2009 BFRL Project Description

Project Title: Quantitative Characterization of Concrete-Making Materials for Performance Prediction and Increased Fly Ash Utilization in Concrete

September 12, 2008

Principal Investigator: Paul Stutzman

Co-Investigator: Edward Garboczi

BFRL Program: HYPERCON: Predicting and Optimizing Concrete Performance

Objective: To develop materials science-based (mineralogy and particle size and shape) quantitative characterization protocols for hydraulic cements and fly ash. Since the measurement of these parameters for concrete-making materials is essential for quantitative concrete performance prediction and increased fly ash utilization leading to performance-based standards.

Problem:

What is the problem? **There is a need to develop materials science-based protocols for mineralogical and particle size and shape characterization for concrete-making materials that can: (1) be used to determine the effects of materials, processing, and environmental variables on the performance of concrete, and (2) provide the basis for significantly increased utilization of fly ash in concrete.** While pieces of this protocol exist, there are many missing parts. Current industry practice utilizes bulk chemistry measurements that serve as a proxy for true mineralogical data. However, the reactants in cement hydration are not the bulk oxides but the mineral constituents. The current practice of transforming chemical to mineralogical data (American Society of Testing Materials, ASTM C150) is inherently biased, limiting the use of these values in evaluating performance predictions. Fly ash classification is even more tenuous, where the distinction of only two ash types is based upon a partial sum of bulk chemical measurements (ASTM C618). For these materials, the reactive constituents include crystalline and amorphous glassy phases, neither of which is currently measured. Direct measures of mineralogical composition and surface area will provide both a more accurate and more useful characterization of these materials.

Particle shape distribution, as well as particle size distribution, plays a large role in early-age reactivity and in rheology and so also needs to be characterized. In fact, particle shape affects how measured particle size distributions, as measured by laser diffraction, the technique of choice, are to be interpreted. In addition, many fly ash particles have internal porosity, so that their 3-D structure needs to be characterized in order to be able to predict fly ash performance.

As new cements are developed that contain supplementary cementitious materials such as fly ash, slag, and calcined clays, direct measurement mineralogical methods will be the only ones

that can be independently applied to assess the true composition and particle size and shape. Technical barriers include the variability and amorphous nature of fly ash and other waste-stream materials, and the multi-mineral phase nature of these materials and also cement. Non-technical barriers are basically the current standards, ASTM C150 and C618, which do not allow for direct mineralogical and size and shape characterization, and the slowness in getting new standards into place.

Why is it hard to solve? Analytical methods for direct mineralogical measurements have seen limited application in cements analysis and no application in the characterization of supplementary cementitious materials such as fly ash. Since the reactive phases of fly ash are mainly amorphous, the powerful tool of X-ray diffraction (XRD) is not very helpful, since it gives information about crystalline phases. Quantitative scanning electron microscopy (SEM) to assess both phase composition and surface area is not being performed on either cements or fly ash due to the difficulties in optimizing the data collection, processing, and analysis. Particle shape measurement of cements, fly ash, and slag, are difficult due to the small average particle size (~15 μm), and the mathematical analysis of this data has not been completely developed and standardized. The modern technique of laser diffraction size analysis, while used extensively by the cement industry, has not been standardized or systematically compared to the Blaine fineness standard, an empirical and biased indirect measure of particle size.

How is it solved today, and by whom? Cements (ASTM C150, American Association of State Highway and Traffic Officials - AASHTO M-85, ASTM C1157, ASTM C595, and European EN197) and supplementary mineral admixtures (ASTM C618, C989) today are classified by their bulk chemical composition and an indirect measure of particle size distribution (e.g., Blaine fineness). The situation is similar in Japan and Europe. Current cement specifications utilize mineral estimates that may be highly biased so their relationships to performance are tenuous. Fly ash classification standards are based upon bulk oxide analysis without any reference to mineralogical phase composition, ignoring mineral and glassy components that are the actual reactive and inert constituents. There is not any particle shape analysis for these materials at present outside of NIST, and there is no standard particle shape determination for cement or any mineral admixture like fly ash. The major cement and concrete research thrust in Europe, the Nanocem consortium (www.nanocem.org), has one small project that partly addresses particle shape, but not in 3-D with X-ray computed tomography (CT) techniques, and no project addresses the mineralogy of fly ash.

Why NIST? NIST participation in ASTM has resulted in the first in the world XRD method for portland cements. This method will need to be extended to accommodate supplementary mineral admixtures, with their glassy phases that complicate the analyses. Developing a protocol for direct analysis and quantification of cement and waste-stream materials addresses the historic limitations in both ASTM and international specifications of these materials that use bulk chemistry and not mineralogy and texture. Quantitative scanning electron microscopy of cements, pioneered by NIST, provides a means to measure phase composition and texture of these materials that, coupled with our mineralogical and particle size and shape data, will allow us to examine performance attributes. As hydraulic cements become more complicated in response to economic, environmental and performance demands, these methods will be the only ones capable of characterizing the reactive phases of these materials.

Developing a protocol for accurate characterizations will allow performance prediction, improve our standards and specifications and, ultimately, provide a path to performance specifications. NIST has state-of-the-art equipment and expertise in XRD, SEM and X-ray microprobe, LD particle size analysis, and X-ray CT. This project is fulfilling a measurement science need of the US concrete construction community, in line with the BFRL mission, and by developing standardized measurement characterization protocols for cement and fly ash, this project is also aligns with the BFRL vision of developing critical solution-enabling tools and performance-based standards. This material characterization project is aligned with the BFRL strategic goal of "Measurement Science for Sustainable Infrastructural Materials."

Approach:

What is the new technical idea? The new idea is to use mineralogical and textural characterization of cements and supplementary cementitious materials, along with particle size and shape analysis, for performance prediction to support performance-based standards and model development. Using image analysis methods adopted from the satellite imagery and analysis codes, we are processing scanning electron microscopy data sets to extract phase and textural data on these multi-phase particulate materials. Using X-ray CT and spherical harmonic analysis, we can also measure the 3-D particle shape information for these materials. Using laser diffraction particle size analysis, interpreted by particle shape analysis, we can characterize the particle size distribution. Because of the inherent difficulty in image and particle shape analysis, and a lack of standardized quantitative particle size measurements, few efforts outside of our laboratory have been applied to these materials. Additionally, we can couple the SEM data with quantitative XRD analysis to provide an independent assessment of the mineralogy and a means to quantitatively assess the glassy phase portion of mineral admixtures like fly ash. The synergy in combining these methods will result in our being able to quantify both the mineralogy and texture of the crystalline and glassy portions of these materials, as well as their particle size and shape.

Why can we succeed now? Developments in hardware and software now allow these measurements but the protocols need to be established and documented to assess precision and bias. Traditionally these analytical methods have been utilized for qualitative analysis. The acceptance of the ASTM XRD standard marked an acceptance from the industrial community of a direct mineralogical method for analysis. BFRL now has its own X-ray CT instrument, and along with mathematical techniques that have been developed in BFRL over the last several years under HYPERCON funding, can now readily analyze particle shape and generate particle shape databases. We have demonstrated how laser diffraction particle size measurements can be interpreted by particle shape analysis, so that this method can be standardized and made available to the cement and concrete community. The growing desire in the cement and concrete industry for performance-based standards demands these kinds of measurements, since quantitative performance prediction capabilities can only be based, for diverse materials, on such fundamental materials characterization.

What is the research plan? (XRD, SEM with X-ray microanalysis and image analysis, particle size distribution (PSD) measurement, isothermal calorimetry, and X-ray CT provide the

core methods for characterization of the cement or fly ash materials' phase and textural characteristics, particle size and shape, and reactivity. Each of these measurement tools provides data for mineralogy, texture of the constituent phases, particle size and shape distributions, and reactivity that will be used to thoroughly characterize concrete-making materials and determine the composition - performance property relationships and hydration kinetics of cements and blends of cements with supplementary cementitious materials.

The first task is to develop protocols for the XRD and microscopy methods of phase analysis and recommendations on reconciling their data. These protocols will be the basis for future standards and will be further tested on the NIST fly ash SRMs 2689-2691, which are already well-characterized by traditional methods and so will serve as good test cases. The next task is to examine a large set of fly ash samples, using these new measurement protocols, from across North America to determine what similarities and differences exist that may be useful in devising a new classification scheme. Quantitative analyses on this material set will form the basis for understanding their phase composition and will provide data to assess compositional effects on performance. These assessments will follow the exploratory statistical data analysis procedures outlined below in more detail for portland cements. Quantitative microscopy coupled with quantitative XRD will provide data on both the crystalline phases and the types and amounts of glassy phases in fly ashes, and the means to develop a new classification based upon these constituents.

A significant part of this project is directed toward relating the experimental mineralogy and texture data for cements to their performance attributes via a statistical model (Integrated Computational Materials Engineering[1] (ICME) mode of research). The Cement and Concrete Reference Laboratory (CCRL) proficiency test program generates cement performance data from hundreds of testing laboratories using a set of ASTM and their equivalent AASHTO standard test methods. An accurate predictive model is possible using the more accurate XRD data and including particle size distribution data, reducing the need for experimental procedures.

Performance data from the CCRL Proficiency Test Program will be compiled into a master database for exploratory statistical analysis using the more complete details on phase composition and particle size analysis. This exploratory analysis will be carried out by: 1) evaluating combinations of variables to select the best statistical predictive models (All Possible Subsets Regression), 2) exploring data transformations on the best models to maximize predictive capability (Alternating Conditional Expectations), and 3) evaluating the resulting statistical predictive model and developing a validation data set.

In parallel with this mineralogical and statistical work on fly ash and cements, X-ray CT will be used to determine the internal, 3-D structure of many fly ash particles. Some particles seem to have smaller, spherical particles inside them as well as air voids. Knowing this structure and especially the porosity makes mass-based fly ash substitution more accurate, since mistakes can be made if all the particles are assumed to be totally solid. Then particle shape ideas will be

[1] *Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security* (National Research Council, National Academies Press, in press, 2008)

further used to interpret LD results, so that a simple correction factor can be used to get a truer measure of particle size from laser diffraction. The Blaine fineness, which is a completely empirical and non-linear test of the ill-defined concept of cement "fineness" will be quantitatively compared, for a range of materials, with nitrogen BET, laser diffraction, and X-ray CT results to be able to conclusively state the limitations of the Blaine test. Previous statistical examination of cement data has shown that mean particle size is a major variable, and the Blaine test does not give that and is poorly correlated to the statistical data. Armed with these results, we will submit the corrected LD procedure to ASTM for standardization.

Recent Results:

- **Outcome:** Developed image analysis method for scanning electron microscopy to characterize multi-phase clinker particles
  Outcome: Renewal (twice) of the NIST cement clinker Standard Reference Materials (SRMs), which are among the top sellers in the SRM program.
  Outcome: Improved phase characterization of the SRM clinkers demonstrated by significantly lower measurement uncertainty

- **Outcome:** Developed a combined X-ray powder diffraction and scanning electron microscopy characterization method for hydraulic cements
  Outcome: Mineralogical characterization of cements now used as the foundation of the VCCTL hydration code, and the CEMHYD3D model before that.

- **Output:** Developed and coordinated an international inter-laboratory study on precision and bias of the method as detailed in the paper entitled "Phase Analysis of Hydraulic Cements by X-Ray Powder Diffraction: Precision, Bias, and Qualification" in the Journal of ASTM International (2007).
  Impact: The first XRD test method for direct mineralogical analysis of portland cements, Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction, ASTM C 1365-06, was adopted by ASTM in 2007. The paper (citation above) and symposium presentation was selected for the 2008 ASTM C01 P.H. Bates award.
  Impact: Industry use of NIST measurement science tool for more accurate and complete analyses of hydraulic cements.

- **Outcome:** A web-based crystal structure database directed towards portland cement analysis has been developed and is in the final testing stages, providing structure models to the cement and concrete industry necessary for quantitative X-ray powder diffraction analysis. Will provide industry with a cementitious materials-specific database on crystal structure models
  Impact: Industry use of NIST measurement science tools and databases facilitating the use of X-ray powder diffraction analysis within the industry

- **Output:** The effect of particle shape on laser diffraction particle size results has been clearly shown in the paper "Shape and size of microfine aggregates: X-ray microcomputed tomography vs. laser diffraction" published in Powder Technology **177**, 53-63 (2007).
  Outcome: Demonstrating bias in laser diffraction measurements stemming from particle shape characteristics demonstrates a potential for calibration of laser diffraction measurements based upon particle habit
  Impact: An improved understanding of potential bias in laser diffraction measurements and potential for calibration

- **Outcome:** Developed a test protocol for measurement and quantifying 3-dimensional particle shape characteristics of fine-grained industrial materials.
  Outcome: 3-D particle shape for cements, slag, and fly ash have been measured for the first time in the world by X-ray CT at Brookhaven National Laboratory

- **Output:** The NIST stone wall web site has been developed, delivering stone wall durability research and historical development of the stone collection to the US dimension stone industry and to the National Park Service, who partially funded the work (http://stonewall.nist.gov).
  Impact: At NIST, we regularly receive physical and virtual visitors from industry and government involved in historical restoration to view stone degradation in the wall and the web page has been adopted by numerous secondary schools Earth Science classes as an exercise in stone durability.

Standards and Codes: This project develops new standard methods for direct analysis of cements and supplementary mineral admixtures. The combined SEM-XRD analysis protocol that will generate the data for developing a new classification scheme for fly ash, based on direct analyses of the mineral and glassy constituents, will be offered for ASTM standardization. Test development will be coordinated with applicable subcommittees within ASTM C01 (Cement) and C09 (Concrete). The principal investigator is chair of the characterization subcommittee (C01.23) of ASTM C01, on the executive subcommittee of C01, and is an active member of other subcommittees. We also have representation on the subcommittee and task force responsible for particle size measurement.