete can be controlled and manipulated during processing to produce optimal properties. Second, concrete itself can be "compositionally" redesigned to make the concrete less sensitive to process parameters that are difficult to control while yielding superior performance.

SYSTEMS APPROACH

In a systems approach, concrete must be viewed as a totally interactive and complex system. This system must be considered over all length-scales, meaning that one must be concerned about the constituents of the cement, the constituents of the concrete, and the assembly methods used to create the entire engineered structure. This implies that one needs to be concerned with materials and their behavior, and the models that describe them, over perhaps 10 orders of magnitude of length, from less than a nanometer to more than a meter (Figure 1-4). One significant challenge will be to extend the models so that each addresses a different length scale. Another major challenge in modern condensed matter physics, and one that has yet to be completely met even for simple metallic, ceramic, and biological systems, is the melding of these various models in order to understand the effects of the different length scales on the entire engineered structure. The systems approach also needs to consider the entire system as it is manufactured as well as considering its performance after it is put into service. For example, interactions between the concrete and the gravel subsurface or steel structure, as well as interactions between the completed structure and vehicular traffic, must be considered in a systems approach. Finally, the concrete system must be designed to avoid or eliminate the durability problems experienced by conventional concrete and those potential degradation mechanisms introduced by the inclusion of new materials.

At the atomic length scale, the role of the electronic structure of the elements comprising the cement is important. The electronic structure controls the ionic and molecular behavior of cement and therefore is central to the gelation and hydration process. The possibility of molecular engineering of cement by the appropriate and intelligent introduction of other basic elements is an option that should not be cavalierly dismissed. The elements and their amounts that must be added to cement to modify its behavior at any point in time cannot be determined experimentally because of the large number of possibilities. However, molecular dynamics calculations—although probably unable to predict the exact changes in performance that would occur due to the addition of particular elements—could be used to guide experimental design work and make the problem tractable in the laboratory.

On the nanometer length scale, the inherent lower limit of the size of atoms means that structure and processes would have to be considered differently from larger length scales, in which matter can be regarded as continuous.

On the molecular level, particles grow by various random processes that generate fractal structures. There is then a crossover to different growth processes involving the impingement of the fractal cluster, which in turn gives different fractal structures. At the molecular to micrometer length scale, the role of the size of feedstock particles and fine aggregate on rates of interfacial reactions must be considered. One may be able to engineer and tailor the gelation reaction, for example, by manipulating the size and morphology of the cement particles before water is added or perhaps even by using a controlled distribution of particle morphology so that one part of the structure has different gelation kinetics from those of another. Historically, in the structural hierarchy, this regime has been one of the most difficult to study, and it presents a significant and potentially rewarding research opportunity.

The systems perspective must also be extended to larger length scales. Changing the aggregate, for example, produces a first-order effect related to the properties of the aggregate itself, but the system is also influenced by the nature of the interface between the aggregate and the cement matrix. As another example, silica fume is increasingly being added to make a higher-strength or less permeable concrete. This can also reduce the material's toughness, however, resulting in a material that is more brittle and requires more care during emplacement to prevent cracking. In a systems approach, all of the materials and unit processes used to create a structure would be considered synergistically and not independently.

Finally, the system perspective must be extended to the engineered structure itself. This implies that one needs to consider interactions between the gravel roadbed, the steel superstructure (if any), the concrete, and minor structural components (e.g., expansion joints).

The systems approach must also be implemented over all length scales within two different contexts. First, it must be implemented during the fabrication of concrete and the construction of the structure. The systems approach will optimize jointly the manufacturability of the system and its cost. Optimal combination of manufacturability and cost does not necessarily mean minimizing either one. One special advantage of concrete relative to other manufactured materials is the longer length of time required for processing (i.e., initial mixing through transport to pouring), which offers ample opportunity to adjust material composition and mixing conditions. Second, the systems approach should optimize the performance and reliability of the concrete and the structure. The goal of the optimized system is to minimize the life-cycle costs of the structure by creating an inherently longer lifetime and minimizing the need for maintenance and repair.

The benefits of the systems approach cannot be realized haphazardly. The methods needed to achieve an optimized system may

not be intuitively obvious, as human intuition may be unable to quantitatively comprehend the interactions and influences among all of the materials in these structures over 10 orders of magnitude of length. As a consequence, the key to realizing a systems approach to the materials, the processes, and the structures created from concrete lies in the ability to model the different facets of the entire system rigorously and to meld these models in order to achieve a reasonable understanding of the studied phenomena in the broader context.

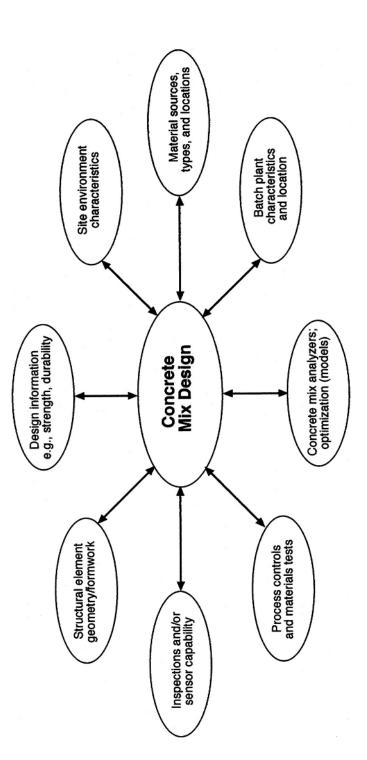
MODEL-BASED DESIGN

Model-based design is a new approach now being used in the manufacturing industry. By definition, it is simply the designing of new materials, structures, and systems quantitatively rather than intuitively. The quantitative nature of the concept allows all pertinent information to be considered simultaneously and synergistically. Each aspect of the design process (i.e., materials and process knowledge) must be rigorously and quantitatively understood, as must the first and higher order interactions between each component of the process. In other words, model-based design uses the right quantitative information at the right place and at the right time. Done properly, model-based design will produce higher-quality products faster and cheaper, especially when considered within the context of life-cycle cost. The concept of model-based design within the context of a systems approach is not a new concept. It has been slowly evolving as computational power increases and is being increasingly applied to the fabrication of "high-tech" systems, including weapons systems, aircraft, and automobiles (NRC, 1988, 1989, 1993, 1995a, 1995c).

The model-based design concept is the next logical step in the systems approach. In order to apply the concept, the materials and the processes used to fabricate the final product must be understood in detail. This complex and quantitative understanding encompasses the fabrication of the material and the structure as well as the performance and long-term reliability of the material and structure. Ultimately, it must be understood that these two aspects of model-based design—the synthesis of the materials and the fabrication of the structure, and its performance and reliability—are themselves coupled.

The first consideration in the use of model-based design is the design of the structure and the processes used to construct it. In such complex cases as a structure fabricated from concrete, sufficient detail may range from the subtle physics and chemistry of interfacial interactions at the atomic level to the macroscopic behavior of the elastic deformation of the steel tendons used in prestressing. Figure 5-1 shows the interplay of the various aspects of model-based design. Fundamental understanding of the materials and processes will allow the processes to be optimized, but it is necessary to model the process mechanistically and perform computational simulations to reduce the number of experimental attempts that must be made to optimize the process. Experiments should be used to validate the process model and not to optimize the process directly. Once an optimal process has been designed, it is possible to apply intelligent control to the process. To maintain control of the process, it is necessary to monitor explicitly the changes occurring to the materials (in the case of concrete, the temperature, viscosity, pH, etc.) and its microstructure, which requires a system of appropriate sensors. Overlaying the intrinsic behavior of the material during processing is the influence of the external environment. For example, the experimentation required to determine strength development, rates of ingress of chlorides, and resistance to freezing and thawing for each concrete mix design takes several months, and these tests must be repeated as the mix is modified. Model-based design would allow the effects of each mix parameter to be evaluated quantitatively prior to experimentation.

The second issue in model-based design is predicting the performance and reliability of the final structure. This requires a quantitative understanding of the performance of the materials and the structure, based on fundamentals to the maximum extent possible and minimizing reliance on observations of empirical behavior. The impact of the environment on performance and reliability is perhaps even greater than its impact on the original processing due to the much longer time periods involved. Coupling the role of the environment with a quantitative understanding of reliability (e.g., explicit description of how salts degrade reinforced concrete) can be used to develop a fundamental understanding of degradation and to construct appropriate models of the entire system. Empirical knowledge is generally insufficient because it is not possible to perform empirical experiments on the full system under every condition. But understanding, for example, how chlorides penetrate the concrete and attack the reinforcement fundamentally allows one to combine higher-order effects computationally in model-based performance and reliability assessments, including requirements for earthquake zones, fire resistance, lightweight applications, etc.





The performance criteria for nonconventional concrete must be based in part on its interaction with companion materials. For example, earthquake loading is resisted by design of steel reinforcements and related connections that are compatible with the properties of the concrete. These interactions would have to be optimized to determine the required performance of nonconventional concrete.

The ultimate contribution of model-based design within a systems approach is to allow the interactions within and among all of the constituents over all length scales to be quantitatively modeled, permitting an understanding of a particular phenomenon in the broader context. It would be impossible to explore experimentally all possible variables of the materials and processes used to create the structure and then to measure all possible performance variables. Given adequate models, however, it is possible to explore computationally the effects of most, if not all, parameter interactions and to identify specific validation experiments.

The replacement of existing systems with new materials must take into account the conventions that have developed over time to normalize secondary design factors. When new systems are developed, these factors must be identified and addressed.

To realize a model-based approach to concrete and the structures created from it, several key enablers are required. First and foremost, a more complete understanding of all structural features and chemistries is needed at all length scales of the materials and processes used to create the concrete and the engineered structure. This implies that far more extensive research into the theoretical interrelationship among synthesis and processing, structure and composition, properties, and performance of concrete materials is required (Figure 1–1). Second, given more extensive materials and process knowledge, better mechanistic computational models are needed to understand the behavior of the materials and structures during fabrication and in-service. Third, the concept of system optimization through intelligent processing or intelligent systems requires a better suite of capable and inexpensive sensors and actuators.

KEY ENABLERS FOR THE APPLICATION OF A SYSTEMS APPROACH

As detailed in Chapter 2, Chapter 3, through Chapter 4 and discussed above, the most fundamental need for realizing a systems approach to concrete and concrete-base structures design is more extensive fundamental knowledge of materials and processes. As discussed in earlier chapters, the fundamental nature of the physics and chemistry of the gelation process is yet to be understood, the fundamental interfacial interactions between cement and aggregate have not been determined, and the physics and chemistry of the interactions between cement and reinforcement have not been explored in quantitative detail. The constitutive properties (e.g., mechanical behavior) of the cement, aggregate, reinforcements, and their interfaces have not been determined either. Without this fundamental understanding, any significant advance in the science of concrete and its applications will not be forthcoming. Model-based design within the construct of a systems approach will not happen until the fundamental knowledge base is significantly expanded.

Fundamental Issues and Computational Models

If one assumes that the required fundamental materials information described above is available, the next issue is how to use this information to optimize the fabrication and manufacturing processes and to enhance the properties and performance of the final structure. Once again, optimization requires the development of mechanistic models and computational tools that span all length scales, from atomic/molecular to macroscopic. At the most fundamental level, understanding of the electronic/atomic/molecular level is needed. Although it might seem abstract to investigate materials behavior at the atomic and molecular levels for concrete, such information is the key to modeling the interfaces and related interfacial behavior within gels and between gels and aggregate. The models are required for length scales far smaller than a micrometer.

Microstructural evolution models are also required to understand the more macroscopic nature of hydration and gelation. This will be the key to understanding the formation of the various crystalline phases that form in concrete as it sets. In the absence of closed-form physical models of microstructure evolution, computational materials-science methods have been applied (Bentz et al., 1994). This involves treating each particle of material in the microstructure as a cellular automaton. The growth or transformation of each particle during a time cycle is determined by a set of simple transition rules that are based on chemical reactions.

Finally, continuum models are needed for finite-element models to understand the macroscopic aspects of flowing unset concrete, the heat transport in setting concrete, and the elastic/plastic/fracture behavior of the set material and the engineered structure. Although such models have been infrequently applied to concrete, they have been widely used in the study of metals, ceramics, polymers, semiconductors, and the structures created from these materials, as well as composites from various groups of these materials. Once the fundamental materials knowledge is available, modeling will follow naturally. Given that concrete systems and the structures created from them are more complex than the materials and structures for which these models have been successfully used, increased computational power will probably be needed. However, advances in computational engines are occurring rapidly. Continuum models have been run under massively parallel computational architectures with ever-increasing speeds. Terraflop¹ computing will be achieved in the very near future, with three and ten terraflops soon thereafter; and pentaflop computing may well be less than a decade away. Given this massive computational ability, it is only a matter of time before all pertinent models can and will be run.

Many of the parameters used in these models are not discrete but are described by probability distributions. As such, the problem becomes stochastic in nature and must be solved repeatedly to produce a statistically sound solution. Such problems are also very amenable to solution through parallel computation.

Smart Processing and Intelligent Systems

As stated in chapter 3 and chapter 4, sensors will be required to fulfill the vision of intelligent or smart processing as well as the vision of an intelligent system, which in this case would be an intelligent highway or bridge (Davis et al., 1996). Rapid advances in materials knowledge and microelectronics technology have revolutionized the world of sensors. More and more capable sensors are being built at ever-decreasing size and cost. Modern integrated sensors can be produced in a modern semiconductor device fabrication facility at a per-device incremental cost of as low as a few cents. Low cost produces the

⁸²

¹10¹² arithmetic operations per second.

option of using sensors to assess the processing (and allow feedback control) that could simply be left in the concrete after their work is done. A multitude of properties can be readily measured with embedded sensors, including temperature, viscosity, pH, and organic and chemical contaminants. Devices can be built that measure a number of these parameters, digitize and preprocess the data using on-chip processors, and then communicate the information to the outside world through a network addressable architecture. Several examples of modern sensors that would be particularly sensitive to parameters that might change in concrete during processing and setting are discussed in Appendix B.

Much of what has been discussed above with respect to sensors has dealt with sensors to monitor the concrete as it is being mixed or cured. Sensors might also be used to provide data on roads and bridges while in use. Such sensors would permit damage to be observed at its earliest stages and repairs to be made at minimal cost. Once again, advanced computational models would be needed. The notion of self-aware systems is also not novel, having been explored for weapons systems, aircraft, and, albeit in a more simplistic way, automobiles.

The same technology that is used to fabricate microsensors and microelectronics could be used to fabricate microelectromechanical systems (MEMS). MEMS-based actuators could then be used to control the injection of chemicals into the structure to control or mitigate corrosion and other degradation.

The vast array of sensors now becoming available can produce large quantities of data. Intelligent use of this data requires advanced processing techniques that can include neural networks, expert systems, etc.

LIFE-CYCLE COSTS

To implement a model-based design methodology, concrete and concrete structures must be viewed within a total life-cycle cost context. Although the use of sensors and on-line computational tools to adjust materials, processes, and in-service performance would be expensive, this approach will greatly increase the life of the material and structure and thereby potentially reduce total life-cycle costs. For this approach to succeed, the costs of structure must not be viewed just from the perspective of the lowest cost of original construction. A favorable trend currently evident in major engineering and construction projects is the increased use of net-present-value estimates over the lifetime of a project in order to provide realistic justification of higher up-front costs and quantify the downstream savings provided by innovations in materials or technologies.

SUMMARY

This chapter has attempted to clarify the need for concrete to be considered within the context of model-based design. The methodology is one predicated on a solid understanding of the materials at all length scales and their behaviors from the processing of the initial raw materials to the preparation of actual concrete to be used for pouring or casting, to the setting of the material, to the understanding of the behavior and durability of the concrete during its inservice life. A materials understanding at all length scales means that the behavior of the material is understood quantitatively from the atomistic level to the microscopic level, and on up to the macroscopic or continuum level. This understanding allows one to control the material and its processing continuously.

The implementation of model-based design relies extensively on a sensorrich environment to allow the development of an explicit quantitative understanding of the materials, the processes, and the degradation mechanisms. Monitoring of the materials and processes would allow for computer-controlled adjustments during placement. Monitoring of the final product in-service would help determine degradation mechanisms and permit the accumulation of data that could be fed back into the model-based design methodology as well as allow cost-effective, localized repairs that would minimize maintenance costs while maximizing in-service time by eliminating routine preventative maintenance. Such a system is often called "smart," "intelligent," or "self-aware."

The technology discussed above, when considered incrementally, is not inexpensive. The materials data that needs to be generated, the models that need to be created, and the sensors that need to be developed will require substantial investment. The use of these enabling technologies to design and construct roadways and bridges and to monitor them during their life will also increase costs. However, there is every likelihood that building the structure using smart processing embedded in a model-based design methodology and building the structure so that it too is "smart," "intelligent," or "self-aware" should significantly extend the life of the structure, greatly minimize repair costs, reduce the amount of time the structure is taken out of service for repairs during its life, and thereby reduce lost opportunity costs. This is a large and complex issue, since the "systems approach" paradigm requires that the discussed technology enablers be considered over all length scales for the cement, the concrete, and then the structure itself. Hence, while the initial investment to build the structure may be substantially greater, the annualized cost of ownership should be significantly reduced. The costs of designing, constructing, monitoring, and maintaining the structure must be summed and amortized over the design life. This yields the predicted annualized life-cycle cost and should be the key financial information given in the original bid.

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APPENDICES

Appendix A

Workshop Participants

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DK 2900 Hellerup Denmark Dr. Richard Hughes Celanese Hoechst Research Division Summit, NJ 07901 Professor D. Lynn Johnson Department of Materials Science and Engineering Northwestern University 2225 North Sheridan Road Evanston, IL 60208-3108 Dr. James E. Martin Mailstop 1421 Sandia National Laboratories Albuquerque, NM 87185 Professor J. William Morris, Jr. Department of Materials Science and Mineral Engineering University of California Berkeley, CA 94720 Professor Gregory Olson Department of Materials Science and Engineering MLSF 2021 Northwestern University 2225 North Campus Drive Evanston, IL 60208-3108 Dr. Larry Schwartz Schlumberger-Doll Research Old Quarry Road Ridgefield, CT 06877-4108

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Appendix B

Modern Sensor Technology

This appendix presents several examples of sensors that would be particularly sensitive to the parameters that might change in concrete during processing and setting.

Figure B-1 shows a densitometer/viscometer for measuring the density and viscosity of a fluid. Although the sketch of the prototype shown in this figure was originally developed to measure the density and viscosity of oil, it could easily be modified to measure the density and viscosity of unset concrete. This would allow such measurements to be made in situ and in line for concrete in the mixing and pumping equipment. In this device, the response of the high-frequency electrodes on the rough resonator differs from the smooth resonator as a function of the viscosity and density of the fluid. Given calibration data, viscosity and density can be measured. The RTD measures temperature to accommodate for density and viscosity changes with temperature.

Figure B-2 shows a sensor based on a Surface Acoustic Wave (SAW) device. In a SAW, the input electrode is oscillated at a high frequency. The mechanical wave created by the electrode is transmitted across the surface of the SAW and received by the other electrode. If the nature of the surface across which the wave is transmitted changes, the amplitude and frequency of the wave will be altered. Typically, a selective film is deposited on the surface that absorbs/adsorbs only a limited number of chemical species. The adsorption/ absorption of these species will change the characteristics of the transmitted wave. A variety of films could be used to sense various components in the concrete. For example, films sensitive to pH could be made.

Measuring a certain parameter on a small cheap sensor is only half of the desired total functionality. It is desirable to perform some, if not all, of the data processing on the chip. This creates an integrated microsystem. Properly configured, the microsystem will process and digitize the data and pass it into a network. Figure B-3 shows an example of an integrated sensor designed to detect hydrogen gas.

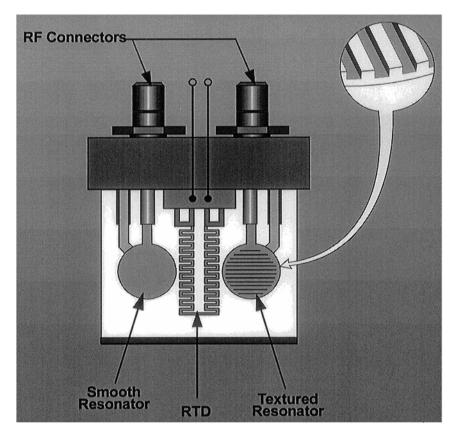
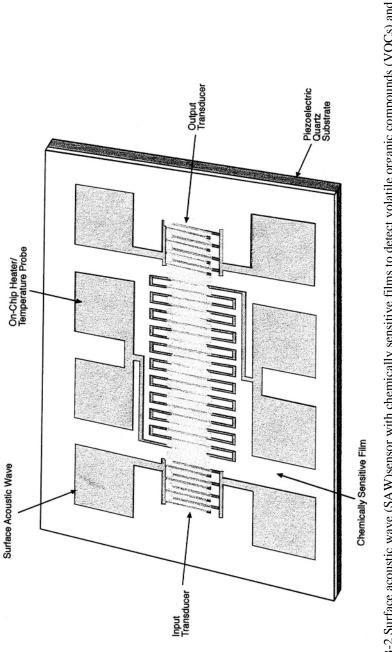
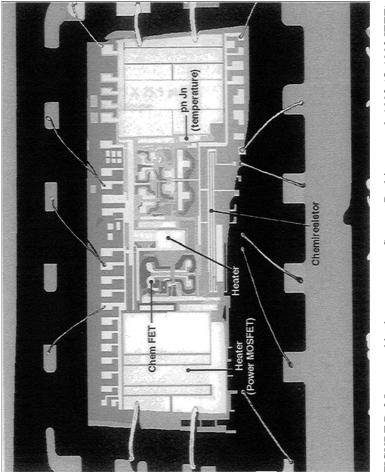


FIGURE B-1 The Sandia densitometer/viscometer. Source: Martin et al, 1994. Reprinted with kind permission from Elsevier Science S.A., P.O. Box 564, 1001 Lausanne, Switzerland.

In some applications, it may not be possible to place the sensor at the desired location, regardless of its miniaturized size. In such cases, it is possible to construct a sensor that senses remotely, as shown in Figure B-4. This particular sensor is designed to detect gaseous species, but it could be constructed to detect liquids as well. The optical fiber has a thin layer of reflective materials, often a metal, deposited onto the end. The film has an intrinsic reflectivity, and light transmitted down the fiber is reflected back up the fiber to a photodetector. If a chemical species is absorbed/adsorbed onto the film, the reflectivity will be changed and measured. Given the proper calibrations, chemical composition can be determined. In this case, it would be possible to embed the sensor in setting concrete so that the cure could be observed and appropriate environmental adjustments made.









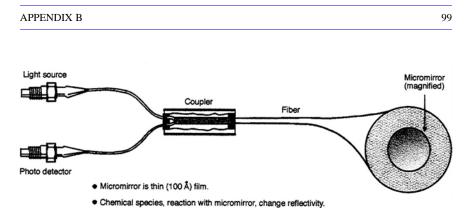


FIGURE B-4 Micromirror sensor. Source: Butler, 1994. Reprinted with kind permission from Elsevier Science S.A., P.O. Box 564, 1001 Lausanne, Switzerland.

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Appendix C

Conventional Concrete Test Procedures

This appendix lists the main test procedures for conventional concrete. The data was compiled from Klieger and Lamond (1994).

- 1. Cement Content Analysis Procedures
- 1.1 Standard Procedure ASTM C1078
- 1.2 Non-Standard Procedures
- 1.2.1 Constant Neutralization Method (Chemical)
- 1.2.2 Absorption Method (Chemical)
- 1.2.3 Rapid Analysis Machine (Separation)
- 1.2.4 Flotation Method (Separation)
- 1.2.5 Willis and Hime Method (Separation)
- 1.2.6 Dunagan Buoyancy Method (Separation)
- 1.2.7 Nuclear Cement Gage (Nuclear)
- 1.2.8 Thermal Neutron Activation (Nuclear)
- 1.2.9 Hydrometer Analysis Method
- 1.2.10 Concrete Consistency Method
- 1.2.11 Conductrimetric Method
 - 2. Water Content Analysis Procedures
- 2.1 Standard Procedure ASTM C1079
- 2.2 Non-Standard Procedures
- 2.2.1 Concrete Consistency Method
- 2.2.2 Thermal Conductivity Methods
- 2.2.3 Microwave Oven Method (Separation)
- 2.2.4 Dunagan Buoyancy Method (Separation)
- 2.2.5 Flotation Method (Separation)
- 2.2.6 Capacitance Methods (Electrical)
- 2.2.7 Electrical Resistance Method (Electrical)
- 2.2.8 Microwave-Absorption Method (Method)
- 2.2.9 Neutron-Scattering Methods (Nuclear)

- 3. **Concrete Strength Testing Procedures** 3.1 Preparing Compression Test Specimens 3.1.1 Standard ASTM C 192 (Laboratory) 3.1.2 Standard ASTM C 31 (Field) 3.2 Compressive Strength Test Standard ASTM C 39 3.3 Preparing Tension Test Specimens 3.3.1 Standard ASTM C 192 (Laboratory) 3.3.2 Standard ASTM C 31 (Field) **3.4 Tension Strength Test Procedures** 3.4.1 Flexural Center-Point Load Standard ASTM C 293 3.4.2 Flexural Third-Point Load Standard ASTM C 78 3.4.3 Splitting Tensile Strength Standard ASTM C 496 3.4.4 Direct Tensile Strength Standard ASTM D 2936 3.4.5 Non-Standard Double Punch Test 3.5 Triaxial Loading Strength Standard ASTM C 801 4. Concrete Uniformity and Workability Tests
- 4.1 Cement Content Standard ASTM C 1078
- 4.2 Water Content Standard ASTM C 1079
- 4.3 Air Content Tests
- 4.3.1 Pressure Method ASTM C 231
- 4.3.2 Volumetric Method ASTM C 173
- 4.3.3 Gravimetric Method ASTM C 138
- 4.4 Unit Weight Standard ASTM C 138
- 4.5 Temperature Test Standard ASTM C 1064
- 4.6 Standard Workability Test Slump ASTM C 143
- 4.7 Non-Standard Workability Tests
- 4.7.1 K-Slump Tester
- 4.7.2 Placeability Apparatus
- 4.7.3 Remolding Test
- 4.7.4 Kelly Ball Penetration Test
- 4.7.5 Thaulow Concrete Tester
- 4.7.6 Vebe Apparatus
- 4.7.7 Compacting Factor Test
- 4.7.8 Wigmore Consistometer
- 4.7.9 Flow Cone Apparatus
- 4.7.10 Grout Consistency Meter
- 4.7.11 Otto Graf Viscosimeter

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Appendix D

Biographies of Committee Members and Technical Consultants

CAROLYN M. HANSSON (chair) is vice president of university research at the University of Waterloo, Ontario. She received a B.Sc. and Ph.D. in metallurgy from Imperial College, London University. Her research concerns the corrosion, erosion, and wear of materials, specifically the corrosion of concrete reinforcement and the properties of concrete that influence it. Dr. Hansson is currently a member of the National Materials Advisory Board.

NORBERT S. BAER is Hagop Kevorkian Professor of Conservation at New York University. He received an M.S. from the University of Wisconsin and a Ph.D. from New York University in physical chemistry. His research interests include the application of physicochemical methods to the examination and preservation of artistic and historical works and structures. He chaired the National Materials Advisory Board Committee on Conservation of Historic Stone Buildings and Monuments in 1980. He also served on the National Materials Advisory Board from 1986 to 1993.

EZRA D. EHRENKRANTZ holds the Sponsored Chair/Executive Director of the Center for Architecture & Building Science Research at the New Jersey Institute of Technology, and is a principal in the New York-based architecture and planning firm of Ehrenkrantz & Eckstut. He received a B.Arch. from the Massachusetts Institute of Technology and a M.Arch. from the University of Liverpool. His research activities include infrastructure planning, building technology, and healthcare.

HERBERT A. FRANKLIN is a senior engineering supervisor in the Advanced Civil Department of Bechtel's Research and Development

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organization. He received a B.S. from the University of New Zealand, a M.A.Sc. from the University of British Columbia, and a Ph.D. in structural mechanics from the University of California, Berkeley. He is responsible for directing internal R&D at Bechtel related to space construction technologies, space materials processing, and planetary surface exploration and prospecting.

KEITH KEEFER is lead technologist for waste forms science and engineering for tank waste remediation at the Pacific Northwest National Laboratory. He received a B.A. from Carleton College and a Ph.D. from Stanford University in geology. His current areas of research concern the structure and stability of vitreous and cementitious waste forms for U.S. Department of Energy radioactive fuel reprocessing waste and the long and short-range atomic structures and synthesis of crystalline and amorphous silicates. materials. particularly oxides and His expertise includes crystallography, crystal chemistry, glass chemistry, high-temperature chemistry, and colloid and gel chemistry.

KATHRYN V. LOGAN is principal research engineer and director of research at Georgia Institute of Technology. She received a BCerE and a MSCerE from the Georgia Institute of Technology. Her current research involves pilot plant scale-up of powder synthesis and forming processes using self-propagating high-temperature synthesis, development of high-performance materials, development of refractory materials for application as boiler liners, and mechanical and analytical microstructural characterization of materials. Ms. Logan is author and co-author of over 30 major reports and publications, editor of two books, and inventor and holder of six patents and co-inventor and holder of one patent.

JOHN NEERHOUT, JR., was previously executive vice president of Bechtel Group, Inc. He is currently a senior of Bechtel and a member of the company's board of directors. He received a B.A. in mechanical engineering from the University of California, Berkeley, and is a licensed mechanical and industrial engineer in California and a chartered engineer in the United Kingdom. Mr. Neerhout is the project chief executive for Eurotunnel, owner of the Channel Tunnel, which is the largest private construction project on record. He is a member of the National Academy of Engineering and a Foreign Member of the Royal Academy of Engineering. ALTON D. ROMIG, JR., is director of microelectronics and photonics at Sandia National Laboratories. He received a B.S., M.S., and Ph.D. in metallurgy and materials engineering from Lehigh University. His personal technology interests include materials and processes for electronic packaging, materials characterization via electron microscopy, and the modeling of microstructural evolution during materials processing and in-service aging. Dr. Romig has more than 150 technical publications, has been a co-author of three textbooks, and holds two patents.

DELLA M. ROY is a professor in the Materials Research Laboratory at Pennsylvania State University. She received a B.S. from the University of Oregon and a M.S. and Ph.D. from Pennsylvania State University. Her research includes phase equilibria, materials synthesis, crystal chemistry and phase transitions, crystal growth, cement chemistry, hydration and microstructure, concrete durability, biomaterials, special glasses, radioactive waste management, geologic isolation, and chemically bonded ceramics. Dr. Roy is a member of the National Academy of Engineering.

MEHMET SARIKAYA is an associate professor in the Materials Science and Engineering Department at the University of Washington, Seattle. He received his M.S. and Ph.D. degrees from the University of California, Berkeley. His research focuses on nanostructural affects (studied via transmission electron and scanning probe microscopies) on physical properties of materials, including nanocomposites, high-temperature superconductors and semiconductors, perovskites, ceramic-metal composites, with current emphasis in biomimetic design and processing of materials.

Chemical Formulas of Cement Materials

C	CaO
	H ₂ O
	SiO ₂
<u>s</u>	SO ₃
Α	Al_2O_3
Ν	Na ₂ O
	Fe_2O_3
K	K ₂ O
М	MgO
C ₃ S	$3CaO \cdot SiO_2 = tricalcium silicate = alite$
C_2S	$2CaO \cdot SiO_2 = dicalcium silicate = belite$
C ₃ A	$3CaO \cdot Al_2O_3 = tricalcium aluminate$
C ₄ AF	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe2O}_3 = \text{calcium alumino ferrite}$
C-S-H	Calcium silicate hydrate, a colloidal and
	mostly amorphous gel with a variable
	composition; this is the major hydration
	product of Portland cement, constituting
	approximately 70 percent of the paste, and is
	the phase providing most of the strength and
	binding
СН	Calcium hydroxide, a hydration product
	constituting approximately 20 percent of the
	paste and, while contributing little to the
	overall strength, buffers the paste pore
	solution to a pH of approximately 12.5
Afm	Tetra-calcium aluminate trisulfate hydrate,
	usually with some substitution of Al by Fe
	and SO ₄ substituting for hydroxyl

CHEMICAL FORMULAS OF CEMENT MATERIALS

Aft	Ettringite, a calcium trialuminate hydrate, usually with some substitution of Al by Fe
	$(C_3A \cdot 3C\overline{S}H_{32} = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O)$
Monosulfate	$C_3A \cdot C\overline{S} \cdot DH_{12} = 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ (Afm with
	complete SO_4 substitution)
w/c or w/b	Mass ratio of water to cement or binder (cement + mineral
	admixtures)

Glossary¹

Air Void Distribution	Air voids are incorporated in the cement-paste phase of concrete to provide space into which the water can flow as it expands on freezing, thereby reducing the possibility of internal stressing and cracking. The size and distribution of these voids to allow minimal distance between any water molecule and the nearest air void are the parameters that determine the
Aggregate	resistance of the concrete to freeze/thaw cracking.
Aggregate	Granular material (e.g., sand, stone, gravel, crushed stone, or iron blast- furnace slag) that is used with a cementing medium to form hydraulic- cement concrete or mortar (see ASTM C125-94).
Agglomerate Small particles bonded together into an integral mass.	
Bleeding	Settling of solid particles in concrete with a concurrent increase in proportion of mixing water at the surface.
Clinker	Nodular manufactured product that is ground to produce cement powder.
Cement	Viscous paste and hardened product of a mixture of cement powder and
Paste	water.
Concrete	A composite material that consists essentially of a binding medium in which are embedded particles or fragments of aggregate; in a hydraulic- cement concrete, the binder is formed from a mixture of hydraulic cement and water (see ASTM-C125-94).

¹Definitions compiled from various sources. Where appropriate, an ASTM Standard is cited.

Cover	Layer of concrete covering a reinforcement.
Fly Ash	Finely divided residue that results from the combustion of ground or powdered coal.
High-Range Water Re- ducer	e Surfactants that allow a workable mix to be produced at low w/c ratios.
Law of Mix tures	- The property, P, of a composite mixture of materials A and B is equal to the sum of the values of that property for each component multiplied by the volume fraction of the component: $P_{composite} = P_A V_A + P_B V_B$.
Model- Based Design	Method of designing new materials, structures, and systems quantitatively rather than intuitively, using all pertinent information simultaneously and synergistically.
Mortar	A product of the mixture of cement powder, water, and sand that is used to bond large blocks (e.g., bricks, cement blocks).
Portland Cement	A hydraulic cement produced by pulverizing clinker consisting essentially of hydraulic calcium silicates and usually containing one or more of the forms of calcium sulfate as an interground addition (see ASTM 150-95).
Pozzolans	Siliceous and aluminous materials that possess little or no cementitious value in themselves but that will—in finely divided form and in the presence of moisture—chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (e.g., fly ash, silica fume, rice husk ash, volcanic ash).
Rebar	Steel bars used to reinforce concrete.
Slump	A measure of the workability of fresh concrete, determined by tamping the concrete into a cone, removing the cone, and measuring the decrease in height of the concrete mass.
Stucco	A plaster of any composition used to coat the outside walls of buildings.
Thixotropy	The prospensity of gels to become fluid when disturbed.