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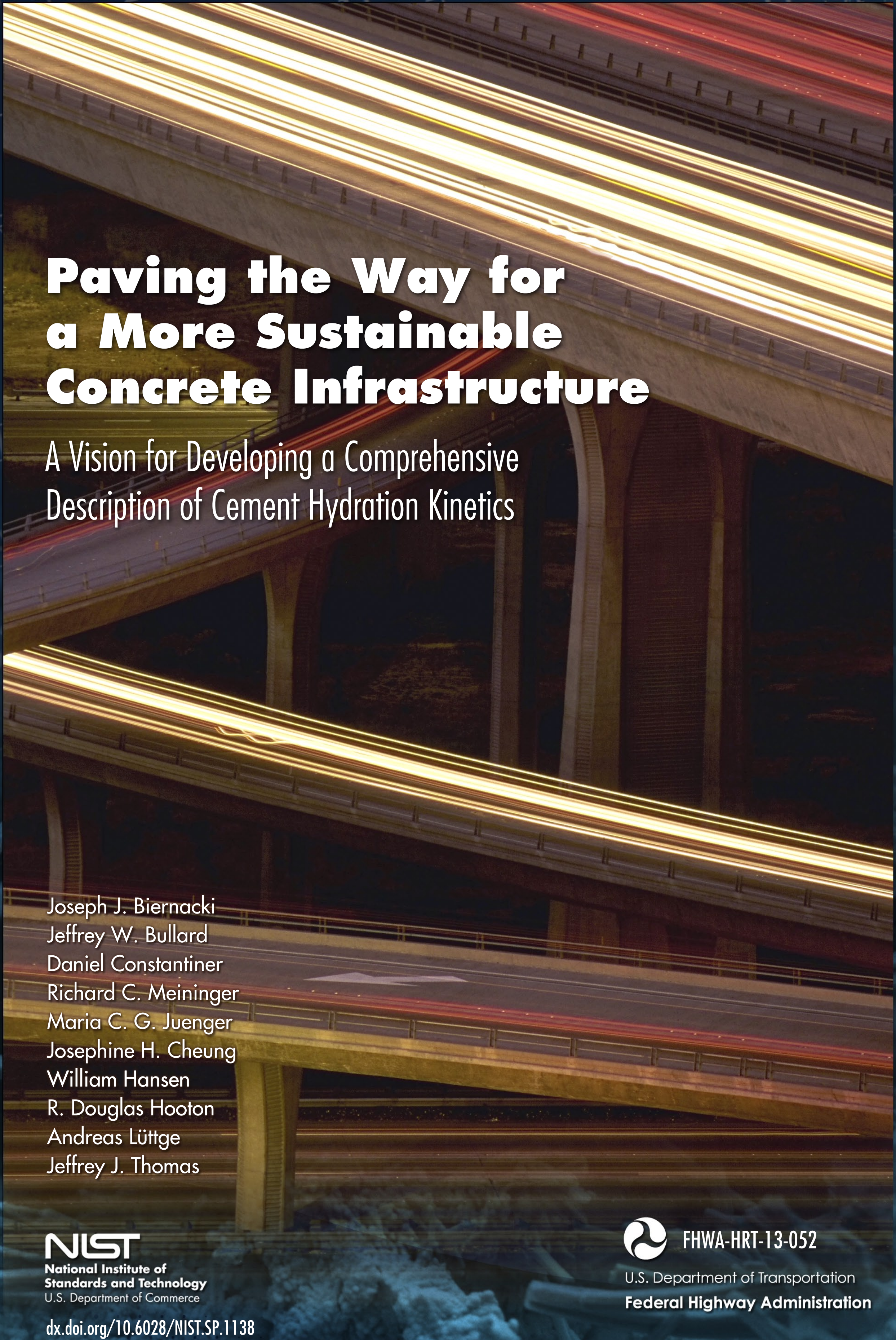

Paving the Way for a More Sustainable Concrete Infrastructure

A Vision for Developing a Comprehensive Description of Cement Hydration Kinetics

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Foreword

Concrete is far and away the most abundantly used man-made material on the planet. As a construction material, it is unique in its capacity to be formed and finished into an almost unlimited variety of shapes, textures, and colors. It can be made on demand with portland cement and inexpensive local materials. With correct placement and use, concrete can have a service life of 50 years to more than 200 years. Improving the proper and efficient use of concrete and portland cement requires better understanding of the chemical process of hydration, and how that process can be characterized and modeled – both for pure portland systems and for those containing admixtures and supplemental cementitious materials such as fly ash, slag cement, and others. Having interactive computer models, based on sound experimental data, for the chemical and physical interaction of cementing compounds, molecules, and ions in the concrete pore-water solutions will help both to improve cement manufacture and to optimize sustainable concrete mixtures.

Importantly, concrete has the *lowest* embodied CO_2 content of any major material used in construction, including glass, steel, and wood. But so much concrete is produced annually that it still accounts for about 8 of industrial CO_2 production. Therefore, reducing both the CO_2 contribution and embodied energy of concrete is a societal challenge that must be addressed to ensure a sustainable built environment and transportation infrastructure. One way to reduce concrete's CO_2 contribution is to lower its embodied CO_2 and energy content and even further, typically by both more efficient production of cement binder and partial replacement with supplementary cementitious materials or fine mineral fillers. This approach is already being used, but often with uncertainty in the way the binder will perform. Concrete is typically *overdesigned* by at least 10 % because of the inability to ensure the exact performance of the binder material. Therefore, the ability to accurately model cement hydration kinetics and predict and improve the performance of concrete as it hydrates could lead to a 1 % reduction in the mass of cement and concrete used each year and significantly reduce concrete's embodied CO_2 content. Achieving these objectives will require more comprehensive and fundamental knowledge of the hydration process that is responsible for the hardening, strength gain, and ultimate durability of concrete.

The National Institute of Standards and Technology (NIST) and the U.S. Federal Highway Administration (FHWA) recognize the importance of obtaining that knowledge through sustained and coordinated research. *Paving the Way for a More Sustainable Concrete Infrastructure* is a joint NIST/FHWA report that provides a detailed vision for focused experimental and computational modeling research that will provide the knowledge and translate it to industry tools for improved cements, mixture design, and service life prediction of concrete in service. The document is the direct outcome of the "International Summit on Cement Hydration Kinetics and Modeling," which assembled hydration experts from academia, government, and industry to identify the most important gaps in knowledge and to formulate strategies for filling those gaps. Their findings have been distilled in this document. NIST and FHWA therefore view this as a foundational resource and roadmap for coordinated concrete research and to secure the necessary sustained funding and focus for ensuring a sustainable national infrastructure.

Paving the Way for a More Sustainable Concrete Infrastructure

A Vision for Developing Comprehensive Description of Cement Hydration Kinetics

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Abstract

Hydration of portland cement is the cornerstone of the process responsible for microstructure development in concrete and ultimately controls the kinetics of all materials properties that make concrete such a useful product for society (properties such as setting, strength, permeability, and durability). comprehensive understanding of, and model for, cement hydration will enable new applications that require better control of concrete properties. Recent advances both in experimental and in computational technology are providing unprecedented insights into the nature of cement hydration. While a comprehensive theory is not yet available, recent progress suggests that what were once thought to be the most elusive hurdles are now within reach. number of simulation platforms are now available, along with emerging modeling strategies that could provide multi-scale linkages for the development of engineering models and computational research tools. Similarly, new experimental methods are yet to be fully exploited, although some are now positioned to offer real insights and breakthroughs. Ultimately, a more coordinated effort must be undertaken that will enable research teams to assemble and focus on specific tasks identified within a Roadmap for developing a comprehensive description of cement hydration kinetics, rather than individual efforts being spent on isolated tasks. The objective of this document is to establish an outline for the efficient development of data and related models that will enable predictive approaches for concrete materials use and new materials realization. This new path is needed for the continued technical leadership of the U.S. in the development and maintenance of a sustainable civil infrastructure.

This report is not intended to be scholarly review on hydration kinetics, but rather a summary that articulates what appears to be some of the most important aspects of cement hydration that currently are limiting our ability to quantitatively describe an mathematically model hydration phenomena. The summary herein is being published in conjunction an as companion to series of recent scholarly reviews [1–5].

Executive Summary

The following document is the direct outcome of an international collaboration between the US and Canada entitled, the “International Summit on Cement Hydration Kinetics and Modeling.” Funded by various agencies in the two countries[*] the summit provided a review of the state of knowledge on hydration kinetics in the following seven thematic areas: (1) mechanisms; (2) modeling and simulation; (3) experimental techniques; (4) chemical admixtures; (5) supplementary cementitious materials; (6) alternative cements; and (7) thermochemistry. Fifty-two engineers, scientists and students from six countries, met at Laval University on July 27, 28 and 29, 2009. The contingent overwhelmingly agreed that being able to control the process of cement hydration is key to the development of sustainable concrete materials. The term “sustainable materials” in this context encompasses formulations based o traditional portland cement chemistries as well as new emerging systems that promise smaller carbon footprints. Collectively, the group also agreed that new instrumental and computational tools offer opportunities to tackle the century long pursuit to understand the mechanism of portland cement hydration and to recreate the process quantitatively and predictably using computer models. Six summit sub-teams were assembled to write state-of-the-art reports that comprised the seven topic areas of the summit. Those papers were used to generate this document, which enumerates and maps the 4 specific research needs or questions that if answered would enable the development of robust tools for predicting hydration kinetics and open the door for the development of next generation concrete infrastructure materials.

Why are kinetics so important? A number of examples should help an answer to emerge. Modern metallurgy utilizes kinetics to manipulate ore processing and to control solidification, crystallization and solid-state phase transformations and, as result, has given us super-alloys, stainless steel, lightweight alloys, corrosion resistant metals and high temperature refractory metallurgy. By controlling the kinetics of organic synthesis, polymer science is able to produce designer macromolecules on demand and the pharmaceutical industry can quickly synthesize new drugs for testing and scale-up to production capacity predictably. Detailed kinetic knowledge of how trace quantities of critical elements react and are transported within semiconductors is required to reliably produce millions of computer chips yearly with astonishing quality control specifications measured in parts per million or parts per billion. Finally, at the heart of modern crude oil refining are numerous kinetically controlled processes including catalytic cracking and hydro-treating. Without sophisticated computational modeling, it would be difficult to control, design and operate refineries to quickly respond to changing market demands and crude feed variations. These examples illustrate that knowledge of kinetics leads to control of outcomes, predictable design, engineered decision making and ability to respond to the changing environmental and economic landscape. Each of the five industries mentioned above, metallurgical, polymer, pharmaceutical, semiconductor and refining, have invested heavily in kinetics and kinetic modeling research in an effort to establish control of product quality and the evolution of their technology.

Equipped with extensive knowledge of cement hydration kinetics, the cement and concrete industry could be revolutionized. Cement manufacturers would be able to tune their raw material proportions, burning conditions, and grinding to achieve portland cement binders with prescribed, optimized reactivity for market demands in different industry sectors. Chemical admixture suppliers would be able

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[*] National Science Foundation (NSF), Federal Highway Administration (FHWA), W. R. Grace, BASF, Mapei, Canadian Research Center of Concrete Infrastructure (CRIB), and Natural Science and Engineering Research Council of Canada (NSERCC)

to design additives to selectively modify the rates of different reaction mechanisms to achieve tailored induction periods, workability, and setting time. Ready-mixed suppliers would be able to forecast exactly the influence of supplementary cementitious materials on early-age behavior, and would know how to adjust mixture proportions and handling in response to seasonal variations in temperature at the time of placement. Every one of these advantages would lead to more predictable behavior, dramatically less returned concrete and corresponding material waste, and the use of higher proportions of industrial byproducts in cementitious binders, all of which would translate to a more sustainable civil infrastructure. Unfortunately, the cements community has not put forward a coordinated, well-funded effort to understand and control kinetics, though notably there is some high-quality published research on the subject and advances being made. The challenges that lie ahead, including increasing interest in sustainable construction practices, the direct reduction in greenhouse gas emissions and the development of new technologies in response to performance-based specifications, must be met with increased commitment to discover the fundamental principles that govern the transformation of anhydrous cement phases to hydrous materials.

In summary:

Hydration Mechanisms – For over five decades, the prevalent explanation for why cement hydration exhibits an induction period, followed by a main hydration peak and slow hydration that extends for years, has been the barrier layer-diffusion control hypothesis. This hypothesis has never been directly demonstrated and is now seriously under question by most researchers. A layer may exist, but new experimental evidence and modeling results are converging in support of alternative and simpler explanations that involve hydroxylated surfaces, nucleation and a two-step densification, growth and space filling processes. Models as well as new experimental evidence in support of these hypotheses are also emerging. While the quest to experimentally validate or refute the barrier layer hypothesis continues, new experimental methodologies now offer unprecedented insights into surface phenomena at the nanometer scale with time resolutions that will enable researchers to isolate the factors that govern cement phase dissolution, subsequent hydration and how admixtures interact at early ages. Techniques such as vertical scanning interferometry (VSI) and X-ray nanotomography along with molecular dynamic simulations and solution-phase based chemical kinetics models can be new focal points in conjunction with traditional techniques which include various forms of microscopy, chemical microanalysis, calorimetry, X-ray and neutron scattering, and nuclear magnetic resonance (NMR) spectroscopy. These techniques can provide experimental details to validate the modeling predictions.

Modeling and Simulation – The past two decades have been dominated by pixel-based strategy for generating cement microstructure developed at the National Institute of Standards and Technology (NIST). The well-known simulation environment, called CEMHYD3D, uses largely empirical rules and a single, likewise empirical, global rate law with no fundamental connection to solution phase chemistry evolution. The summit participants recognize the great contribution of this pioneering work, yet agree that this strategy must be superseded with one which links solution phase chemistry, transport phenomena and thermochemistry through fundamentally sound kinetic frameworks aligned with past work. As is typical of such endeavors, modeling is somewhat ahead of experiments, but VSI in combination with molecular dynamic simulation is now one route to advance the understanding of basic rate laws and reaction mechanisms. What is clear is that models that link to the basic chemical and physical mechanisms are being, and must continue to be, developed and directed to connect these basic processes to macroscopic behavior so that they will be useful for designing clinker phases, for mixture proportions, for admixture optimization, and for predicting life cycle behavior of concrete. These connections will inevitably require models to bridge length and time scales such that user-friendly models can be produced and widely adopted by the concrete industry.

Experimental Techniques –The past 5 years have been dominated by calorimetry, microscopy (optical, electron and X-ray), microchemical X-ray analysis, X-ray and neutron scattering and, to a lesser extent, NMR and other forms of spectroscopy. Summit participants agree that these tools will continue to be among the mainstream approaches, but that new insights will likely emerge through the application of new and developing analytical methods such as VSI, atomic force microscopy (AFM), nuclear resonance reaction analysis (NRRA), broadband time-domain reflectometry (BTDR), X-ray nanotomography and nano-X-ray chemical analysis, and high resolution electron microscopy. Already, high resolution electron microscopy is providing support for the recent two-stage hydration hypothesis, and X-ray nanotomography is offering a real-time window into the chemical and microstructural changes within cement paste. These newer techniques will complement the more traditional microstructural and macroscopic characterization methods to enable the development of detailed kinetic data sets for cement hydration.

Admixtures –Many chemical compounds are available for altering some property of fresh concrete, and each interacts with hydrating cement phases in mechanistically unique ways. Even when admixtures are used for functions such as altering rheology or controlling shrinkage, they may still effect hydration. Furthermore, even within class, say set-altering admixtures, there may be multiplicity of mechanisms that produce similar effects. This is further complicated by the fact that we do not have a mechanistic understanding of how cement phases hydrate, even in the absence of admixture chemicals. Without that basic understanding it is difficult to determine how admixtures operate. Ultimately, a generalized way to predict chemical interactions with cement phase surfaces and ionic species must be sought so that the effect of any given chemical on hydration can be predicted *priori*. This is a challenging task, one that will benefit greatly from molecular simulation, computer-aided molecular design (CAMD) and focused kinetic experimentation.

Supplementary Cementitious Materials (SCMs) – Most high-performance cementitious systems designed for improved durability characteristics and lower CO_2 consumption contain one or more SCMs at replacement levels ranging from 5 (silica fume) to 50 or more (ground granulated blast furnace slag). SCMs present many challenges since they, like admixtures, vary in composition and physical characteristics. Today, each SCM is typically treated as a unique material. Even within classes of SCMs, individual sources of materials are treated as though they are unique. What key physical and chemical features of an SCM determine its reactivity and how do they impact on the reactivity of cement phases when used as partial cement substitutes in blended cement systems? This question can be answered by developing kinetic models that incorporate solution phase chemistry and the physical and chemical characteristics both of the cement and of the specific SCM in question. However, the basic kinetic and thermodynamic data are not fully available at this point. Computational strategies such as molecular dynamic modeling, together with the application of experimental methods such as VSI, will likely advance progress in this area.

Alternative Cements – Alternative cements, several examples of which are described in Section II.7, might be categorized as engineered variations of existing SCMs or radical modification of clinker chemistry that form cements. To some extent, the chemistry of alternative cements overlaps with that of portland cement, and to some extent it broadens the field. For example, we include in this category portland cements that have been modified by the addition of fine limestone particles to enhance the early-age kinetic behavior. Kinetic data are even scarcer for alternative cements than they are for portland cement, and quantitative models d not exist. The challenges facing this community are daunting. What chemistries might be tested? What are the projected costs o the industrial scale? Which materials will have suitable life cycle performance characteristics? Until these questions can be answered systematically, alternative cements will continue to have limited ranges of applicability, higher cost barriers, and/or performance concerns.

Brief History – Full appreciation of this report's recommendations requires a brief historical review. The Center for Advanced Cement-Based Materials (ACBM) has provided focus for materials science research on cementitious materials in the US since 1989. Though it never included a significant thrust in the area of kinetics, it did emphasize modeling and enabled the development of CEMHYD3D and other modeling tools. In recent years, ACBM has become an independently funded entity and its emphasis has moved away from topics such as the fundamental chemical interactions of cement phases. Efforts for more than a decade at the National Institute of Standards and Technology (NIST) to develop the Virtual Cement and Concrete Testing Laboratory (VCCTL), a platform for the development of fundamental models and their use as practical tools, have contributed the more recent HydratiCA code, the first comprehensive effort to fuse solution phase chemistry, kinetics and transport processes into a generalized modeling environment for cementitious materials. VCCTL has also contributed model-based tools that are used for education and research in the US and around the world. The most recent link in the hydration kinetics chain is the new industry-funded Concrete Sustainability Hub (CSHub@MIT) at the Massachusetts Institute of Technology (MIT). This new thrust promises to be a significant contributor to any effort to develop generalized kinetic theories for cement hydration.

Th Path Forward – It is clear that the cement and concrete manufacturing sectors, as well as the agencies, owners, engineers, and architects using concrete, would benefit greatly from a coordinated multidisciplinary effort o hydration kinetics. Thus, the following single recommendation is made – ***to form an organization for cement hydration kinetics that will act as focal point for relevant research and planning for the concrete materials of the future***. The organization could take the form of a consortium of stakeholders and partners, potentially funded by government and industry and involving the academic community, National Laboratories and private sector research and development interests. A ambitious, cooperative structure is envisioned wherein industrial partners take an active role in the development and deployment of new technologies emerging from research. Industry, rather than having the typical passive role as funder and advisory board member, would be true research partners and, in addition, engage the initiatives as test beds for transferring technology, co-developed by the academic and research community, and offer an early introduction of research findings into the practices of their organizations. Furthermore, the consortium would be the embodiment of an effort that combines cutting edge experimental techniques and modeling to create a process that provides feedback between the two. Through the proposed organization, we hope to begin, "Paving the Way for More Sustainable Concrete Infrastructure."

Context of this Document – The vision for productive future research in cement hydration contained herein is formatted in terms of series of critical, unanswered research questions, along with a description of the activities necessary to make progress on understanding and controlling the kinetics of the reactions in concrete. However, note that this document does not exist in isolation, but instead is tied to other recent roadmaps for the concrete industry. The ACI roadmap "Vision 2030: A Vision for the US Concrete Industry" [6] describes four topics that link directly to specific research needs related to kinetics: *Design and Structural Systems Constituent Materials Research Needs Concrete Production, Delivery, and Placement* and *Repair an Rehabilitation*. In fact, the present document includes a series of tables of research needs for hydration kinetics that are keyed to these four topics. In addition, it addresses research needs that will promote at least two of the key goals articulated in the International Concrete Repair Institute's "Vision 2020" roadmap [7]: *Improve Repair Material Design and Performance* and *Develop a Means for Predicting Repair System Performance*. Finally, the Federal Highway Administration (FHWA) maintains the Concrete Pavement Road Map (called the "CP Road Map"), which was updated in 201 [8]. Volume II of the CP Road Map describes detailed research needs categorized into 12 comprehensive "Tracks" of research. Hydration knowledge, models, and data are called for in several of the tracks and sub-tracks -- such as "Subtrack 1-1. Performance-Based Mix Design and Specifications", which recognizes that "multiscale models are needed to predict and guide the entire concrete paving process, from microstructure to performance." Other research track objectives in the CP Road Map, such as the use of reaction thermal proprieties, more effective curing, and fast-track setting and strength gain for accelerated construction would also be advanced through understanding of hydration kinetics.

I. Introduction

The quest to identify the underlying mechanisms that control cement hydration is among the more enigmatic problems in modern materials science. More importantly, the lack of such knowledge appears to be an obstacle to the development of next generation hydraulic construction materials that have sustainable characteristics and improved life cycle performance as compared to existing portland cement technology. Among materials, portland cement concrete is unique in that the final product, a complex composite made from aggregate (rocks and sand), water, small amounts of other additives known in the industry as admixtures, portland cement and SCMs are formulated on demand and are processed to some extent at the point of use. This recipe is followed thousands of times each day as this most used engineered material on earth is applied to construct mankind's infrastructure across the planet. Our inherent lack of knowledge about how to control the hydration process makes improving, predicting and controlling the performance of portland cement concrete a difficult task that is accomplished today by trial-and-error experimentation combined with the experience of engineers and technologists. But as concrete materials and formulations become more complex to meet the economic and environmental challenges of the future, experience with yesterday's formulations will be of limited use.

It would be incorrect to say that not much research progress has been made o cement hydration kinetics in the past three decades or so, since one might draw that conclusion based on the list of questions that remain, a list that seems to echo the work of Gartner and Gaidis [9]. In contrast, advances in instrumental analysis and careful analytical chemistry have offered considerable insights. The inherent problem is that we simply do not have fundamental, underlying theory that describes how portland cement is transformed into the spectrum of hydrates, particularly the primary hydrates known as calcium silicate hydrates (C-S-H), that make up the binder in concrete. Furthermore, it is unclear how or if the existing database of experimental information can be used to discover such a theory. Breakthroughs in our ability to alter and control material properties and to improve performance have generally come along with understanding about their synthesis and physicochemical behavior at the most fundamental levels. And, while such are largely known for some classes of materials including metals, polymers, and semi-conductors, equivalent theories are not available for concrete and its binding matrix, portland cement.

In recent years, there have been a number of isolated studies of various aspects of hydration but, unfortunately, there has not been a focal point for a large-scale thrust to *clear the remaining hurdles*. In December of 2006, three of the authors, Biernacki, Bullard, and Hansen met to discuss their mutual interests in cement hydration modeling. At that time they crafted an idea that would eventually take shape as an international workshop on hydration kinetics, now known as the ***International Summit on Cement Hydration Kinetics and Modeling*** [10]. This vision document and five companion papers [1–3,5, 11] o various aspects of cement hydration are the outcomes of the Summit.

While the thematic basis of the Summit was cement hydration kinetics, the program was divided into six subthemes that addressed related or enabling topics. Based upon the number of contributions offered at the Summit and the amount of time spent on each, the various subtopics have been divided into three Primary and four Secondary themes, all of which are now summarized.

Primary Themes

Mechanisms – In the field of kinetics, mechanisms define the molecular-scale processes that control the rate at which something happens. Portland cement hydration encompasses both chemical and physical changes, so explanations of how these changes happen likewise must incorporate both chemical and physical mechanisms. In kinetics, mechanisms are the pathways by which chemical or physical changes take place. Knowledge of mechanisms gives engineers the insight needed to intentionally manipulate material behavior. Without such knowledge, engineers must use their past experience to guide them in solving problems and designing new formulations, which is a trial-and-error proposition when formulations change substantially.

Models and Simulations – In the past, models were mathematical devices used to explain experimental data – without the data, models could not be calibrated and parameters could not be estimated. And, while modern models continue to serve this purpose, new tools such as molecular dynamic simulation are now being used to discover mechanisms and to estimate parameters that can be used in other models. In a sense, modern models *beget* models. It turns out that the length and time-scale of the desired information are important in determining what kind of model is used. To predict the behavior of “Y” at length or time scale “x”, “Y” must be described at a scale that is at least as small as “x and likely smaller. Most traditional kinetic models predict macroscopic performance based on microscopic information. Modern modeling strategies utilize tools that can predict nanoscale events, which can then be up-scaled as inputs to micro-scale models, at least in principle if not often in practice. But this kind of multiscale approach is likely to play a significant role in discovering and developing a universal modeling strategy for cement hydration.

Experimental Techniques – Experimental techniques effectively enable hypothesis generation and also limit the extent to which new hypotheses can be validated. New methods are continuously being developed and old ones are being used in new ways to discover mechanisms and observe hydration behaviors at many length scales. Calorimetry, electron microscopy, thermal analysis and x-ray diffraction continue to be primary tools since they are generally available to all researchers in laboratories around the world. Neutron and synchrotron radiation are also being utilized to lesser extent at larger research facilities. NMR, however, is being used for cement by a still smaller number of investigators, probably because of the highly specialized background and facilities that are required and material limitations associated with cement (e.g., paramagnetic materials, such as iron, interferes with NMR). Similarly, transmission electron microscopy is somewhat underutilized because it requires highly specialized training and sample preparation. Atomic force microscopy (AFM), despite its widespread availability, has been somewhat underutilized technology. Newer methods, such as VSI, nano X-ray tomography, broadband time-domain reflectometry spectroscopy (BTDR) and nuclear resonance reaction analysis (NRRA), are just now emerging as potential contributors.

Secondary Themes

Chemical Admixtures – Chemical admixtures are materials that are added to the concrete mix formulation in an effort to alter fresh (fluid) or hardened properties. Some admixtures are deliberately used to change hydration behavior, but others must be designed to change properties such as flowability without altering the rate of hydration or setting kinetics. Admixtures have been used since Roman times and were widely used in the making of pozzolanic cement by the Romans. New admixtures are developed based on a general understanding of mechanisms involved. However, the design of new admixtures and the prediction of how existing ones will behave in various mixture formulations are difficult because the detailed mechanisms required for modeling the interaction of different admixtures with the cementitious components are not known with sufficient accuracy. Ultimately, an understanding of how portland cement hydrates may be obtained through careful study of how admixtures interact with cement phases.

Supplementary Cementitious Materials – The use of waste or byproduct materials that have cementitious properties is an obvious route to more sustainable concrete construction practices. This, however, adds more degrees of freedom and possible interactions that are often understood even less than the hydration of cement clinker phases. Nonetheless, the use of supplementary cementitious materials (SCMs) as they are called, is crucially important for environmental benefits and, in some cases, improvements in performance or service life. Much is known about the empirical responses of concrete to SCMs, but mechanisms that describe the fundamental chemical and physical pathways leading to material property changes are not known with sufficient detail to develop predictive models.

Alternative Cements – The concept of alternatives to portland cement has been around for decades, but economic and performance considerations have limited alternative cements to specialty applications and laboratory curiosities. However, a sustainable future for concrete may be found in formulations that are well outside of the compositions that we presently consider as the norm. Assuming that these cements will still require hydration to achieve their hardened properties, it stands to reason that mechanistic information about reaction pathways and kinetics would pave the way for quicker development and implementation.

Thermochemistry – All chemical and physical transformations are driven by thermodynamic potentials. Without explicit knowledge of the thermochemical and thermophysical limits that govern cement transformation, it is unlikely that we will develop corresponding rate laws that govern the kinetic behavior of cementitious systems. Therefore, thermochemistry and thermodynamics in general is an enabling, crosscutting discipline. Unfortunately, this area was underrepresented at the Summit and will not be reported on here.

II. Hydration

II.I Overview

This document is intended for those with a scientific background but who may not necessarily be familiar with cement hydration and chemistry. Therefore, we provide a brief introduction to the key concepts to aid in understanding the remainder of the document. Portland cement (PC) is made up of five major compounds: tricalcium silicate (C_3S)[†] dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF) and gypsum (calcium sulfate dihydrate, CH_2$). C_3 (actually the impure form of C_3 known as alite, a Mg, Al and Fe bearing combination of the polymorphs) is the major constituent of Type I, II and III cements), so it is frequently used as a model in place of the more complex multiphase system. The hydration of alite, and likewise of portland cement , is a net exothermic process (i.e. it releases heat) so calorimetric methods are often used to monitor the rate of hydration under various conditions. Figure 1 is a typical isothermal calorimetry curve for alite at 25^{o} and a w/c (water to cement mass ratio) of 0.4. Interpreting the shape of this curve has been the subject of debate for decades.

Bullard et al. [1] recently described cement hydration as having the following five stages shown in Figure 1: (1) an initial fast reaction period (Stage 1), (2) a period of slow reaction (Stage 2), sometimes called an induction period, (3) period of accelerating hydration (Stage 3), and (4) subsequent period of progressively decelerating hydration (Stages 4 and 5). While these stages have been described many times in the literature and have become the fingerprint for cement hydration, they are the unexpected result of an extremely complex process that is yet to be fully defined, even for pure cement phases such as C_3S. What follows are brief synopses of the most recent viewpoints concerning hydration of cements, organized by the six sub-themes listed earlier.

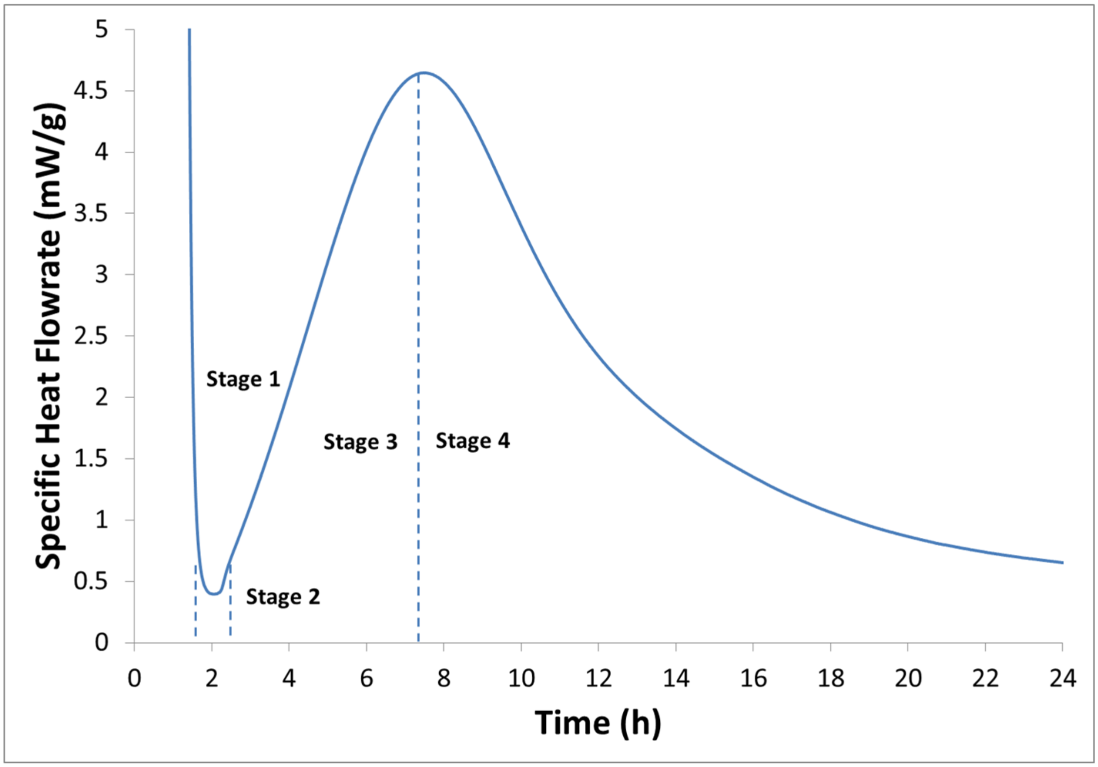

Figure 1. Typical alite calorimetry curve characteristic of C_3S (triclinic)-based hydraulic cements, data after Xie and Biernacki [11].

II.2 Mechanisms

[†] Cement hydration shorthand notation is used throughout wherein: C=CaO, S=SiO_2, H=H_2O, A=Al_2O_3, \$=SO_4, M=MgO, F=Fe_2O_3.

Mechanisms define the fundamental steps in a process. Rate controlling mechanisms are those steps that are slowest, those that control the observable kinetics, where “observable” is a relative term that might be defined by a timeframe and length scale that are relevant to the process and the objectives of the observers. Thus, when studying the kinetics of cement hydration, we ultimately must define events at time and length scales that suitably reconstruct macroscopic behavior in concrete since we, the observers, desire to predict and control the properties of portland cement concrete.

The rather simple looking calorimetry curve in Figure is actually the result of very complex interactions between tricalcium silicate and water. Understanding these events is critical to elucidating the broader problem of portland cement hydration, which involves four additional major components, C_2S, C_3A, $C\$H_2$ and C_4AF modified by the presence of potassium and sodium hydroxides and other trace constituents native to the cement or reactive constituents added to modify the behavior of the concrete. Early attempts to describe cement hydration utilized simple models that mostly ignored solution phase chemistry and assumed one, or a few at most, rate controlling mechanisms. While one could sometimes adequately fit experimentally observed hydration behavior with these models, none of them could be used to design new material chemistries or predictably engineer new microstructures and responses in cement or concrete.

So, where are the problems and what are the obstacles?

Until recently, there have been no quantitative models that could adequately describe the solubility behavior of C_3S. Thermodynamic calculations unequivocally predict that C_3 is extremely soluble in water, with equilibrium solution concentrations of calcium and silicates on the order of 10^2 mM (mmoles/L). This high solubility is clearly responsible for the high dissolution rates and rapid heat liberation during Stage hydration. However, the solution *never attains concentrations as large as* this thermodynamic solubility limit. In fact, the actual activity product is typically about 17 orders of magnitude less than the equilibrium value. The reason for this large discrepancy is a matter of considerable debate.

One hypothesis that has been around since at least 1964 [12] is that of the *metastable barrier layer*. This hypothesis is so well known in the literature and among those having even cursory knowledge of hydration kinetics that it has achieved dogmatic status with many researchers. However, there is no direct evidence that such a layer actually exists. Indirect evidence, from sophisticated experiments involving nuclear resonance reaction analysis [13,14] and recent NMR experiments [15] is compelling but not universally accepted.

What fuels the controversy is not the above stated hypothesis of a low-permeability metastable layer. Rather, the controversy is that there are altogether different hypotheses that can explain the observed behavior just as well. Barret [16], Nonat [17] and others contend that hydroxylated surface forms on the C_3 immediately upon contact with water, with this surface having an apparent solubility product constant on the order of 10^{-17}. To produce an experimentally observed peak in silicate ion concentration, nucleation of a stable form of C-S-H must occur within minutes, which then continues to grow slowly during Stage (2). This has become known as the “steady-state hypothesis.”

Notably, Bullard has demonstrated that either the metastable barrier layer or hydroxylated surface hypothesis can adequately predict alite hydration rates, there being only minor differences in the predicted evolution of the solution chemistry [18]. But there were certain assumptions or implicit mechanistic functionality that were necessary to also make either mechanism work; establishing that such mechanisms are present is a challenge to be proven empirically. This is clear example where modeling results may provide a clear experimental approach to resolve this difficult challenge.

Yet another hypothesis for the early-age kinetic behavior comes from research on the dissolution of various minerals other than alite, which has shown that their rates of dissolution can be abruptly decreased by a change in dissolution mechanism from unwinding of surface defects at high driving forces to step flow motion below a critical driving force. While some evidence exists that supports this hypothesis, such as direct observation of etch pits in alite surfaces, the body of experimental data is small at this time.

While it is generally taught that Stage (2) is a period in which the reaction becomes dormant, it is becoming increasingly clear that a true induction period only occurs when something interrupts or interferes with the ordinary progress of hydration. In actuality, Stage (2) is simply the point at which hydration is slowest. So, the more relevant question is, “What causes the rate of hydration to increase during Stage (3)?”

The main problem with the semipermeable barrier layer hypothesis described above is that on its own, such a layer would suppress dissolution rates, and therefore hydration rates, indefinitely. Thus, a companion hypothesis is necessary. This additional requirement demands that the layer material be metastable with respect to the eventual formation of a more stable form of C-S-H gel. This condition would permit continuous, though slow, hydration to proceed with the layer intact until the more stable form of C-S-H nucleates. How does this work? The metastable C-S-H (C-S-H(m)) has a higher equilibrium solubility than the more stable C-S-H, thus, once the stable form nucleates and begins to grow, the metastable phase simply dissolves. While this seems simple enough, the metastable C-S-H(m) is an elusive material that has yet to be observed directly.

In this case, there are three concepts that follow from the already mentioned mechanisms, any of which could potentially explain Stage behavior:

1. Nucleation and growth of a stable form of C-S-H destabilizes the metastable C-S-H, at least at its outer boundary, permitting large amounts of stable C-S-H to form.
2. Nucleation and growth of a stable form of C-S-H mediated by slowly dissolving C_3S.
3. Mechanical destabilization of a barrier layer (not necessarily chemically metastable layer).

Unfortunately, all three mechanisms can be shown to accommodate at least some of the experimental observations and all can be utilized in part to produce simulations that likewise are consistent with some of the experimental observations. Therefore, it appears that at this time there is no single model or hypothesis that quantitatively explains all observations, nor is there unequivocal experimental evidence to decide which, if any, of the hypotheses just described most closely describes the situation.

Considerable attention has been given in the past decade or so to the mechanisms causing the observed second and major hydration calorimetry peak that is associated with the onset of Stage (4). Since the late 60’s, it had been assumed that the onset of Stage (4) signaled the transition from nucleation and growth kinetics to diffusion-controlled kinetics, but this assumption is now being questioned. A new hypothesis that focuses on volume filling arguments and a two-stage growth C-S-H mechanism wherein low density morphology fills the pore space quickly followed by slow densification has gained credibility as and alternative explanation [19]. Most researchers still agree, however, that diffusion is likely to take over as the rate controlling mechanism at some later age. But the transition to diffusion kinetics is not clearly identifiable and little experimental research is available upon which to draw conclusions or inferences or upon which models can be tested. To be sure, most recent modeling has focused on Stages (0) through (4) in Figure 1. From different perspective, the movement of ions from hydrating cement grains to form hydration products and fill empty spaces in “dense” system (after several days of hydration) would be very similar to the ingress of ions responsible for concrete deterioration (sulfate, carbon dioxide), therefore, the ability to model later-age hydration has broader implications.

Unfortunately, as illustrated and discussed above, there are numerous plausible mechanisms that can explain the observed hydration characteristics for portland cement along with experimental evidence that partially supports each hypothesis. Furthermore, the classic framework for understanding how cement hydrates mechanistically has not changed much in the past three decades. Similarly, mathematical modeling has been shown to render simulations that can be made to behave like experimental observations, comply with thermodynamic constraints and yet be controlled by any number of hypothetical mechanisms. Thus, one can only conclude that there are a number of fundamental questions that must be definitively answered before we can be confident about the mechanism of cement hydration. These questions, unfortunately, have not changed much since about 1989 [9].

At this point, it appears that a great deal of effort has focused on understanding the hydration mechanism for C_3 and alite since tricalcium silicate in the form of alite is the primary component in ordinary portland cement. Even then the questions stated earlier remain. And, while it is necessary to continue to place emphasis on alite hydration, at some point it will become necessary to move towards more complex systems including C_3A, gypsum, etc. Although this statement seems obvious, the hurdles at this point are high, particularly since C_3 hydration is still not understood and there seem to be a number of important interactions between the silicate and aluminate phases that can be decisive in determining the time at which hydration begins to accelerate.

II.3 Models and Simulations

Great strides have been made in modeling cement hydration in the past two decades. The present state of cement hydration models might be best described as either meso-scopic, microscopic or nano-scopic/molecular. The meso-scale work is predominantly driven by the recent discovery by Thomas and coworkers that shows that boundary nucleation and growth (BNG) might be used to explain the induction period (Stage 2), the onset of Stage 3 hydration and the transition to Stage 4 hydration [20,21]. What seems to be rather simple now was obscured for years by our attempt to work with Avrami’s equation, which is mechanistically incorrect [20].

Computational environments that allow modelers to simulate microstructure development have made a significant contribution in the past two decades or so. Two simulation environments are now reasonably well developed: CEMHYD3D, from the National Institute of Standards and Technology (NIST), now embedded in NIST’s Virtual Cement and Concrete Testing Laboratory (VCCTL) [22] and μIC [19]. While different in many respects, both offer the opportunity to build and test various hypotheses in frameworks that can handle ensembles of particles. μIC’s strength is in its rather “open architecture” that allows the user to build kinetic or transport rules to govern phase changes and mass migration. The VCCTL, while primarily constructed around the NIST CEMHYD3D model which uses semi-empirical rules to mimic kinetic-like transformation, has been extensively disseminated in North America through educational programs offered by NIST.

Within the newer developments from VCCTL, microscopic modeling has moved from global kinetic and descriptive approaches towards distributed parameter strategies that account for real kinetics, transport phenomena, solution phase effects and compliance with thermodynamics. Presently, there is one model that excels in this arena, HydratiCA [18]. HydratiCA provides a rigorous computational environment via the application of kinetic cellular automaton that mimics the complex partial differential equations that arise from the microscopic mass continuity equations.

At the nano-scale, researchers are beginning to simulate hydrate structures from solution phase chemistry and have strategies for combining real-time nano-scale experiments with computational approaches that have been shown to offer insights about other through-solution mineral transformations. These new breakthroughs have generated optimism in the modeling community.

Thus, models of various forms and levels of complexity from molecular to those with simple global rate forms are presently being used to decipher experimentally-observed hydration data, which is likewise varied and multi-scale. Though molecular work is limited, it offers the potential for developing insights that could, to some extent, replace presently impossible-to-perform experiments and provide inputs for up-scaling to longer length and time scale models. It appears that a spectrum of modeling strategies is required since the problem is, in fact, multi-scale. Ultimately, useful engineering models may obtain inputs from both experimentally-derived parameters and those computationally-inferred. While this trend is being effectively exploited in other areas of materials science, it is yet to be well developed within the cements community, partially because of the complexity of the problem but primarily because the field of concrete research has historically been defined within the context of civil engineering instead of materials science.

II.4 Experimental Techniques

While the bulk of the experimental work on hydration continues to depend upon calorimetry, various X-ray and neutron diffraction and scattering techniques, electron microscopy, chemical analytical methods (e.g., energy dispersive spectroscopy) and, to much lesser extent, nuclear magnetic resonance spectrosocopy (NMR), there are more recently introduced techniques that are either making or have potential to make novel and critical contributions. Among the newer methods are: vertical scanning interferometry (VSI), atomic force microscopy, nano x-ray tomographic imaging [23], nuclear resonance reaction analysis (NRRA), and broadband time-domain-reflectrometry (BTDR) dielectric spectroscopy (DS). Unfortunately, most of these newer techniques require unique facilities and unique data processing methods that limit their widespread use.

Vertical scanning interferometry is a technique that is being successfully used in the geochemistry field to unravel the complex dissolution-precipitation kinetics of mineral interactions. The same technique should be utilized to study the hydration of cement phases and shows great promise [24]. In general, the technique utilizes visible light, generating interference patterns caused by interaction of two incident beams of monochromatic light. The interference patterns are used to produce a topological map of the scanned surface. High-resolution forms of this technique are capable of sub-micrometer horizontal resolution, and sub-*angstrom* vertical resolution, of surface features in real time and in the ambient aqueous environment. This means that samples can literally be visualized with unprecedented resolution *as they react*. Among the exciting opportunities for this technique is the direct imaging and quantification of rates of dissolution at any stage of hydration, and the imaging of the mechanisms of dissolution and nuclei formation. The technique promises to enable the discovery of the morphology of both dissolution and precipitation events and when combined with related modeling techniques, most recently the use of kinetic Monte Carlo simulations (kMC), there is hope that intrinsic (elementary) kinetic rate laws might be discovered.

Monteiro [25], Artioli [26], and Lange [23] recently reported on a nano X-ray tomographic method wherein individual cement grains could be directly imaged in three-dimensions without drying over a long period of time. This work, while not yet quantitative, shows the evolution of microstructure in a volume that contains only a few cement particles. The qualitative images clearly show the dissolution and conversion of some particles into products, the consumption of pore space (water filled voids), the relative rates of reaction of various particles and various unexpected events such as the production of porosity due to the dissolution of particles that leave voids. If developed into a quantitative tool wherein particles and products can be identified by their chemical composition and volumes of individual phases tracked as a function of time, this technique may offer new insights into the kinetics of at least micro-scale distributed events, and thus generate an entirely new opportunity for combining modeling and experimental datasets.

technique that has already shown considerable promise as a tool for probing very near surface real-time events during hydration is nuclear reaction resonance spectroscopy. Thus far, researchers Livingston and Schweitzer [13] suggest that this technique provides good indirect evidence of a barrier layer forming during the first minutes of hydration, and they have even offered an estimate of its transport properties and thickness. And, while the present data may be interpreted in various ways, the technique may provide transport and microstructure related inputs for model development.

II.5 Admixtures

Admixtures are a broad and complex field, particularly because the range of admixture behaviors and their chemical compositions vary widely from simple inorganic salts such as calcium chloride (a set accelerator) to polycarboxylate comb polymers (used as superplasticizers). And, since the desired behaviors sought from these admixtures are so diverse (e.g., water reduction, set retardation or acceleration, rheology-alteration, air entrainment, strength enhancement, shrinkage reduction), it is unsurprising that the modes or mechanisms of their effects are likewise diverse. Furthermore, since the underlying kinetics of cement hydration are not well understood, it becomes yet more difficult to interpret and predict the behavior of additives and to discover and design new substances with targeted performance characteristics. Among the hypothesized forms of admixture activity are surface adsorption, nucleation site or growth face poisoning, ion chelation, surface tension reduction and solubility alteration. Examples of each of these are well documented in the literature, although in most cases the mechanisms of activity remains the subject of hypothesis only. Virtually nothing has been done to develop chemical-based models for admixture activity and it remains an open field at this point. This is likely because the broader questions regarding the mechanism of alite hydration continue to be unanswered. As a result, new admixtures are most often developed by trial and error, making incremental changes to existing known admixture chemical scaffolds. This is a time-consuming, costly, and inefficient strategy. Mechanistic insights into how cement hydrates as well as how admixtures interject into the process would open up alternative design strategies to advance admixture development, including promising new tools such as computer aided molecular design (CAMD) strategies [27].

In general, the problem is not the lack of data on the impact of admixtures nor the lack of hypotheses to explain some of the most well-characterized interactions (e.g. the retarding effect of sucrose), but rather that these hypotheses have not been reduced to theories, nor has there been any significant effort to quantitatively assemble them into mathematical formalisms. The result is a general absence of experiments designed to directly reveal kinetic insights in coordination with like modeling efforts in the area of admixture-cements interaction. Among the pressing challenges is the general relationship between admixture chemicals, sulfates, aluminates, ferrites and silicates in cementitious systems as well as those containing supplementary cementitious materials.

II.6 Supplementary Cementitious Materials (SCMs)

SCMs typically include silica fume, blast furnace slag, fly ash, and metakaolin. Notably, other natural or synthetic mineral-based materials may also be used, though some are not necessarily cementitious (e.g., fillers such as limestone powder), yet such may interact physically or chemically with hydrating clinker phases. The wide range of materials used as SCMs or as fillers and their likewise wide range of chemical compositions and physical states makes it difficult to generalize their behavior. The grand majority of these may be mapped onto the C-S-A (CaO-SiO_2-Al_2O_3 ternary phase diagram, though they range in crystallinity, and hence solubility and reactivity, from pozzolanic (reactive with CH) and hydraulic (reactive with water alone) to inert or very low reactivity. Adequately characterizing their composition and often amorphous structure, and linking these characteristics to the reactivity, is a technical barrier to using these materials at higher replacement volumes.

II.7 Alternative Cements

There are many chemical alternatives to portland cement, that is, C_3S-dominated cement, but four of the most prevalent alternatives are: (1) calcium aluminate cements; (2) calcium sulfoaluminate cements; (3) alkali-activated binders; and (4) supersulfated cements. The chemistry of these systems might be classified into two groups: (1) those related to the portland cement family, e.g. anhydrous calcium silicates and aluminates or sulfated forms which interact with water via through-solution reaction mechanisms to form various stable and metastable crystalline and amorphous hydrates; and (2) those that are associated with glassy or nano-structured anhydrous phases, such as fly ash and blast furnace slag, metakaolin and similar materials. However, since each is dominated by the hydration of different raw materials, C_3 in the case of calcium aluminate cements, ash, slag and/or metakaolin in the case of alkali-activated cements, it is necessary to understand the hydration pathways likewise. And, while there have been kinetic studies, there have been no significant efforts to systematically reduce the information to mathematical models and interpretations, not even to the extent done for C_3S-based cementitious systems. The primary obstacles to more widespread use of such alternative cements are discussed for each of the four types individually.

Calcium aluminate cements have been shown to have rapid strength development, to be resistant to abrasion and sulfate attack and to produce 50 less CO_2 than portland cement during manufacture. Unfortunately, the hydration pathway passes through metastable hydrates with significant half-lives, measured in years at ambient conditions, which ultimately convert into stable hydrates, thereby releasing water, AH_3 gel and generating porosity. Ways to mitigate, control and or eliminate conversion or its effects are among the most pressing challenges for calcium aluminate cement developers. Presently, the value of bauxite sets the commercial price of aluminum-based cements, making it expensive relative to portland cement. Therefore, modeling the processes would allow for virtual testing of potential solutions.

Calcium sulfoaluminate cements (CSA) are dominated by the presence and hydration of ye'elimite ($C_4A_3\$$) and are generally produced in a belitic (C_2S) or ferritic (C_4AF) form. In general, CSA cements exhibit rapid hardening, high-strength, expansion and self-stressing behavior. Manufacture of CSA requires temperatures that are about 100 °C to 200 °C lower than required for portland cement. In addition, they require less grinding energy to produce the cementitious powder. Overall, production of CSA cement releases less than 50 of the CO_2 on a finished paste volume basis as compared to ordinary portland cement. Currently, the primary obstacles to widespread use of CSA cements are its high cost and low alkalinity (pH of 1 to 12), the latter which may not provide adequate passivation against corrosion of steel rebar.

Alkali-activated cements are typically formulated by mixing fly ash, blast furnace slag and/or metakaolin with a highly alkaline solution. The resulting mixture produces gel phases, of which two forms are generally recognized, a C-(A)-S-H form which is highly cross-linked and mostly amorphous and a zeolitic gel that resembles a zeolite structure on very short length scales, but is largely amorphous as well. By some estimates, the use of such binder systems may reduce CO_2 production by as much as 80 as compared to portland cement. At this time, however, this form of cement, special class of which are sometime referred to as geopolymeric cement, is limited geographically and has uncertain long-term durability properties. Although these systems exhibit through-solution chemistries and produce gelated products, the reaction mechanisms and pathways are somewhat different than those of the portland cement family of crystalline starting materials. Not nearly as much work has been done on the kinetics of such reactions; however, a well-established qualitative reaction path process has been worked out and to some extent portions of the process have been reduced to mathematical formalisms for subsets of materials (high calcium containing systems). Like portland cement, there is no unifying quantitative theory at this time that has been reduced to mathematical expressions. Thermodynamic models, coupled to kinetic expressions via solution phase composition, have been demonstrated to predict the phase assemblage and porosity quite well, though the paucity of thermodynamic data for low calcium systems limits the further development of such models at this time.

Supersulfated cements share kinetic aspects of both the portland cement family of alternative cements and the alkali activated family. This class of alternative binders almost exclusively utilizes blast-furnace slag as a starting raw material. Slags, typically containing higher alumina contents, are mixed with calcium sulfate (or hydrated forms or waste streams containing significant amounts of the same) and an alkaline activator. The resulting products are large amounts of ettringite and C-S-H with smaller amounts of hydrotalcite due to the relatively high MgO content of the slag. The production of ettringite and C-S-H make supersulfated formulations related to portland cements, though the glass phase dissolution process differs from the crystalline C_3 dissolution in portland cements. Interestingly, supersulfated cements exhibit an initial peak, dormant stage and main hydration peak. Once again, use of this alternative binder system is presently driven by CO_2 reduction. It does not appear that a significant effort has been directed towards discovering mechanistic aspects of the hydration process or development of mathematical models, the latter of which follows from the former in most cases.

It appears that these forms of alternative binder systems share many aspects in common with portland cement, including through-solution reaction mechanisms, shrinkage, and metastable products. And, while alkali activated systems are mechanistically different, for those binder systems that are based on aluminate and sulfoaluminate hydrates, there is kinetic commonality with portland cement. Therefore, one might conclude that studies in any of these areas would be cross-cutting among the calcium-silicate-aluminate-sulfate-ferrite systems. More importantly, it is likely that a modeling tool capable of describing the hydration of portand cement at fundamental chemical and physical level would be able to accommodate any of these alternative systems, provided that thermodynamic and kinetic data are provided.

III. Reconciliation with Other Vision Statements

This vision for cement hydration kinetics does not and must not stand in isolation from other industry visions. It must be reconciled with "Roadmap 2030," the concrete industry's plan for achieving a more sustainable, cost effective and improved concrete for the 21st century, published in 2002 [6].

So, how does the vision for cement hydration kinetics relate to Roadmap 2030? The following four "critical research areas necessary to propel the industry forward," were identified by industry experts and reported as the basis of Roadmap 2030:

1. Design and Structural Systems
2. Constituent Materials
3. Concrete Production, Delivery, and Placement
4. Repair and Rehabilitation

Within each of these four areas, numerous subtopics and "specific research needs" were identified. Each of these four areas will be addressed separately to illustrate the intimate relationship between hydration and these focal topics. Collectively, there are 130 specific research needs identified in Roadmap 2030. Of these, 55 appear to be unique needs that are directly related to hydration; these are listed in Tables I through IV. This tabular format mimics the one used in Roadmap 2030 for easier subsequent comparison. It is important, however, to recognize that concrete is a complex material and that hydration is not the only factor that controls its behavior.

Design and Structural Systems

Within Design and Structural Systems, seven research sub-topics were identified and within these seven sub-topics, 38 specific research needs were listed in Roadmap 2030. Among these 38 specific needs, 13 would directly benefit from having a comprehensive understanding of hydration. These 13 specific needs cut across six of the seven sub-topics.

Constituent Materials

Four sub-topics related to Constituent Materials were identified. Thirty-nine unique specific needs were itemized as important enabling technologies. Hydration outcomes can be directly linked to 20 of these specific, excluding those areas that were duplicated or represented under another heading.

Concrete Production, Delivery, an Placement

The topic Concrete Production, Delivery and Placement includes four sub-topics and a total of 26 specific research needs. Of these, 14 are directly related to hydration, all are duplicated under either Design and Structural Systems or Constituent Materials.

Repair an Rehabilitation

There are three sub-topics listed under Repair and Rehabilitation along with 27 specific research needs. Eight of these specific needs are linked to hydration, and all are duplicated under one of the other main topics.

IV. Vision for Cement Hydration

This vision for achieving an understanding of the kinetics of cement hydration was developed to provide the research community with focal points for directing immediate and short-term research that should be undertaken within the next three to five years. Among the most pressing issues at hand are those that will impact the design of cementitious materials and systems that lead to smaller carbon footprints and hence improved life cycle performance. Although significant progress has been made in the past ten years towards development of modeling platforms for cement hydration, thus far they are mostly limited to hydration of neat C_3 (C_3 in the absence of organic or inorganic admixtures or other cement or mineral phases) and even then a unique model is not yet available that describes the range of observed behaviors. Furthermore, the body of existing experimental information is sometimes contradictory or at least can be interpreted using more than one hypothesis. In the absence of clear and detailed mechanistic information, the near term development of modified and new cementitious systems, optimized utilization of waste and by-product materials and discovery of new admixtures, will continue at the present slow and costly pace. The research needs identified by Summit participants are formulated here as either questions or statements. The list of needs is not intended to answer the questions, but rather to pose them. Nor does the list represent a proposed solution but rather supposed elements of the solution. Recognizing also that the topical areas discussed above are not isolated from each other, but rather that they are highly interrelated, the following list is suggested in an effort to “pave the way for more sustainable concrete infrastructure via the development of a comprehensive description of cement hydration kinetics.”

IV.I Hydration Mechanisms

1. Does a semi-permeable layer actually form at early ages? A affirmative answer might lead to pathways for either preventing its formation or prolonging its existence. If there is such a layer, knowledge of the trigger for its disappearance (e.g. thermodynamic or mechanical instability) could lead to the design of admixtures for targeting that trigger.
2. What role is played by surface defects, such as stacking faults and dislocations, in governing the dissolution rates of clinker phases in cement? Answering this question could lead to approaches such as annealing or chemical/mechanical pretreatments that could optimize defect structure and frequency.
3. To what extent do species in solution adsorb on cement phases or hydration product phases and modify the dissolution or growth rates of those phases? There is persuasive evidence that adsorption of calcium sulfate onto active dissolution sites of aluminate phases is responsible for the set-controlling properties of gypsum in cement, but understanding in this area is still in its infancy.
4. What are the transport properties of the bulk C-S-H products formed and how do they evolve with time?
5. Does C-S-H form by a two-stage growth process and what is the bulk density of C-S-H as a function of time?
6. When and where do C-S-H nuclei form and what is the formation rate?
7. What factors are responsible for the strong interactions between silicates and aluminates in cement clinker hydration? There is recent experimental evidence that incorporation of aluminate ions in C-S-H is highly dependent on aluminate concentration in solution, which also can poison its growth rate.
8. What are the forms of the rate laws (e.g., the reaction order)?

9. Along with (8), what are the elementary reactions that control the reaction rates, not only at early age, but at any age?
10. What is the actual morphology of C-S-H growth and what controls the morphology since many forms have been observed?
11. Are there signatures in early-age calorimetry measurements that indicate long-term kinetics and performance?

IV.2 Modeling and Simulation

1. Continue to develop various solution phase driven models that incorporate kinetics, thermochemistry and transport phenomena.
2. Develop multiple modeling paths and strategies that corroborate findings and lead towards useful engineering tools as well as model-based research instruments including fast algorithms for PC and similar platforms.
3. Continue to extend and exploit computational resources as necessary and needed to accommodate changing needs (i.e., utilize massively parallel processing and supercomputer facilities as needed).
4. Pursue alternative computational strategies to accelerate the development of rigorous models, i.e. fast single particle models, representative volume approaches, etc.
5. Exploit the body of knowledge on true multi-scale modeling.
6. Improve the dissemination of modeling tools to promote their use and development.
7. Incorporate more molecular-level modeling strategies (e.g., kinetic Monte Carlo)
8. Develop suitable structural analogs for various anhydrous and hydrated cement phases for use in molecular modeling.
9. Develop focused experimental program driven in part by model development and designed to provide information for parameter estimation and to answer mechanistic questions. Specific questions that must be addressed experimentally and within the construct of existing and new models to be developed were included in Section III (Mechanisms) above.

IV.3 Experimental Techniques

1. Extend as necessary and apply the vertical scanning interferometry (VSI) technique in an attempt to answer at least portion of the questions regarding dissolution mechanisms.
2. Further develop X-ray nanotomography into a quantitative technique and apply it to study the rate of cement phase reaction in both model systems and portland cements and for blended systems containing silica fume, blast furnace slag and fly ash.
3. Further explore the use of nuclear resonance reaction analysis (NRRA) as tool for elucidating the barrier layer hypothesis.
4. Establish an open network with researchers in the broader community, both those doing modeling and experimentation, so that they have access to datasets and instrument time on unique tools such as VSI, X-ray nanotomography, NRRA and TDDS.

IV.4 Admixtures

1. Identify the paths and kinetics of reaction for different admixtures in cements with different amounts and availability of sulfates.

2. Identify the paths and kinetics of reaction for different admixtures with the crystallographic forms seen in typical alite, belite, aluminate and ferrite phases.
3. Build computer models based o knowledge generated in 1 and 2 above to look at how hydration kinetics is impacted by different admixtures in different cementitious systems.
4. Identify the elementary steps (reactions and kinetics) for classic hydration acceleration and retardation (e.g., for $CaCl_2$ and sucrose activity, respectively) at dosage rates practiced by the industry.
5. Identify the elementary steps (reactions and kinetics) for strength enhancement of different alkanolamines and how the differences in solubility of alkanolamines in pore solution impact the paths and kinetics of reaction.
6. Isolate and identify physiochemical interactions of different admixtures with various cement surfaces and quantify the rate controlling processes for each process.
7. Isolate and identify chemical interactions with various cementitious ionic species, for example, the rate of Ca^{+2} chelation by sucrose and other admixtures, the rate of Fe^{3+} chelation by alkanolamines, or the rate of Al^{3+} chelation by other admixtures.
8. Identify and model the fates of dispersant, sulfates, and retarders whether added separately or at the same time.
9. Understand how formation of etch pits or other defects o the silicate and aluminate surfaces are impacted by the different admixtures
10. Design experiments explicitly to be used for kinetic model development with the objective of having quantitative outcomes than can be used to develop and refine models.

IV.5 Supplementary Cementitious Materials

1. Isolating the rate of reaction of SCMs is generally very difficult. Most reactive SCMs are amorphous rather than crystalline and some, such as fly ash, contain more than one reactive constituent; that is, fly ashes may contain more than one reactive glassy phase each having its own reactivity.
2. So called "filler effects" are difficult to separate from chemical effects since both may have similar apparent outcomes, e.g. slightly altered size and location of the primary calorimetry peak (Stage 3 and 4).
3. Generalized solubility models for the range of glassy phases are not readily available.

IV.6 Alternative Cements

1. While there are kinetic datasets for the various classes of cements, there is no cohesive unified theory for the common cement forms (i.e., those that are indirectly derived from the portland family of anhydrous crystalline cements and those derived predominantly from glassy raw materials and requiring high alkali content activator solutions).
2. Although the kinetic processes share features in common with those of C_3S-based cements, it seems that side-by-side studies of these features have not been conducted.
3. There is general lack of information regarding long-term durability for many classes of alternative cements. While somewhat outside of the scope of this document, it should be acknowledged that this is an obstacle to the widespread development and use of such materials.
4. There are number of economic hurdles at this time, including the use of bauxite as raw material and the high cost of alkali agents. Further development or materials engineering might reduce production cost and enable the introduction of alternative cements into various markets where they are presently not economically viable.

IV.7 General Comments

1. There is general lack of resource organization and dissemination of tools for modeling cement hydration. national resource for hydration data should be considered wherein a database of computer models, thermophysical properties (thermodynamic datasets and thermodynamic models), crystallographic information files (CIF), kinetic datasets, models and modeling tools and their associated source codes, etc., can be easily accessed by the research community at large. Huge amounts of time are spent by research teams searching for, reviewing and assembling such information independently.
2. There is presently no focal point for hydration research in the US, but there should be. Concrete is the primary building material for the world's infrastructure and the US must continue to remain competitive and be a global leader in concrete materials technology. The lack of a generalized, universal theory governing chemical transformation kinetics, microstructure development rates and properties of complex hydrate synthetic mineral-based materials impedes the pace of development.
3. It appears that some alternative cement systems exhibit kinetic features that are like those of the C_3S-based portland cement system, including behaviors such as an early dissolution peak, dormancy and a main hydration peak, i.e. super-sulfated cements and calcium sulfoaluminate cements. While this is well known among the community of researchers, it might be beneficial to study such systems side-by-side in an effort to resolve common or dissimilar features that could lead to a more refilled and clarified mechanistic theory of cement hydration.

Table I. Design and Structural Systems*

Specific Research Needs
Structural Concrete • **Chemical bonds** *Altering the strength of such bonds requires detailed knowledge of the chemical structure of the surfaces involved.* • **Changes due to relaxation, creep and shrinkage** *Current models for relaxation, creep and shrinkage are mostly empirical or linked to poorly defined material, microstructure and hydration definitions.* • **Chemical factors such as freeze/thaw, chlorides, and sulfates** *Interactions between concrete and the environment are dependent upon detailed knowledge of the pore structure and the chemistry of the nano- and micro-scale composite nature of hydrated cement.* • **Direction, speed, location and cycling of external loading or internal forces** *Multi-scale models for the prediction of load transference and resulting mechanical properties and performance of concrete will not be possible until a comprehensive description of hydrated cement is available.*
Reinforced Concrete • **Improved ductility of high-performance concrete** *Ductility is not just a reinforcement issue, but involves understanding the nature of the matrix that supports the reinforcement. Presently, we have almost no way to modify the matrix. If, however, we had knowledge of how hydration happens and what factors can be changed to alter the chemical and physical structure of the hydrates, it may be possible to engineer ductility via matrix modifications rather than depending solely on reinforcement-based approaches.* • **Corrosion- and reinforcement-free bridge deck** *The concept of corrosion and reinforcement-free decking materials will only be possible through controlled cement hydration and modification of the concrete from the matrix (cement) perspective.*
Modeling and Measurement • **Service life design models** *Service life design models are only as good as the underlying models for prediction of properties, i.e. permeability, strength, creep, shrinkage. While models are presently available, most are empirical and require calibration against large datasets of experimental information. Ultimately, service life depends upon the chemistry and microstructure of concrete, neither of which can be adequately predicted without knowledge of hydration mechanisms.* • **Durability models that predict interaction of stress and environmental factors** *Similarly, the weakness in present durability predictions is identical to the weakness in present service life models. At the heart of these durability models are poorly predictive hydration models or no models whatsoever.* • **Smart materials** *Altering concrete to produce “smart” materials will be greatly accelerated by hydration information.*
High-Performance Concrete • **Curing technologies** *Curing is a hydration and hydration kinetics related phenomena.* • **HPC mixture optimization software** *While there are many forms of mix optimization software, none will ever achieve predictability without detailed knowledge of hydration kinetics.*
Technology Transfer • **Accelerate[d] technology transfer** *The ambition here is to reduce the time to bring new technology to practice from 1 years to two years by 2030. Hydration models would enable this by making it possible to simulate material performance and to run only a limited number of targeted field tests based on reliable predictions.*
Fire-, Blast-, and Earthquake-Resistant Materials and Systems • **Fire-resistant, high-strength concrete** *Fire resistance is a complex problem for composite materials and depends upon detailed knowledge of the composite structure at all length-scales.*

*Text in **bold** print matches or is paraphrased from Roadmap 2030.

Table II. Constituent Materials Research Needs

Specific Research Needs
New Materials *To achieve the following list of "specific needs" it will be critical to understand how to control cement hydration. These "needs" can be summarized as controlling and predicting the performance of concrete and explicitly call for manipulation of chemical factors that are directly linked to hydration of the cement matrix and its resulting structure.* • **Families of innovatively manufactured concrete with predictable performance** *Concrete will not be predictable without predictable cement hydration kinetics.* • **New materials to reduce shrinkage and cracking** *Shrinkage and cracking begin at early age and various forms continue throughout the lifecycle of the concrete structure. Both shrinkage and cracking are linked to hydration kinetics and microstructural outcomes.* • **Reduction of alkali-silica reactions in concrete** *This is a fundamentally chemical and chemical kinetic problem.* • **Materials for active and passive corrosion prevention** *Corrosion of embedded steel is associated with the matrix chemistry and microstructure.* • **Reactive powder concretes** *Reactive powder concretes begin with highly reactive cements that have engineered particle distributions and in some cases chemical compositions. The performance of such is a classic problem in chemical kinetics.* • **New admixtures, e.g., corrosion-inhibiting, self-consolidating [and] leveling, reduce reinforcement** *Though there is a large body of literature on admixture behavior, it is mostly qualitative. The research community at large would agree that little is known about the mechanistic interactions of admixtures and hydrating cement. Knowledge of such would greatly accelerate the pace of admixture discovery and design.* • **Cements of specified performances** *This is fundamentally a chemical design problem and cannot be achieved until a more mechanistic description is available for cement hydration.* • **Cement produced with improved energy efficiency and reduced environmental impact** *The design of new low-environmental impact cements will come along with our ability to control the properties and performance at the hydration stage. Producing concrete that is more durable and lasts longer, for example, is one way to reduce environmental impact.* • **Performance-based standards** *This concept is difficult to achieve reliably without better predictability and control of the materials.* • **New materials from novel waste streams** *The problem with using waste stream materials is linked to chemical interactions with cement during hydration. Limitations on the use of fly ash and narrow specifications for suitable ash compositions are directly linked to our inability to predict and control chemical reactions during hydration.* • **Supercritical carbon dioxide research for rapid strength** *The use of supercritical carbon dioxide for modification of cement properties is a chemical reaction and likely transport phenomena controlled process.*
Performance Measurement and Prediction *Achieving the following "specific needs" are all dependent upon having detailed knowledge of hydration and hydration kinetics. Predictability of properties will only come with confident, mechanistic-based hydration models. "Modeling" is a theme throughout these specific needs.* • **Prediction methods and models for permeability, cracking, durability, and performance (including environmental interactions)** • **Tools and data for quantifying benefits of using alternative materials** • **Measurement and prediction of self-desiccation in concrete** • **Multi-scale modeling to connect microstructure with engineering properties** • **Predictive models to augment/replace QC tests**
Reuse and Recycling *Hydration kinetics will ultimately govern how and if these specific needs can be addressed. At this point, most of what we know about the following four areas is qualitative or empirical at best. Hydration kinetic studies will eventually provide opportunities to realize these needs or impose constraint which govern the limits of applicability.* • **Reuse of high-alkali wastewater** • **Aggregate recycling** • **Incorporation of waste and by-product materials from other industries** • **Reuse of cementitious materials, cement kiln dust, and other waste products**

Table III. Concrete Production, Delivery, and Placement

Specific Research Needs

Information and Control

- **Techniques to optimize, predict, and verify concrete performance (see Constituent Materials)**
- **Modeling and measurement systems to predict and control properties (see Constituent Materials)**

Production, Delivery, and Placement

- **Controlling curing**
- **DEF as relates to accelerated curing**
  Delayed ettringite formation is a chemical reaction and transport problem.

Test Methods and Sensors

- **Procedures and technologies for tests in the curing process (see Design and Structural Systems)**
- **Improved on-site monitoring of concrete during early age**
  The early age period is dominated by hydration kinetics.
- **Tests and models to predict cracking and strength development immediately after setting**
  The period immediately after setting is very dynamic period still dominated by hydration kinetics. The mechanical response of concrete during this time frame is intimately coupled with the rate at which cement is hydrating.

Energy and Environment

- **Aggregate and alkaline water reuse (see Constituent Materials)**
- **Increased use of waste streams via the use of validated, integrated models to optimize concrete formulation (see Construction Materials)**
- **"Cradle to grave" assessments (see Design and Structural Systems)**
- **Recycling of concrete (see Construction Materials)**
- **Carbon dioxide reduction (see Construction Materials)**
- **Admixtures to eliminate steam cleaning/curing precast (see Construction Materials)**
- **Frost-resistant, non air-entrained concrete (see Construction Materials)**

Table IV. Repair and Rehabilitation

Specific Research Needs
New Repair Materials • **Self-repairing (damage-insensitive) concrete** *Self healing is a chemical phenomenon which will be difficult if not impossible to predict and model without detail microstructural, transport and kinetic information for cement paste and concrete at a broad spectrum of ages.* • **Heat-resistant pavements (see Design and Structural Systems)** • **Adhesives to improve bond between repair layers and substrate (see Design and Structural Systems)** • **Repair of sulfate damage with sulfate-resistant concrete (see Design and Structural Systems)**
Assessment Tools and Modeling/Measurement Technologies • **Model development (see Construction Materials)**
Repair Field Process Technologies • **Mitigation of alkali-silica reactivity in existing structures (see Construction Materials)** • **Corrosion-Canceling technologies (see Construction Materials)** • **Admixture research to stay abreast of changing performance requirements (see Construction Materials)**

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