2009 BFRL Project Description

Project Title: Doubling Concrete Service Life

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BFRL Program: HYPERCON: Predicting and Optimizing Concrete Performance

Objective: Develop and validate a novel new technology that doubles concrete service life by increasing the hardened cement paste pore solution hydrodynamic drag coefficient, and use measurement science to facilitate industry acceptance of this new concrete performance enhancement paradigm known as VERDiCT: Viscosity Enhancers Reducing Diffusion in Concrete Technology.

What is the problem? The American Society of Civil Engineers (ASCE) infrastructure report card[1] gives the Nation's infrastructure a grade of D, and states that $1.6 T is needed over five years to bring the Nation's infrastructure, many of the critical elements of which are made of concrete, to a good condition. The cost of concrete infrastructure repair depends directly upon the duration of serviceable life; doubling the service life would halve the long-term cost of repair and replacement. **Since most concrete degradation mechanisms depend directly on the diffusion of ions through concrete, developing new technologies to improve concrete resistance to diffusion is a key way of addressing concrete durability. This must be done, however, without significantly degrading other aspects of concrete performance and constructability.** Because most concrete requirements are prescriptive, the concrete industry tends to be technologically conservative, and is often skeptical of new technologies without extensive testing under practical conditions. The American Concrete Institute (ACI) Strategic Development Council (SDC) has acknowledged this, and its mission[2] includes the, "…timely adoption of innovative technologies, problem solutions, and best practices."

Why is it hard to solve? Concrete is a highly variable commodity building material in which microscopic phenomena impact macroscopic behavior. Technologies that extend service life, and the measurements that demonstrate the efficacy of that technology, must be broadly applicable. The new technology cannot negatively impact the chemistry and physics of cement hydration, the quantitative measurements that demonstrate performance must be applicable across a wide range of length scales, and the data analysis must consider transport, reaction, and binding.

[1] http://www.asce.org/reportcard/2005 (Updated for 2008)
[2] http://www.concretesdc.org/about/mission.htm

How is it solved today, and by whom? The typical industry approach to improving durability is to reduce diffusive transport by modifying the solid phase: reduce the porosity while increasing its tortuosity. Historically, this is achieved by reducing water:cement (mass) ratio and/or adding supplemental mineral admixtures. These approaches can lead to other problems such as cracking, which can otherwise destroy any gains in the hardened cement paste durability. Laboratory measurements that characterize performance typically use subjective measures of ingress or rely upon macroscopic measurements of physical degradation, neither of which elucidate the underlying phenomena. Standard practice in these areas are similar in Europe, the US, and Japan.

Why NIST? The inception of the VERDiCT technology originated as a logical extension of the decade-long NIST basic research behind the development of the computer program 4SIGHT,[3,4] which models transport and reaction as part of a cementitious barrier *life-cycle performance assessment tool* for the Nuclear Regulatory Commission (NRC). 4SIGHT combines microscopic and macroscopic transport behavior at a fundamental level, which are essential to understanding and improving concrete durability. Without the fundamental understanding of ionic transport in concrete achieved by this decade-long basic research project in the HYPERCON program, the technical idea behind VERDiCT would not have been conceived.

BFRL has received written support from the concrete industry for developing a patent based on VERDiCT because subsequent patent licensing will ensure intellectual property (IP) protection to the company that develops the patented technology into a marketable product. BFRL will now take a leadership role in establishing the practical viability of the VERDiCT technology that will ultimately promote industrial innovation, and the objective of doubling the service life of concrete will improve the Nation's economic security, both of which fall under the BFRL mission. This project is aligned with the BFRL strategic goal of "Measurement Science for Sustainable Infrastructural Materials."

Approach:

What is the new technical idea? Virtually all concrete degradation mechanisms begin with the diffusion of deleterious ionic species through the pore solution within the hardened cement paste in concrete. The new approach increases the hydrodynamic drag (related to viscosity) on the diffusing species within the pore solution, slowing the rate of diffusion, thereby increasing the time required before chemical and physical degradation begins. Reducing the rate of diffusion by factor of two will lengthen the service life of the structure by a factor of two for most common degradation mechanisms.

This concept is consistent with the microscopic theory of diffusion in concentrated electrolyte solutions in which the high concentration of ionic species increases the bulk viscosity of the solution. Here, chemically inert molecules are to be added to the pore solution to increase

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[3] K.A. Snyder and J.R. Clifton, "4SIGHT Manual: A Computer Program for Modelling Degradation of Underground Low Level Waste Concrete Vaults", *NISTIR 5612*, National Institute of Standards and Technology, (Gaithersburg, MD) 1995.

[4] K.A. Snyder, "Validation and Modification of the 4SIGHT Computer Program," *NISTIR 6747*, National Institute of Standards and Technology, May 2001.

the hydrodynamic friction. For this approach to work, these inert molecules must have sufficiently low molecular weight to increase the hydrodynamic drag on relevant diffusing species. Conversely, the dosage required to increase the hydrodynamic friction by a fixed amount is (generally) inversely proportional to the molecular weight of the additive. An ideal additive will have a sufficiently small molecular mass to increase hydrodynamic friction, yet require a sufficiently moderate dosage so that the kinetics of hydration do not change appreciably. Fortunately, microscopic models of transport indicate that changes in hydrodynamic friction also affect electrical conductivity by the same proportion. These rapid electrical measurements on solutions have been used to demonstrate the efficacy of viable VERDiCT additives.

Why can we succeed now? Building on the basic research of the HYPERCON program, by exploiting the hydrodynamic friction dependence on electrical mobility, the concept of modifying the hydrodynamic drag of inorganic ionic species has been demonstrated in solutions using rapid electrical conductivity measurements. There are many potentially viable VERDiCT additives because many viscosity-modifying additives already exist for the construction and food industries. Moreover, recent advances in quantitative X-ray microfluorescence in concrete specimens will help to validate the practical effectiveness of trial VERDiCT admixtures.

What is the research plan? The two-year research plan consists of demonstrating the VERDiCT concepts through chloride exposure to both mortars and concrete. Candidate VERDiCT chemical admixtures will be identified through rapid assessment of changes in solution viscosity and electrical conductivity, and three different delivery mechanisms will be considered: addition to the mix water; external application as a curing compound; and incorporation into pre-wetted lightweight aggregates. These three delivery mechanisms represent the most practical delivery approaches consistent with present industry practices. Chloride ion penetration will be monitored periodically over the course of a year. Penetration will be determined on fracture surfaces, and characterized using both silver nitrate spray (visual) and X-ray microfluorescence (CSTL) in combination with theoretical analysis. In addition, the effects of the chemical additive on hydration kinetics will be quantified using isothermal and semi-adiabatic calorimetry.

The first experiments will be conducted on mortars to demonstration the concept in a cementitious material. Mortars having varying water: cement (mass) ratios will be made using each of the aforementioned delivery methods. The samples will be exposed to a chloride solution at room temperature. Samples will be extracted periodically, fractured using the split-cylinder testing method, the fracture surface analyzed, and the degree of chloride penetration quantified.

The second set of experiments involves concrete exposure, and is an important component of this project because it will demonstrate efficacy under real-world batching conditions. The sample characteristics, VERDiCT delivery mechanisms, and exposure of concrete experiment will be a replication of the mortar experiment. The laboratory demands for large-scale concrete production will either use the Inorganic Group's planned facility upgrade or will coordinate with an external agency or organization (e.g., Federal Highway Administration (FHWA), National Ready-Mixed Concete Association (NRMCA)) having large-scale concrete facilities.

Recent Results:

- **Output**: Viable VERDiCT additives that balance dosage and efficacy were identified, and the results published in a paper that has been accepted for publication: "Doubling the Service Life of Concrete. I: Reducing Ion Mobility Using Nanoscale Viscosity Modifiers", accepted for publication by *Cement and Concrete Composites (2008).*
- **Outcome**: A key element to ensuring industrial innovation is to patent the VERDiCT technology and then license the patent to a private company, thereby protecting any further product development on the part of the private company. The NIST Patent Review Committee and BFRL management have agreed to proceed with NIST patenting of VERDiCT in May 2008.
- **Output**: Positive preliminary results for potential VERDiCT additives have been achieved from experiments on mortars, based on visual examination of silver nitrate spray. The results have been summarized in a paper prepared for submission: "VERDiCT: Viscosity Enhancers Reducing Diffusion in Concrete Technology" submitted to *Concrete International* (2008).

Standards and Codes: None planned at present.