

2009 BFRL Project Description

Project Title: Modeling of Hydration and Microstructure Development for Concrete-Making Materials

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BFRL Program: HYPERCON: Predicting and Optimizing Concrete Performance

Objective: To enable the reduction of expensive physical testing of cementitious binder formulations, and assist the acceleration of design and troubleshooting of new binders, by developing and implementing the next generation of microstructure models of cement hydration.

Problem:

What is the problem? The U.S. concrete industry faces increasing challenges to optimize short-term performance, extend service life, and reduce the environmental impact of concrete. Faced with these challenges, the concrete industry lacks the measurement science capability, specifically a modeling framework, to *understand* and *predict* the chemical and structural changes that occur during cement hydration or concrete curing. Without this capability, optimizing the design of cementitious materials is becoming increasingly difficult because the increased use in binders of fillers and waste materials like fly ash, slag, and recycled washwater make the design space difficult to explore by trial-and-error experimentation. And without adequate knowledge of the design space, potential chemical incompatibilities among these materials can go undetected and lead to major performance problems in the field. According to the U.S. Concrete Industry Technology Roadmap¹, the concrete industry "... requires the development of tools for measurement and prediction of performance. The fact that ... concrete is complex ... can lead to confusion about concrete's performance. A concrete modeling initiative aimed at producing a meso-to-macro statistical performance prediction model could greatly benefit the concrete industry."

Why is it hard to solve? Understanding and predicting the changes in cement binder properties requires a fundamental modeling framework, grounded in thermodynamics and kinetics of reaction mechanisms, which can track the chemical and structural changes of a wide range of cement-based materials. Our current cement hydration model, for all its successes, does not incorporate or predict real kinetics. Even for simpler materials like porous ceramics and metals, simulating the evolution of their 3-D geometry at the microscopic scale is a notoriously

¹ "Roadmap 2030: The U.S. Concrete Industry Technology Roadmap, Version 1.0" American Concrete Institute Strategic Development Council (2002), p. 16.

difficult computational task. And cement-based materials are much more chemically complex than ceramics or metals, having extremely diverse chemical and physical properties, and involving dozens of strongly coupled nonlinear reactions that are incompletely understood. The underlying computational challenges and the poorly characterized chemical landscape of cement-based materials make this a difficult measurement science problem to solve.

How is it solved today, and by whom? In the U.S. industry, the problem is solved mostly by trial-and-error experimentation. Research is guided largely by empirical equations, data fits on existing mixes, or by the personal experience of engineers. The need for accurate microstructure models is recognized in industry, and BFRL has been the world leader in cement microstructure modeling for almost two decades with its CEMHYD3D model. In recognition of BFRL's expertise, several companies and industry associations—representing about 75 % of the U.S. concrete industry—are sponsoring the Virtual Cement and Concrete Testing Laboratory (VCCTL) Consortium to support and guide the next generation of cement hydration models that can then be used in the VCCTL software to make predictions of full concrete performance. Outside the U.S., both Europe and Japan are working to improve their measurement science capability for engaged in cement hydration modeling research. In particular, the Nanocem consortium in Europe is vigorously sponsoring a research program in the basic materials science of cement. Nanocem researchers currently are producing the world's best experimental work on cement hydration kinetics. Their modeling research is also improving rapidly and already is competitive with CEMHYD3D.

Why NIST? A comprehensive microstructure model of cement hydration or concrete curing with real chemical kinetics will advance the measurement science capability of the U.S. concrete industry by enabling engineers to expedite the design and physical testing of cement-based materials. BFRL is unique in having the technical expertise in materials and scientific programming and visualization combined with the computational power to achieve success with this project. It will be a critical solution-enabling tool for reducing the design-to-market cycle for new building materials. This project addresses the prediction of the properties of concrete, and is therefore aligned with a BFRL core competency, "Performance, durability and service life prediction of building materials" and with the strategic goal of "Measurement science for sustainable infrastructural materials." The success of this project will enable BFRL to retain and strengthen its historic global leadership in cement microstructure modeling. Finally, this project is a key component of the VCCTL Consortium, which is one of BFRL's direct contacts with the U.S. building materials industry.

Approach:

What is the new technical idea? The most important, and most complex, changes that occur in cement binder happen within the first day after mixing. The transition from fluid to load-bearing solid is governed by myriad details of chemical interactions, mix proportions, and environmental conditions. To accurately capture these early-age details, a new model called HydratiCA is being developed on statistical mechanical principles, specifically transition state theory, which unifies the kinetic and thermodynamic aspects of microstructure development. HydratiCA will have several unique advantages over all existing hydration models. Among these are (1) an intrinsic time scale and real kinetics, (2) numerical convergence to the relevant rate equations, (3) a more explicit connection between material properties and model parameters,

(4) a natural accommodation of temperature effects, and (5) a unifying principle for simulating coupled phenomena including diffusion, dissolution, and nucleation and growth.

HydratiCA is computationally intensive and will be used only to predict early-age behavior. At later ages, cement binders are governed more by thermodynamic principles, and changes occur much more slowly. For this regime, early-age microstructures predicted by HydratiCA will be used as input to a second model, called THAMES (Thermodynamic Hydration And Microstructure Evolution Software), to be developed partly under DOE funding, which will combine powerful thermodynamic modeling principles used in environmental geochemistry with BFRL expertise on digital-image microstructure development algorithms. This second model will provide extremely rapid forecasts of paste microstructure for extended times.

Why can we succeed now? The NIST-led VCCTL Consortium is composed of nine industry and government partners who support the development of a next-generation cement hydration model that is the core of a larger concrete performance prediction tool, and they are helping to ensure that it will be a solution-enabling tool for industry when it is completed. Several research groups in Europe are now generating critical experimental data and scientific understanding that are being used to validate HydratiCA. NIST researchers in ITL are providing their expertise in parallelization of the model and scientific visualization of its predictions. The computing power of BFRL's Hercules cluster will enable HydratiCA to run in reasonable times. In addition, NASA has granted 200K hours on their Columbia supercomputer to test the scalability of HydratiCA. Recent thermodynamic modeling work conducted in Switzerland (at the EMPA laboratory) has enabled the feasibility of developing the THAMES model.

What is the research plan? High-level overview. The major tasks are to develop, test, and validate the two hydration models, HydratiCA and THAMES, for early-age and later-age microstructure development, respectively. Work on HydratiCA began in FY06, and all its major algorithms have been developed and verified on small, idealized systems. The remaining work on that model is to validate it against progressively larger and more chemically complex systems, exploiting the ongoing work with NIST ITL personnel on parallelizing HydratiCA. Alongside this ongoing work on HydratiCA, initial development of THAMES. The thermodynamic engine of THAMES will be based on a model already completed at EMPA in Switzerland, and the major tasks for THAMES are therefore to make its input compatible with a digitized 3-D representation of microstructure and to develop and test algorithms for projecting microstructure changes based on the output of the thermodynamic calculations.

For both HydratiCA and THAMES, validation will occur in two stages: (1) preliminary validation at NIST against published experimental data, and (2) further validation by VCCTL Consortium members using their own experimental measurements. Preliminary validation of both models for ordinary Portland cement binders. While further validation is conducted in industry, work at NIST in remaining years of the project will focus on incorporating fly ash and silica fume chemistry into both HydratiCA and THAMES. Preliminary validation for these more complex chemistries should be completed by the end of FY11. The ultimate outcome of the project will be a software tool combining HydratiCA and THAMES in a package that will provide industrial researchers with the measurement science capability to virtually test cement paste formulations and reduce physical testing requirements, over short and long times, for cement, silica fume, limestone, and some kinds of fly ash.

HydratiCA will be tested on calcium aluminate-calcium sulfate systems, comparing against experimental data generated recently at the Université de Bourgogne. HydratiCA will be used to predict influences of particle size distribution on tricalcium silicate hydration rates, comparing against existing experimental data from Université de Bourgogne and from NIST. HydratiCA will be used to predict hydration rates and setting times for selected ordinary Portland cement pastes, comparing against existing experimental data generated at NIST. For THAMES, the thermodynamic model developed at EMPA will be refitted to accept initial conditions from a 3-D digitized paste microstructure, and algorithms will be developed for projecting the state of microstructure to later times using tabular output of the thermodynamic algorithms. Preliminary validation of the THAMES algorithms will be completed on ordinary Portland cement.

Recent Results:

Output: J.W. Bullard, “Approximate rate constants for nonideal diffusion and their application in a stochastic model,” *J. Phys. Chem. A*, **111** [11] 2084-2092 (2007).

Output: J.W. Bullard, “A three-dimensional microstructural model of reactions and transport in aqueous mineral systems,” *Mod. Sim. Mater. Sci. Eng.*, **15** 711-738 (2007).

Output: J.W. Bullard, “Fundamental reaction-transport model for simulating microstructure development in hydrating cement pastes,” Proceedings of the Twelfth International Congress on the Chemistry of Cement, TH1-0.85, (2007).

Output: H.M. Jennings, J.W. Bullard, J.J. Thomas, J.E. Andrade, J.J. Chen, G.W. Scherer, “Characterization and modeling of pores and surfaces in cement paste: correlations to processing and properties,” *J. Adv. Concrete Tech.*, **6** [1] 1-25 (2008).

Outcome: Roadmap and guidance to concrete materials community about the most important and promising areas of research for understanding and controlling the structure-processing-properties relationships in concrete.

Impact (anticipated): Concrete materials community (industrial and academic) uses NIST guidance to better focus future research efforts for controlling the structure/processing/properties of concrete.

Output: J.W. Bullard, “A determination of hydration mechanisms for tricalcium silicate using a kinetic cellular automaton model,” *J. Am. Ceram. Soc.*, **92** [7] 2088-2097 (2008).

Outcome: First demonstrated use of a computer model to determine reaction paths in early-age cement paste.

Impact (anticipated): Industry adoption of NIST measurement science tools for more effective/efficient design of chemical accelerators and retarders for controlling the setting time of concrete.

Standards and Codes: None at present.