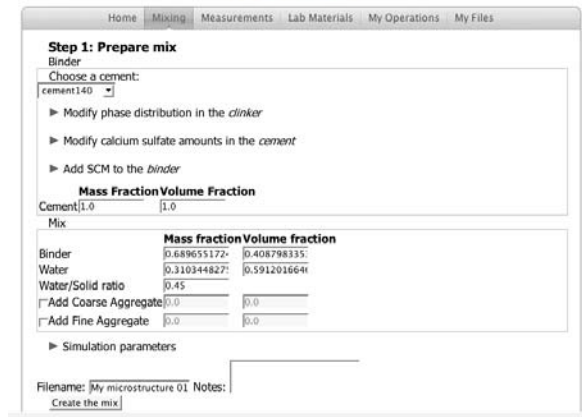
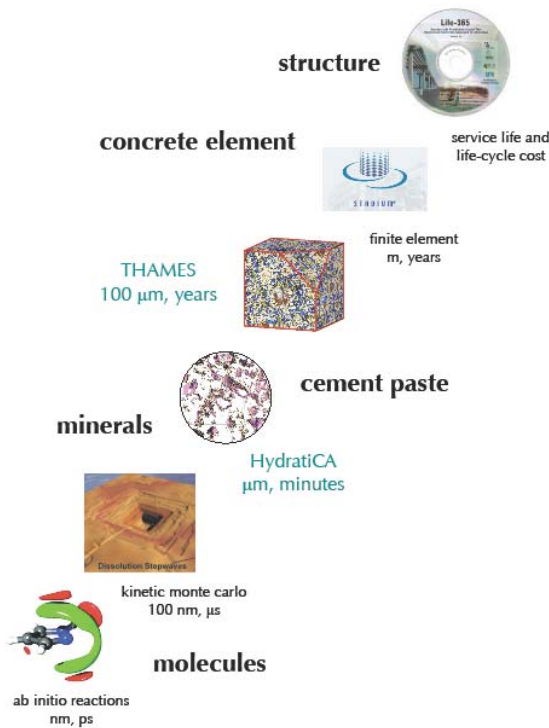


VCCTL 2001-2009: Accomplishments and Prospectus

December 24, 2009

Hydration

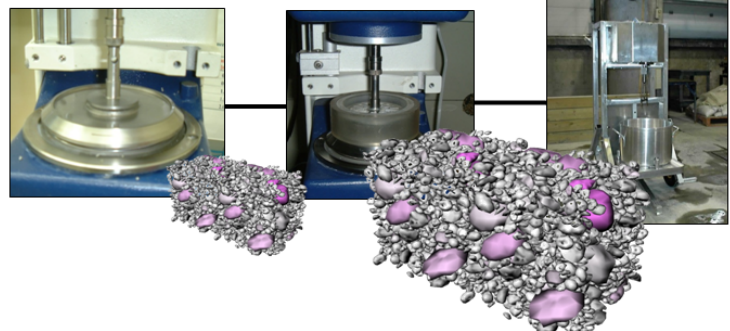


Rheology

Cement paste

Mortar

Concrete



I. Introduction and Executive Summary

The Virtual Cement and Concrete Laboratory (VCCTL) Consortium started in 2001, with six companies and organizations as the charter members. Version 1.0 of the virtual lab software was written in the HTML language and built on top of the CEMHYD3D cement paste microstructure model as it existed at that time. The goal was to carry out joint research involving cement hydration and concrete rheology, and to systematically improve the virtual lab software over time in tune to industrial needs. The research has won several awards (see Appendix), the virtual lab software is now at v8.0, and new hydration and rheology models have been created and are proving to very useful in understanding and therefore providing the means of optimizing concrete. The models developed in the VCCTL consortium fit extremely well into a complete multi-scale approach to solving the problems arising in the use of concrete – such a multi-scale approach is the only one that will ultimately work to fundamentally solve real problems, since concrete is very much a multi-scale materials, from atoms to meters, with different phenomena to model at each scale. A collaboration that has promise for carrying out this multi-scale vision is being built with the newly-formed MIT Concrete Sustainability Hub (CSHub) – the existing VCCTL models and the MIT CSHub models to be developed are complementary and united will form this multi-scale approach (see above cover picture for hydration or Fig. 1 below). New data and models will be built into the VCCTL virtual lab software, making it even more powerful for solving real problems.

Current VCCTL consortium members, at the end of 2009, include the Ready-Mixed Concrete Research and Education Foundation (RMC), W.R. Grace, Sika, Mapei, and the Turner-Fairbanks Laboratory of the U.S. Federal Highway Administration (FHWA). For 2010, the member list so far (as of December 15, 2009) stands at FHWA Turner-Fairbanks, Mapei, and Florida Department of Transportation, with other members to be determined. The complete list of members over the last nine years is in the Appendix, as well as information on progress made in material characterization, scientific visualization and parallel programming, and the production of new ASTM standards based on VCCTL research. A companion document lists all the presentations, informational articles, and journal articles published on the VCCTL research over the last nine years.

In the following, the work over nine years is briefly reviewed with emphasis on what has been learned and what has been accomplished in the various areas of research, in order to give a context for the prospectus for cement hydration, rheology, and the virtual lab software.

II. Cement Hydration: Accomplishments

CEMHYD3D was systematically improved in response to member concerns and this increased sophistication was brought to the VCCTL software. However, around 2005, it became clear the members' desire for a better coupling of chemistry and kinetics, and increased flexibility in introducing new materials could not be satisfied by the CEMHYD3D model. Development work on the new model HydratiCA was then started, and has resulted in several fundamental insights into the chemical mechanisms of hydration (see below). However, more realistic physics and chemistry have made the computational requirements for HydratiCA much more intense so that it could not be brought into the VCCTL virtual lab software as a replacement for CEMHYD3D. While HydratiCA continues to give insight into early-age hydration mechanisms, which is of great interest to the

chemical admixture industry, current model development work focuses on THAMES, which is similar to CEMHYD3D except that it is based on real thermodynamics and more realistic kinetics, and is more accurate in its phase development. It is being designed to eventually replace CEMHYD3D in the VCCTL virtual lab software.

What we have learned from VCCTL hydration research includes the following important points.

- The induction period for cement hydration can be plausibly explained by either of two hypotheses; the metastable passivation layer hypothesis and the slow dissolution step hypothesis. HydratiCA has shown that current experimental data are not conclusive on the mechanism, and has begun to point toward new experiments that could give greater insight into the mechanism. This question is practically important because the induction mechanism will dictate the required action of a chemical additive in retarding or accelerating hydration.
- The hydration kinetics of C_3A in the presence of calcium sulfate cannot be explained quantitatively by the formation of a protective layer of ettringite around C_3A particles, but can be explained in terms of the adsorption of a calcium sulfate complex on active dissolution sites of C_3A .
- Most importantly, hydration rates are sensitive to a wide range of chemical and physical phenomena that before VCCTL may not have been thought important, such as ion speciation in solution, selective adsorption, and the exact nature of the growth law and morphology of C-S-H embryos.

III. Cement Hydration: Prospectus

The International Summit on Cement Hydration Kinetics was held on the campus of the University of Laval in Quebec City, Canada, from July 27-29, 2009 and provided an ideal multidisciplinary forum for identifying hydration research needs and clearly identified the VCCTL cement hydration research, in the form of HydratiCA and THAMES, as a world leader. Figure 1 below shows a schematic of a true multi-scale hydration modeling scheme from atoms to macroscale applications. THAMES and HydratiCA fit neatly into the multi-scale scheme, coupling the nanometer length scale to the meter scale, and the μs time scale to the time scale of years. Collaborative research with the MIT CSHub molecular and nanoscale models will enable this multi-scale scheme to be realized for the first time ever.

IV. Concrete Rheology: Accomplishments

Since concrete is a suspension of particles in various fluids at many length scales, the only way to gain materials science-based insight into concrete rheology is to develop models at the particle scale. Early on in the VCCTL consortium, it was found that accurate computational rheology modeling, involving real particle shapes, lubrication forces between aggregates (required for dense suspensions like concrete), and inter-particle forces, required increasing amounts of computation

power in the form of massively parallel machines. Several grants of supercomputer time from NASA (Columbia supercomputer) and the Department of Energy (Blue Gene supercomputer at Argonne National Laboratory) have been received, totaling several million hours of time, allowing runs using up to 1000 processors at a time in massively parallel mode.

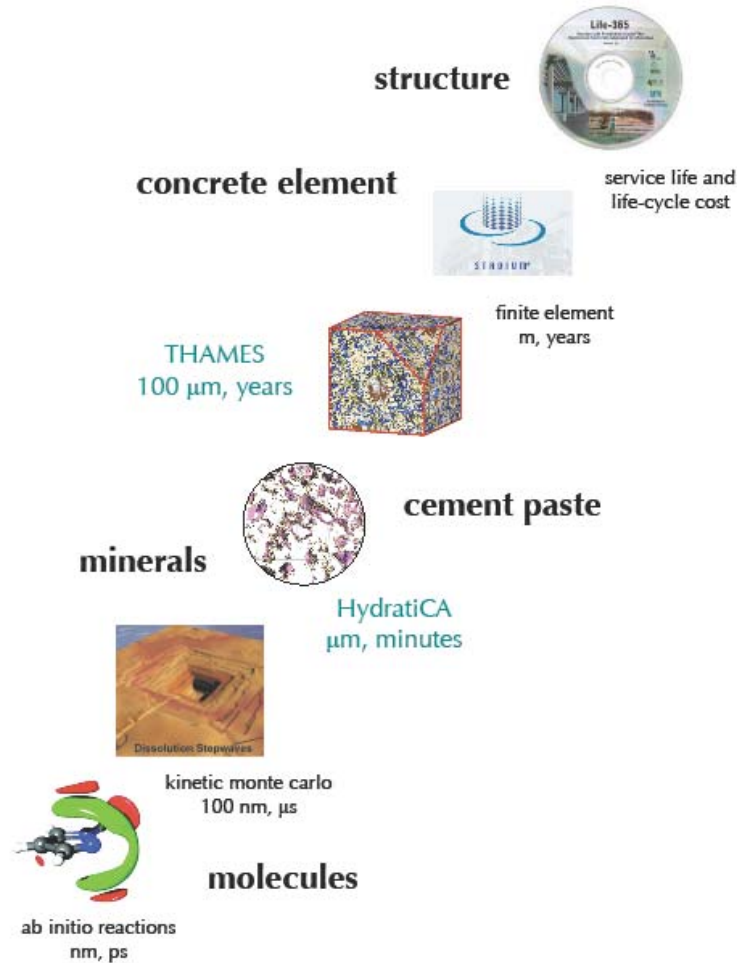


Figure 1: Multi-scale modeling schematic for cement hydration and prediction of hardened concrete properties

These computer runs have resulted in a lot of good results, but because of this need for large computational resources, it would not be useful to incorporate the rheology software into the virtual lab software. However, the VCCTL virtual lab software was modified to be able to set up the initial files needed for large rheology simulation computer runs. At present, the state-of-the-art code is based on smooth particle hydrodynamics (SPH), which can model a non-Newtonian fluid matrix with the exact fluid properties as measured for cement paste and which accurately treats the dynamics of the aggregates.

Many fundamental insights into concrete rheology have been produced in the VCCTL research program. The first is improved understanding of the role of aggregate shape and size distribution in controlling the flow of concrete - it was demonstrated that concrete with crushed aggregates typically has a higher viscosity than concrete composed with more spherical aggregates. This can be understood in terms of the transmission of stress across chains of larger aggregates that span the system. Replacing the crushed aggregate with spherical particles was shown to decrease yield stress and plastic viscosity. Such an effect was also seen for the case of partially replacing angular cement particles with more spherical fly ash particles.

VCCTL rheology research has also advanced understanding of the fundamental mechanisms that control yield stress. It was found that at low volume fractions, the strength of the interparticle interaction controls the magnitude of the yield stress. But, as the volume fraction increases, there is an increase of stress that is transmitted in compression, something akin to a jamming phenomenon, which increases the yield stress. This stress transmission in the compression quadrant is not normally accounted for in the usual treatment of yield stress. The lesson learned here is that at high volume fractions it may make more sense to modify cement particles with coatings instead of changing the interaction potential between particles to improve flowability. We have shown that the rheology of suspensions like cement-based materials is strongly controlled by the local shear rates found near the inter particle contacts, which are considerably higher than in the bulk matrix fluid. Hence, the rheology of concrete is strongly dependent on the high shear rate behavior of the matrix fluid = cement paste.

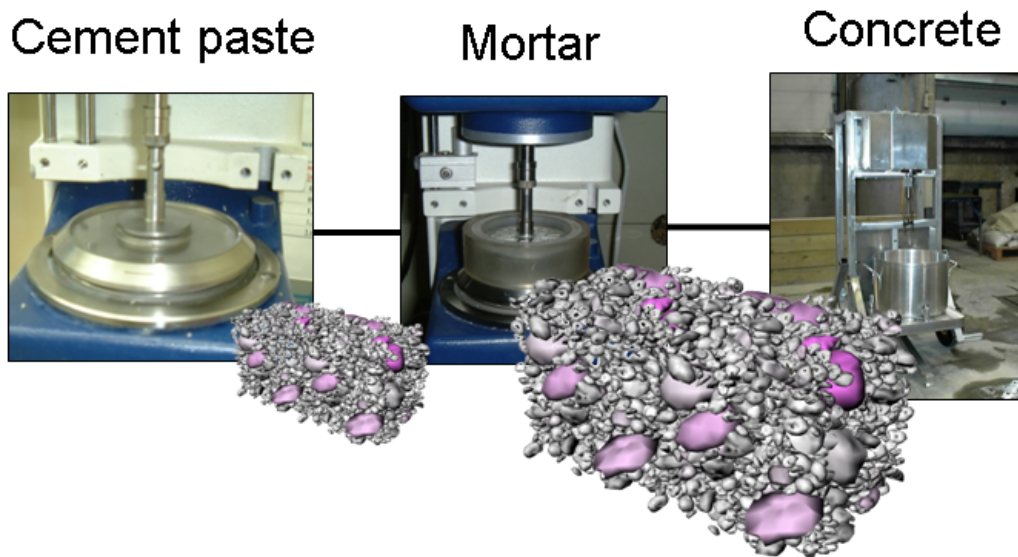


Figure 2: Multi-scale modeling schematic for concrete rheology

V. Concrete rheology: Prospectus

The functioning rheology code that we have in VCCTL is multi-scale, since it works from the length scale of cement particles in water, sand grains in cement paste, and coarse aggregate in

mortar (see Figure 2 above), tying together these length scales with accurate model predictions. This is a unique-in-the-world and very powerful tool for exploring the effect of various variables on concrete rheology, and should be used as such. Coupled with rheology models at the meter scale, and determination of interparticle forces at the nanoscale, it can serve as the heart of a true multi-scale approach to concrete rheology/workability.

Some topics that can be further explored include the modeling of flow in rheometers to sedimentation to better connect to measurements. A data base of the rheological properties of concrete suspensions should be constructed, using supercomputer time, which can be incorporated into the VCCTL virtual lab software – this will be the focus of the 4th phase of the VCCTL consortium. This data base would be useful for estimating rheological properties as a function of particle shape and size distributions. Other possible future research is to extend the rheology code to model viscoelastic behavior, which will help us better understand the early stages of gel formation or setting.

VI. VCCTL Virtual Lab Software Prospectus

The VCCTL virtual lab software package is a powerful piece of software, and can now be used in its version 8.0. We expect in the fourth three-year phase of the VCCTL consortium to focus on applying hydration models like THAMES and HydratiCA and the rheology models to build up the databases and tools inside the VCCTL virtual lab software. We plan to make the VCCTL virtual lab software available to a larger number of companies, via some kind of organization that is either attached to the main consortium or else forms a second consortium.

However, there are issues involving ease of installation and stability of use of VCCTL 8.0, since it is still in the form of a web server. The interface needs to be improved by rebuilding the foundation in Java, to make it in the form of a stand-alone application, which will run under Windows, Linux, and Macintosh. We fully expect that this will solve the vast majority of stability problems and allow for easier incorporation of new algorithms and other improvements. Once this is done, it will be straightforward to channel its power and generality and get out eVCCTL, an educational version that we expect will be highly used in civil engineering curricula and will spread the VCCTL ideas and techniques to a wide audience of future industrial, academic, and governmental leaders. A number of academic beta testers are already lined up.

VII. Conclusion

The VCCTL consortium is healthy after its nine year (so far) run. The virtual lab software is poised to become much more powerful, soon to be based on the greatly improved THAMES hydration model, and easier to use, based on its soon-to-be Java foundation. HydratiCA and the rheology code will be able to link up with other models, some of which to be developed by the exciting new MIT CSHub, so that we can finally form a true multi-scale model of hydration and rheology that will be able to solve the often-thorny problems encountered in the real world of concrete.

Appendix: Member List, Material Characterization, Scientific Visualization and Parallel Programming, VCCTL Technical Notes and New ASTM Standards

A1. Complete Member List Since 2001

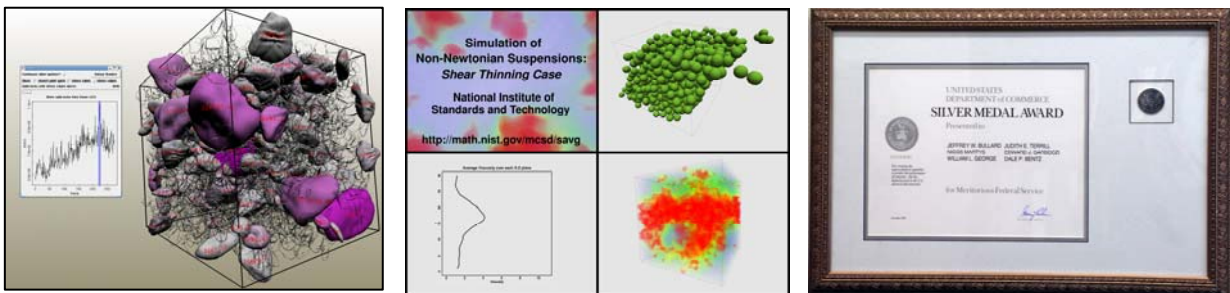
The complete list of members over the nine years, to whom we owe many thanks for financial and intellectual support, includes: the Portland Cement Association (PCA), the Ready-Mixed Concrete Research and Education Foundation (RMC), Holcim, W.R. Grace, Sika, BASF, Mapei, ATILH, VDZ, Dyckerhoff Zement, the Turner-Fairbanks Laboratory of the U.S. Federal Highway Administration (FHWA), Cemex, and the National Stone Sand and Gravel Association (NSSGA). So all the main aspects of concrete have been represented in the VCCTL consortium, at one time or the other – cement, aggregates, chemical admixtures, ready-mixed concrete, and the transportation infrastructure – lending their special insights and guidance to the work.

A2. Awards for VCCTL Research

VCCTL researchers won a Department of Energy Office of Advanced Scientific Computing Research (OASCR) Award for their visualization (left side of picture below) demonstrated at the 2008 SciDAC Conference, held in Seattle, Washington, from July 13-17, 2008. The SciDAC Conference brings together about 350 scientists participating in the Department of Energy (DOE) SciDAC Program along with other prominent researchers from the computational science community. The winning visualization presented the results of a high-performance computer simulation of the flow of a particular complex suspension: concrete.

A short movie entitled “Simulation of Non-Newtonian Suspensions: Shear Thinning Case,” developed by ITL’s Scientific Applications and Visualization Group in collaboration with BFRl scientists, received an OASCR Award at the 2009 Scientific Discovery through Advanced Computing (SciDAC) Conference in San Diego on June 14-18, 2009 (middle of picture below).

The NIST VCCTL team consisting of D.P. Bentz, J.W. Bullard, E.J. Garboczi, W.L. George, N.S. Martys, and J.E. Terrill have won a Department of Commerce Silver Medal in 2009 for their technical work over nine years on the VCCTL software and consortium. This is the second-highest technical award from the Department of Commerce (of which NIST is an agency), and shows the high regard that NIST and Department of Commerce management have for the VCCTL program (right side of picture below).



A3. Progress in Material Characterization

The requirements of the VCCTL models has driven advances in cement and aggregate characterization, since such accurate characterization is needed for the sophisticated VCCTL models to work. Mineralogical characterization at the individual cement particle level was required to obtain accurate results from CEMHYD3D, as well as global mineral phase volume fractions. Both of these needs were taken care of by developing new SEM and XRD techniques. The XRD technique required is now an ASTM standard (see below). The mortar and concrete-level predictive models that are part of the VCCTL software, as well as accurate predictions by the concrete rheology models, required knowledge of particle shape. An X-ray CT technique was developed to fulfill this need, and then was extended to cement particles to add more realism to the cement hydration models, both for CEMHYD3D and for HydratiCA. The particle size distribution of the cement particles (and any other cementitious materials) is crucial for predicting reaction over time, so a standard method using laser diffraction was developed at NIST under VCCTL auspices. This method is available in a VCCTL Technical Note, and has been introduced into the appropriate ASTM sub-committee.

A4. Progress in Scientific Visualization and Parallel Programming

From the inception, the VCCTL research has made good use of the parallel programming and scientific visualization capability at NIST. In fact, without parallel programming, the hydration and rheology models would not be possible. But the requirements of the rheology and hydration modeling research have also driven the development of new visualization techniques. The challenging cement and concrete problems 3-D visualization problems have been used to inspire and test out new kinds of visualization (e.g. GPU programming for shaders) in 3-D. These 3-D visualization techniques have in turn been used to help see the consequences of computer code changes and have greatly accelerated hydration and rheology model development. The many visualization demonstrations for VCCTL consortium members have shown this capability.

A5. VCCTL Technical Notes and New ASTM Standards

For the first few years of the consortium, NIST, often in collaboration with VCCTL members, generated Technical Notes on new experimental procedures that had been developed to support VCCTL model development. A number of these have now been turned into ASTM standards, so that these measurement techniques are now widely available for others to use to support their use of the VCCTL software.

Technical Note 1: Estimation of the Degree of Hydration of Portland Cement by Determination of the Non-Evaporable Water Content

Technical Note 2: SEM-X-ray Imaging of Cement Powders

Work to make this a standard practice is proceeding in ASTM C01.23

Technical Note 3: Quantitative Determination of Calciumsulfate Dihydrate and Calciumsulfate Hemihydrate in Cement by Means of Thermogravimetric Analysis

Technical Note 4: Estimation of the Degree of Hydration of Cement by Measurement of Chemical Shrinkage

ASTM C1608-07 Standard Test Method for Chemical Shrinkage of Hydraulic Cement Paste.

Technical Note 5: Rheological Measurement of Cement Paste/Mortar Using a Parallel Plate Rheometer

In ASTM C01.22, these methods were balloted and were expected to be accepted by the end of 2009 (WK17835 New Practice for High Shear Mixing of Hydraulic Cement Pastes and WK17836 New Test Method for Rheological Properties of Hydraulic Cementitious Paste Using a Rotational Rheometer).

The current ACI 238 state-of-the-art report has some of this experimental rheological material, and this report has been placed into the ACI Manual of Concrete Practice

Technical Note 6: Standard Test Method for Particle Size Distribution of Hydraulic Cement and Related Compounds by Light Scattering

First balloted in 2006, test method slowly proceeding through ASTM

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. This procedure is crucial for characterizing cements so that they can be used in the VCCTL software, including HydratiCA.