



Concrete Science Platform Phase I Summary White Paper

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EXECUTIVE SUMMARY

Concrete sustainability begins at the most fundamental level: understanding the molecular structure of cement paste—calcium-silicate-hydrate (C-S-H). The mechanisms that govern C-S-H's hardness and cement powder's reactivity to water occur at the nanoscale and have thus been challenging to study. Researchers in the Concrete Science Platform (CSP) of the MIT Concrete Sustainability Hub (CSHub) have created innovative, atomic-scale models of C-S-H that shed new light on its molecular dynamics.

The goal of these studies is to discover ways to make a more resilient concrete that lasts longer and requires fewer repairs over its use phase, and perhaps to reduce the amount of cement needed to make concrete. Both would reduce the material's carbon footprint.

The CSP has been divided into three thrust areas: 1) dissolution, 2) precipitation, and 3) hardened paste. During the CSHub's first five years, each of these areas has produced a new model, based on first principles, that fills a critical gap that has previously eluded scientists. The value of this type of model, in addition to being based on first scientific principles, is that it is flexible and can be used both to answer a huge array of questions at nano- to micro-scales directly, and to provide input for models that upscale to micro- to macro-scale engineering practice, such as the VCCTL model at NIST.

1) The first ever quantum model of tricalcium silicate and dicalcium silicate, the two most abundant and important minerals in cement, are now being used to understand the reactivities of these phases, and the influences of elemental point defects. This type of model will be developed to include increasingly complex phases relevant to cement and to understand interactions with liquid water and soluble ions (electrolytes).

2) Building on models of the nanostructure of cement paste, a new approach to understanding setting and hardening has been developed. This percolation-based concept among nanoscale particles forms the basis for modeling the distribution of products at larger scales and, therefore, it is a platform that begins to bridge the gap known as the mesoscale, the bridge to engineering properties. This is a scale that is little understood but is the scale typically observed under a microscope without much of a first-principles understanding. This is fundamentally the next challenge for our research.

3) The molecular model of C-S-H has been validated by chemical, mechanical and structural experiments, expanded, and refined. Illusive questions about water within the structure, the influence of chemical composition of C-S-H on its water content, the influence and binding potential of substitution ions, and the interaction forces among C-S-H particles have been explored. Relationships between structure and properties are emerging, and they are based on first principles.

The models allow researchers to probe how cracks begin to form in concrete at the atomic scale, the role water molecules play in shrinkage, creep and corrosion of hardened cement, and how supplementary cementitious materials, such as fly ash from electric coal power plants, affect the hydration phase of C-S-H.

CSHub findings could allow industry to make a clinker that relies more on belite than alite, thus lowering the sintering temperature and decreasing carbon dioxide emissions. Silicate phases also impact the energy required for grinding clinker into cement powder. More reactive alite and belite could enable coarser cements—requiring less grinding—with no loss of early strength development or other performance characteristics.

Research in the CSP has also applied rigidity theory, an analytical tool from glass science, to C-S-H with various ratios of calcium to silicate. The method enabled them to determine the optimal ratio that would make concrete structures impervious to cracks and other deformations.

The discoveries and validations that the CSHub’s models have made possible would have taken decades to achieve experimentally. Further refinement of these models and validation of their predictions—using commercial clinkers with realistic compositions—is the next logical phase of this work.

CSP ROADMAP

Table 1 shows the concrete science platform roadmap for Phase I. This report presents brief summaries of the key outcomes and remaining gaps in each topic area. **THE SHADED BOXES REPRESENT AREAS FOR WHICH THERE WERE NO RESULTS AND THEREFORE NO SUMMARIES.**

Table 1: The Concrete Science Platform Phase I roadmap.

| Science Across Industry Down | Dissolution | Precipitation and Setting | Hardened Paste |
|---|---|---|---|
| Alite/belite reactivity | 1.1 Surface energy in vacuum Impurities in mineral Interaction with water Admixtures in water | 1.2 Precipitation of product Condensation model Influence of seed Accelerators/retarders | 1.3 Distribution of products Micro texture |
| Aluminate reactivity/sulfate optimization | 2.1 Surface energies in vacuum Interaction with water Interaction with water and sulfate | 2.2 Precipitation of products Sulfate in C-S-H | 2.3 Distribution of products Micro texture Aluminates and silicates together |
| Alkali effects | 3.1 Influence of alkalis in water on surface energy of phases | 3.2 Precipitation of product Alkali in C-S-H | 3.3 Micro texture |
| Water and dissolved components | 4.1 Experimental pico-volume study of the dissolution reaction | 4.2 Electrolytes Interparticle potentials | 4.3 Water within particles Water between particles Predictive water isotherms Water in pores under applied load |
| Mechanical properties | 5.1 Grinding additions and surface energy | 5.2 Very early age strength – liquid to solid | 5.3 Modulus of particles Strength of particles Cohesion Friction Creep Drying shrinkage Toughness at micron scale Multiscale predictions |

DISSOLUTION

The goals of this thrust area have been:

- (1) To provide a fundamental understanding of the relationship between the reactivity (in this case surface energy) of cement phases (the phases in clinker) and their electronic structure using quantum mechanics-based simulations, and
- (2) To use this new knowledge to suggest new strategies for modifying clinker minerals to increase surface energy, and thereby increase reactivity. Our focus has been initially on C_3S (with some of the impurities normally in alite having been studied) and C_2S (with some of the impurities normally in belite also having been studied), but will extend to other cement phases in the future, to give a complete picture.

Topic 1.1: Surface energy in vacuum, interaction with water

What was accomplished in the project?

- For the first time, we modeled and examined the molecular structure of cement clinkers using a quantum mechanical analysis.
- We elucidated the key factors that cause the difference in reaction rates between alite and belite. We showed that the high reactivity of C_3S is mainly related to the reactive sites around the more ionic oxygen atoms, which are loosely bound to the system.
- We studied the effects of impurities in alite and belite phases/polymorphs on mechanical and chemical properties and related our findings to the reactivity of clinkers.
- We provided a fundamental link between the electronic structure of the calcium silicate phases and their reactivity and predicted several novel candidate dopants that could improve the reactivity of belite (see Durgun and Manzano, Chem. Mat. 2012).
- We performed an extensive quantum mechanics-based surface analysis of C_3S and C_2S for all possible orientations and stable crystal surfaces. We classified the most and least stable surfaces, which play a significant role in grinding energies and reactivity. We suggested surface engineering methods to modify these properties (see Durgun and Manzano, Chem. Mat. 2012).
- We clarified reasons for the reducing rate of reactivity of alite hydration. We showed that not only the highly reactive C_3S surface transforms into a low reactivity C_2S -like surface, but also that the protonation of Ca atoms can result in more stable surfaces, which decreases the reactivity of the alite surface during the induction period.
- We have understood from the electronic structure why gamma belite is not reactive, and proposed ways to increase the reactivity of this polymorph. Alkali metal atoms passivate the gamma belite surface

significantly and reduce the reactivity of this polymorph. The effects of alkalies on beta-belite polymorph are not as pronounced as gamma-belite.

- We applied accurate quantum mechanics-based methods to large supercells of clinker using the cluster expansion method. For the first time simulations have been carried out at varying concentrations with a wide range of different impurities including the effects of temperature in the same simulation cell.
- We developed a reactive empirical force field (ReaxFF) for the main elements involved in clinker hydration. The novel methodology fills the gap between accurate but expensive (time consuming) quantum mechanical methods, and faster empirical potentials that did not capture the necessary chemical reactions with suitable accuracy.
- Starting from the interaction of water molecules with calcium silicate surfaces (adsorption and dissociation) we developed a dynamic model on the early period of dissolution for the first time at the nanoscale. This analysis revealed complex cooperative mechanisms and helped us to better understand each of these stages of reaction to lead to improved control and optimization of hydration.
- We also experimentally measured and quantified dissolution of pure C_3S in water, demonstrating key length scale effects that promote the hydration reaction over the competing carbonation reaction.

What are the remaining gaps?

- Using cluster expansion method, realistic quantum mechanical models of clinker phases could be engineered in different ways depending on desired properties.
- The effects of impurities on the surfaces can be more dramatic than in the bulk phase. We are already working on impurities at the surfaces of belite polymorphs, but similar calculations should be conducted for alite polymorph surfaces.
- We are conducting experiments to understand the reactivity at surfaces of belite polymorphs and to use these to benchmark our simulation results.
- The relation of thermal properties (heat capacity, heat of hydration, etc.) to impurity defects in cement phases deserves attention.
- We focused on the two most dominant phases of cement clinker. Similar studies on the Aluminate and Ferrite phases should be conducted.
- The link between the computed reactivity descriptors, the effect of impurities, etc., and quantitative dissolution rates remains a challenge.

Topic 4.1: Effect of electrolyte composition on hydration products

The goals of project are:

- (1) To adapt an existing experiment developed at CINaM (CNRS-Marseille) to study under an optical microscope the dissolution of a single grain of clinker in a pico-liter droplet
- (2) To measure rates of dissolution and precipitations from industrial clinker samples provided by the industry
- (3) Interface this “droplet” experiment with electronic SEM and TEM measurements for phase identifications

What was accomplished in the project?

- We experimentally varied the electrolyte composition by adding sodium hydroxide and other salts to degassed water, and imaged the rate of formation of products upon reaction with a model C_3S phase. These experiments were conducted on pico-volume droplets with microscopic imaging.
- We found that variation of the electrolyte composition changed the rate of dissolution and morphology of hydration products, as reported in a CSHub newsletter (month year) and as expected from empirical macroscale cement paste production reports in the literature or unpublished by CSHub member companies. However, the reaction product composition was not known from these initial experiments.

Topic 5.1: Quantitative analysis of clinker composition, crystal morphology and impact on the grinding process

The goals of project are:

- (1) To provide a cost effective and reliable methodology for the quantification of the phase composition, phase abundance and bulk composition of clinker
- (2) To provide qualitative and quantitative relationships between the clinker composition, micro-texture, processing conditions and grinding energy

What was accomplished in the project?

- Within this project we developed a new methodology based on the grid electron probe micro-analyses (EPMA) to measure simultaneously the chemistry of the clinker phases, their relative abundance, and the bulk clinker chemistry. Prior to this method, the industry needed three independent measurements to obtain similar results. The method has been tested with industrial clinkers and different sample preparation methods (see **Fig. 1**).

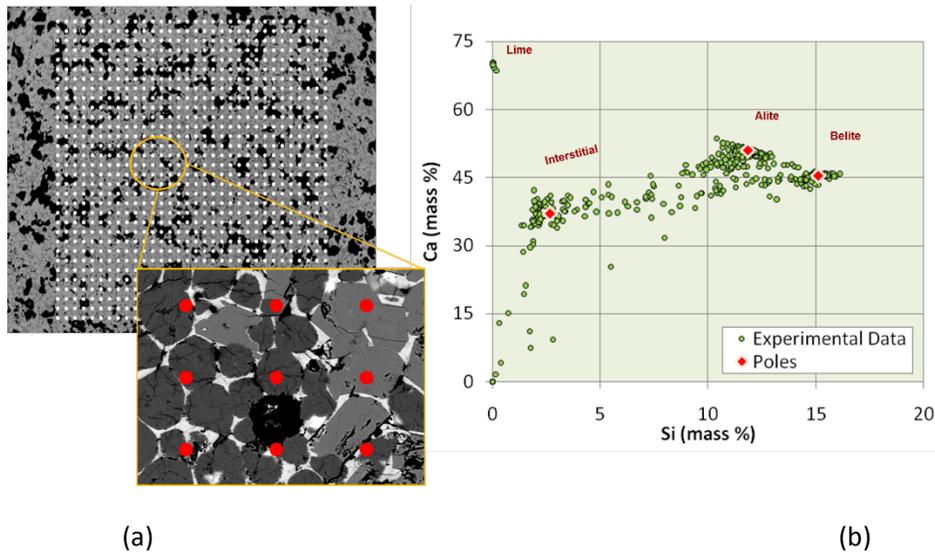


Fig. 1: Grid electron probe micro-analysis technique. (a) Schematic of the EPMA grid superposed on a BSE image of bulk clinker sample, the dots represent the sampling grid, which covers a clinker surface composed of the clinker matrix in gray and the porosity in black, (b) Si vs. Ca representation of the micro-probes obtained on the polished clinker surface.

- A qualitative model of the multi-scale microstructure has been proposed and validated in the experimental investigation. The model consists of three different observation levels, each associated with the unique microstructural features.

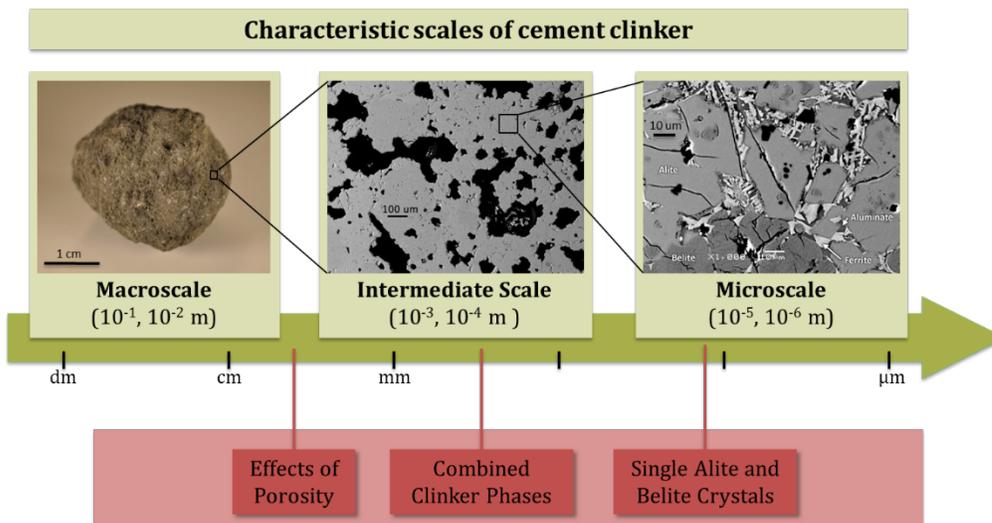


Fig. 2: Schematic of the multi-level model of the clinker micro-texture relevant for the grinding processes, from clinker nodules toward the clusters of individual clinker phases.

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- Different toughening mechanisms and micro-texture effects were identified and may be correlated to clinker grinding stages at industrial scale e.g. coarse and fine grinding (see **Fig. 2**).

What are the remaining gaps?

- Quantification of the amount of amorphous matter in industrial clinkers and its impact on the grinding characteristics of clinker. The earlier investigation shows an important contribution of the phases on typical clinker minerals, including amorphous matter. Its impact on the grinding performance is not quantified as well as its effects on the clinker reactivity
- Quantitative modeling of clinker fracture across multiple levels is postulated in the proposed model. Several important mechanisms of toughening have been identified. However, the quantitative description of these mechanisms and their impact on clinker grindability is lacking, especially in comparison to the Bond work index.

PRECIPITATION AND SETTING

The goals of this thrust area were:

- (1) To model the rate of precipitation of C-S-H during the early stages of reaction, and
- (2) To model the development of elastic modulus and strength in C-S-H.

Topic 1.2: Precipitation of product, condensation model, influence of seed accelerators/retarders (kinetics of reaction rate for cement based materials)

The challenge: The hydration kinetics of tricalcium silicate (C_3S) has been the subject of much study, yet the experimentally observed effects of the water-to-cement (w/c) ratio and particle size distribution have been difficult to explain with models.

The solution: We have developed simple hypothesis that provides an explanation of the lack of any significant effect of w/c on the kinetics and for the strong effect of the particle size distribution on the amount of early hydration associated with the main hydration peak. The hypothesis is that during the early hydration period, C-S-H forms only in a reaction zone close to the surface of the C_3S particles. We also quantified the chemical composition of the dominant reaction products, via microRaman spectroscopy and image analysis.

Validation: To test the hypothesis, a new microstructure-based kinetics (MBK) model has been developed. The MBK model treats the C_3S particle size distribution in a statistical way to save computation time and treats the early hydration as essentially a boundary nucleation and growth process. The MBK model is used to fit kinetic data from two published studies for C_3S with different size distributions, one for alite (impure C_3S) pastes and one for stirred C_3S suspensions. The model is able to fit all the data sets with parameters that show no significant trend with particle size, providing support for the reaction zone hypothesis.

What was accomplished in the project?

- We developed a new hypothesis for the kinetics of hydration of C_3S that fundamentally takes into account the influence of water-to-cement ratio and particle size.
- We measured the rate of reaction of C_3S with differing particle sizes and mixed at different water-to-cement ratios.
- We developed the hypothesis into an executable computer model and compared predicted results to experimental.
- We compared the model predictions to experimental results to validate the essential correctness of the model.
- In separate experiments, we quantified the hydration products of C_3S mixed with water, in both microscale volumes of electrolyte and in bulk hardened pastes. Initial experiments within picovolumes of water droplets were conducted and reported in a CSHub newsletter (May 2012). Product formation

extending from the C_3S particles was visible and tracked over time, but the composition of the hydration product(s) was unknown (for a description of the technique see Grossier, Phys. Rev. Lett 2011).

- To identify the reaction products and reaction kinetics, we then used microRaman spectroscopy to quantify the hydration products with microscale volumes and cement pastes (see Fig.3). We found that carbonation rather than hydration dominates the dissolution reaction under poor hydration conditions or appreciable evaporation conditions. Although C-S-H formation is expected to occur, and does occur on weeks' time scale, within the first hours and days even miniscule carbon dioxide concentrations within the water result in calcium carbonate domination. This quantitative in situ analysis also showed the kinetics of clinker dissolution to be surface-reaction dominated. These experiments provide fundamental understanding of reaction modes and in situ chemical identification of reaction products to validate clinker reactivity simulations, as well as the experimental conditions required to suppress carbonation and thus study hydration. These results lay the basis for further comparison of reactivity of clinker compositions.

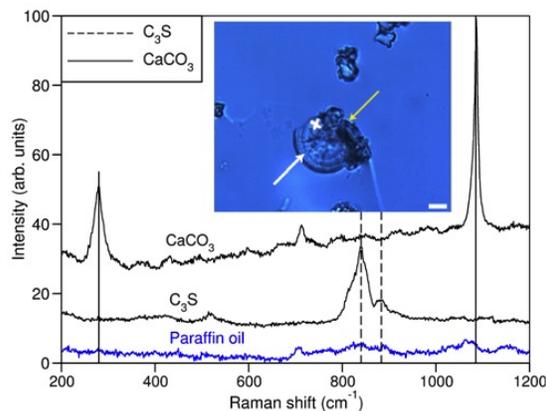


Fig. 3: Raman spectra of system comprising C_3S particles in NaOH pH 12 after 2.5 h of hydration. Micro-Raman characterization of the chemical nature of the reaction byproducts of hydration of tricalcium silicate C_3S , for which growth rates were computed from time-lapse image analysis.

What are the remaining gaps?

The next steps are to extend this MKC model to portland cement and in particular to cement with admixtures. An admixture of particular interest is the seed that can accelerate hydration and redistribute the products, but generally accelerators and retarders are of interest. Finally the study of supplementary cementitious materials is important. Next steps for in situ chemical identification of reaction products, including for more complex and industrially relevant clinker and electrolyte compositions, are possible.

Topic 4.2: Electrolytes, inter-particle potentials

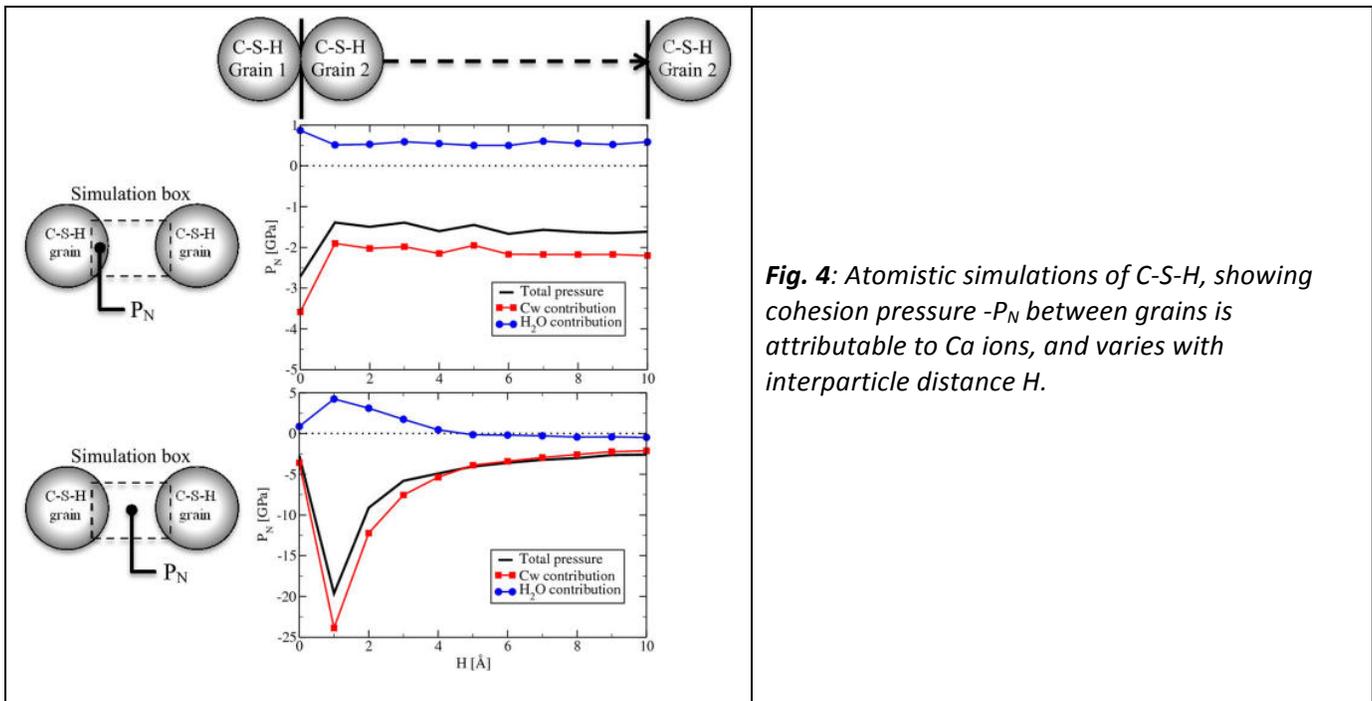
The goals of this project were:

The CSHub aimed to develop mesoscale simulations that describe cement structure and properties beyond the atomistic scale of C-S-H. This mesoscale would describe higher length scales including many C-S-H particles and other phases, and thus required an accurate description of the interaction forces between particles. Interaction forces between these nanoparticles are at the origin of C-S-H mechanical properties at the meso- and

macroscales. These particle interactions and resulting properties may be affected significantly by particle density and environmental conditions such as temperature, relative humidity, or concentration of chemical species within a solution. We thus constructed a potential of mean force between C-S-H nanoparticles, as input into ongoing C-S-Hub mesoscale simulations.

What was accomplished in the project?

- Based on the idea that the CSH grain-grain inter-particle potential has to account for the Hertz contact concept, we built a CSH grain effective potential incorporating grain size effect and carried on the first mesoscale simulations of CSH. We shown that accounting for grain size polydispersity is key reconciling many experiments from mechanical testing, to neutron small angle scattering and water adsorption.
- At a second stage, we used atomistic GCMC simulations and thermodynamic integration, to construct a potential of mean force (PMF) between C-S-H particles that can account for specific particle volume fractions and physical conditions such as humidity and temperature. This allowed us to realistically simulate an environment in which C-S-H particles are immersed at specified humidity and temperature.
- With this approach, we constructed Grand Potential energy profiles and PMFs for C-S-H particles for three distinct mis-orientations between particles; these three configurations allowed us to quantify the extent to which PMF depends on whether the silicate layers within the different particles are aligned. Via thermodynamic integration (TI) of these energy profiles, PMFs were reported for 10%RH and a particle density of 2.2 mmol/L, demonstrating the general method that can now be used for a wider range of physical conditions and C-S-H or electrolyte compositions (see **Fig. 4**). Such PMFs will be key to mesoscale simulations of microstructural and mechanical changes during cement paste curing, as well as changes in the hardened pastes in response to varied physical environments.



What are the remaining gaps?

Such PMFs will be key to mesoscale simulations of microstructural and mechanical changes during cement paste curing, as well as changes in the hardened pastes in response to varied physical environments. Remaining gaps include:

- Inclusion of this model's PMF into mesoscale simulations, and
- Application of this GCMC/TI approach to obtain the PMF for other compositions and conditions of interest.
- Study creep at the mesoscale from existing granular polydisperse models. Implement the rigidity theory for predicting aging mechanism.

Topic 5.2: Very early age strength – liquid to solid

The goals of this project were:

Fracture properties of cementitious materials are difficult to determine with classical experimental means, as size effect tests require setups that are difficult to realize within normal laboratory settings. It is thus not surprising that most engineering design methods, from materials to structures, are geared toward structural and/or materials strength; despite the fact that it is fracture, which ultimately limits serviceability and longevity of most concrete structures. A typical and critical example is the property development of cementitious materials at early ages. As cement paste hardens, molecular bonds are formed between precipitating calcium-silicate-hydrates particles; eventually reinforced by residual clinker grains. Since Powers, a great deal of research efforts have been dedicated to pinning down functional relations between strength and stiffness properties and intensive variables that capture the hydration process of cementitious materials, such as the hydration degree. But the development of fracture properties, namely fracture energy and fracture toughness, have not (to the best of our knowledge) been addressed in the open literature. This is recognized as a serious limitation for engineers to design materials and structures against early-age concrete cracking, and provides enough motivation for this experimental chemomechanics investigation of early-age fracture properties of cement paste.

What was accomplished in the project?

- Experiments were carried out that determined the fracture toughness and splitting tensile strength of white cement at very early ages (see **Fig. 5**).
- We concluded that the microscratch test was the only test method in which the fracture toughness could be assessed on the microscale for a wide range of curing times (or degree of hydration). Typical structural testing would not have been possible at very early ages because of difficulties in instrumentation and the fragility (very low strength, stiffness and toughness) of the material.
- We also show that the classical Brazilian Split Cylinder test, as recommended by ASTM C496/C496M-11, was sufficient to determine the splitting strength of the cement cylinders at all ages, with a correction for the bearing strip width effect.
- We show a fundamental link between the curing time (and hydration degree, as determined with an isothermal calorimeter) and the evolution of fracture toughness and splitting strength. Both properties increase with increasing curing time and degree of hydration, and appear to follow a ‘power law’ type trend.

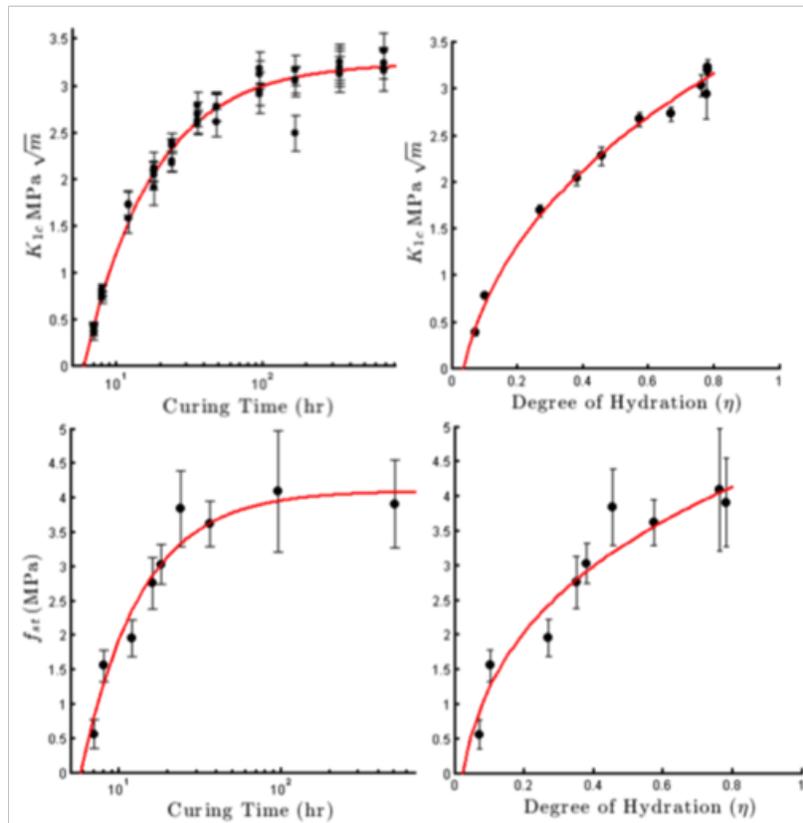


Fig. 5: The evolution of the cement paste fracture toughness with time or degree of hydration.

We determined the effects of curing time and degree of hydration on the evolution of the fracture process zone (FPZ) size, determined from calculation of Irwin’s characteristic length. We show that the FPZ size also increases, which indicates an increase in the ductility of the microstructure, with increasing curing time (and degree of hydration), and seems to follow a ‘power law’ type trend.

HARDENED PASTE

The goals of this thrust area are:

- (1) To understand the atomic structure of C-S-H,
- (2) To quantify how this structure and physical/mechanical properties change with C/S and water content,
- (3) To understand the water within multiscale porosity (binding energy of interlayer water and water in the smallest pores),
- (4) To understand how the binding of impurities into the structure of C-S-H affects the atomic structure and physical/mechanical properties.

Topics 1.3 & 2.3: Distribution of products' microtexture

Subtopic a: Nanotexture of C-S-H

What was accomplished in the project?

- For the first time, we modeled and examined the molecular structure of C-S-H at the atomistic scale probing all possible compositions measured in terms of the Ca/Si ratio using simulations. Initial simulations using classical molecular dynamics suggested high stiffness and hardness of C-S-H with C/S = 1.5. We then refined the computational method by developing and employing reactive force fields (ReaxFF). The overall approach to simulate C-S-H of varying C/S composition entails screening a computationally generated database of atomic structures of C-S-H, against a set of three defect attributes: calcium-to-silicon ratio (C/S) as compositional index, and two correlation distances describing medium-range silicon-oxygen and calcium-oxygen environments. As we consider here C-S-H at the nanoscale, this is referred to in some parts below as “nanotexture.”

For experimental validation of these simulations, cement pastes of varying clinker composition, electrolyte composition, and water/solid ratios were produced. The composition of C-S-H as a function of experimental conditions was quantified by wavelength dispersive spectroscopy in massive grid arrays over the hardened cement pastes surface, and correlated with the elastic modulus and hardness of C-S-H in Project 5. 3. We also extensively validated the simulated models with available (published) nanotexture experimental data (**Fig.6**).

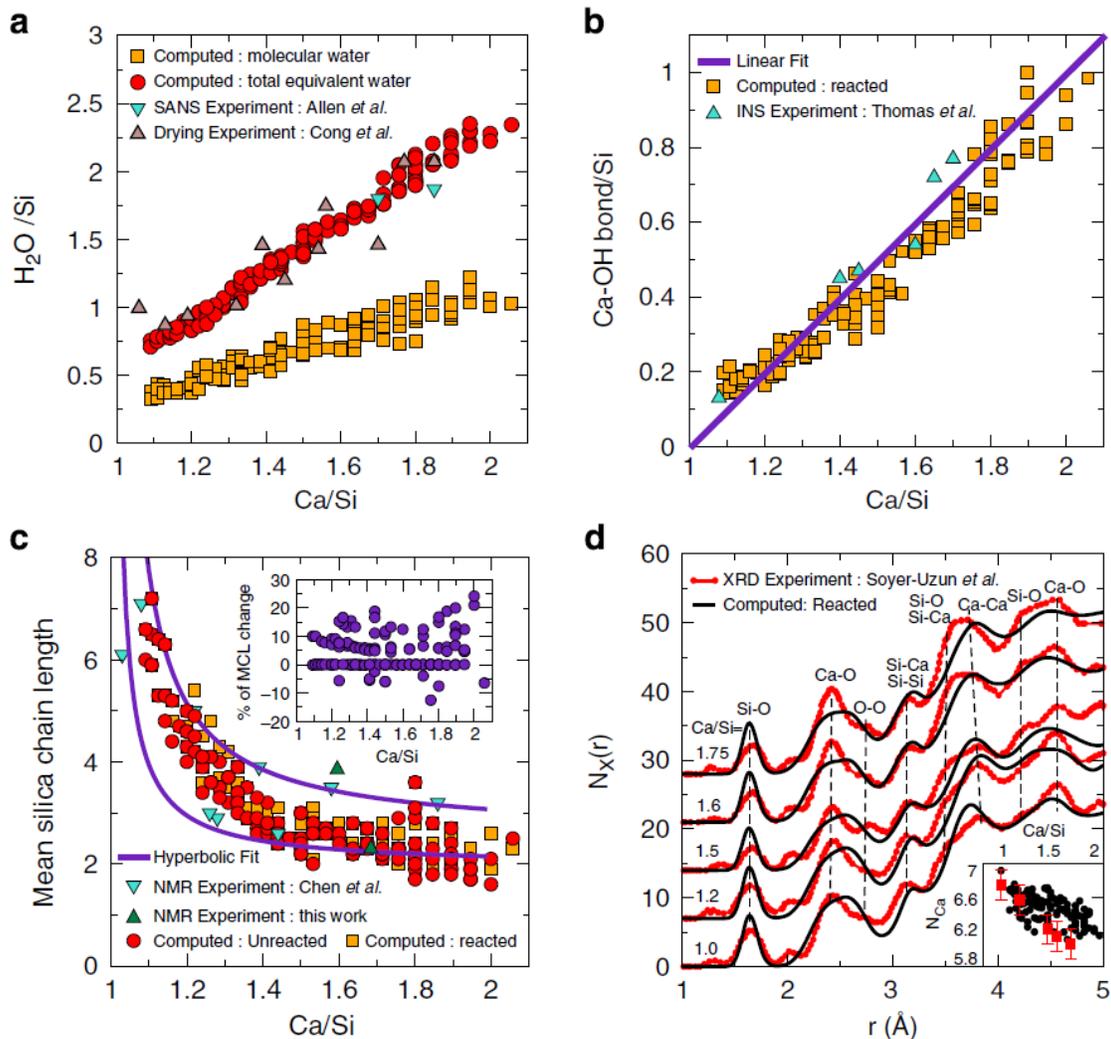


Fig.6: Effect of C/S on the nano-texture of C-S-H. (a) The state of water in C-S-H interlayers at 300 K. The total equivalent water contains both the hydroxyl groups and molecular water in the interlayer spacing. The water content is comparable with total equivalent water measured in SANS and a set of controlled drying experiments. (b) Number of Ca-OH bonds measured via topological analysis at 300 K along with linear fit to the simulation data and their comparison with INS experiments (c) The effect of C/S ratio on the mean silicate chain length in reacted and unreacted models at room temperature compared with NMR experiments of this work and those carried out by Chen and Jennings and hyperbolic fits to the experimental data. The inset presents the variation of MCL before and after reactive modeling. About 20% of molecular models exhibit extra silica condensation and 5% show silica chains dissociations. (d) The total pair correlation function calculated from molecular dynamics trajectory at 300 K and the comparison with X-ray diffraction experiments. The inset provides the comparison between coordination number of calcium ion as calculated from atomistic simulation and measured from X-ray diffraction.

- Mechanical properties of the hardened pastes were examined experimentally via instrumented nanoindentation for a range of cement pastes of varying clinker composition and electrolyte composition. The C/S composition of the C-S-H within these pastes was measured separately via wavelength dispersive spectroscopy, and correlations between C/S and the mechanical properties of C-S-H were explored (see Fig. 7). These data show that stiffness and hardness could vary significantly even for a fixed C/S composition of C-S-H, which was the experimental concept and validation of the computational supposition of C-S-H “polymorphs.”

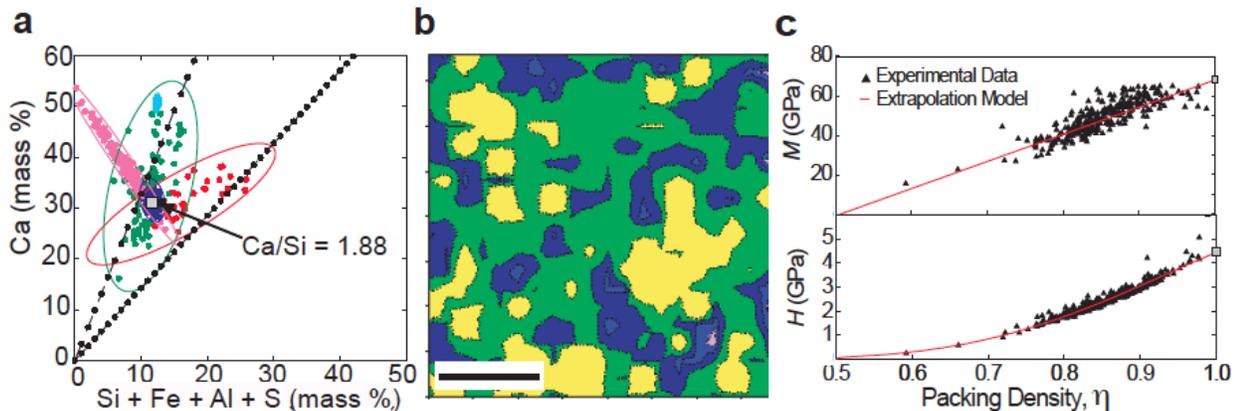


Fig. 7: Experimental characterization of chemistry and mechanics in hardened cement pastes. (a) Wavelength dispersive spectroscopy identifies calcium/silicon ratio of C-S-H; (b) instrumented nanoindentation grids identify elastic moduli M and hardness H of C-S-H regions of finite packing density; and (c) micromechanics models are used to infer mechanical properties of the monolithic C-S-H phase that is computed in atomistic experiments by others within the CSHub.

- These data showed that the calcium/silicon ratio of C-S-H varied strongly with alite and belite fractions (i.e., with clinker reactivity), as well as with electrolyte composition, water/solid ratio, and curing temperature; but not with the initial electrolyte pH.
- Further analysis of chemomechanical properties of C-S-H was conducted with cement pastes that varied systematically the alite or belite composition, water/solid ratio, initial solution pH, and curing time according to a Taguchi matrix. These results also confirmed that mechanical properties of C-S-H were not defined singly by the C/S composition, and also showed that $C/S = 1.5$ did not necessarily result in a phase of maximum in the M/H quantity (that can be seen as an overall mechanical resistance). An original aim of this Taguchi matrix was to obtain conditions that would maximize the stiffness and hardness of C-S-H, and this was partially realized. The addition of fly ash within the range of conditions explored confounded results in terms of only alite or belite reactivity.

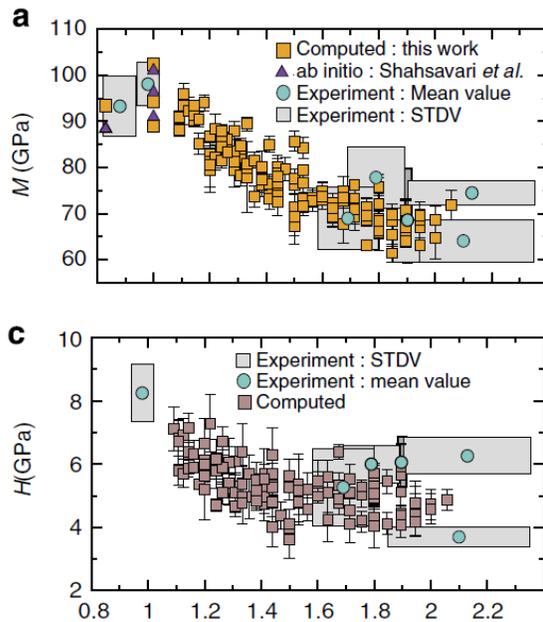


Fig. 8: Experimentally measured elastic moduli (a) and hardness (b) for various cement paste samples (black points with gray boxes indicating experimental and analytical uncertainty), as compared to simulated points via reactive MD.

In both, experiments and simulations, composition C/S does not uniquely define the mechanical properties of the C-S-H phase.

- These correlations were demonstrated by a Taguchi matrix of processing variables, in which our goal was to identify conditions that would attain a calcium/silicon (C/S) ratio of 1.5 in C-S-H. That goal was not realized in the absence of fly ash (see Table), which is consistent with our computational findings that these phases of varying C/S with pure C-S-H were energetically comparable. Further, this work confirmed that conditions which maximize stiffness (m_s) and hardness (h_s) of C-S-H are similar (Table 2): 20°C, water/cement ratio of ~0.4, and grey clinker.

| Objective | Optimal levels of factors | | | |
|----------------|---------------------------|------|---------|----------|
| | T (°C) | w/c | clinker | Additive |
| Maximize m_s | 20 | 0.4 | Grey | None |
| Maximize h_s | 20 | 0.43 | Grey | None |
| Ca/Si = 1.5 | 20 | 0.4 | Grey | FH |

Table 2: Taguchi matrix results, showing that maximum C-S-H stiffness and hardness are attained for slightly different conditions, and a specific C/S ratio requires addition of fly ash.

- The above results show that micro- to macroscale porosity of the cement pastes was strongly affected by processing conditions. Macroscale measurement of the hardened paste’s elastic modulus and hardness showed no significant correlation between the stiffness and hardness of C-S-H and the stiffness and hardness of the macroscale cement paste. Such findings are also discussed below in terms of outstanding gaps.
- We identified a crystal to glass transition for a C/S ratio =1.5 that corresponds to a maximum in the material fracture toughness (see Fig. 9).

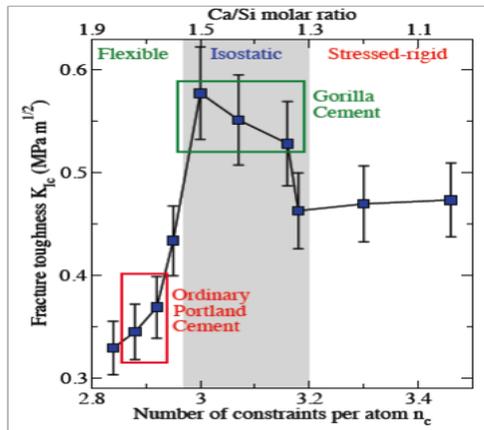


Fig. 9: Effect of C/S ratio on the fracture toughness of C-S-H at nano-scale. A Stressed rigid to flexible phase transition is observed with a peculiar "isostatic" composition at C/S = 1.5 that we call Gorilla Cement as it has a fracture resistance almost 70% larger compared to that of "normal" CSH at C/S=1.7.

- The combinatorial approach introduced here contributes to optimized concrete design that may reduce material consumption and associated CO₂ production. Indeed, while the CO₂ emission of cement clinker production scales with the volume of the concrete structural elements (beams, columns, etc.), the structural strength scales with their cross-sectional area. It is thus expected that an increase of the material strength by a factor of δ allows reducing the environmental footprint to δ^{-1} for pure compressive members such as columns and shells, $\delta^{-2/3}$ for beams, and $\delta^{-1/2}$ for plates.
- As contemporary concretes are characterized, on average, by high C/S ratios, it is expected that the estimated 60% increase in C-S-H strength achieved by reducing C/S from 1.7 to 1.1 (for instance with silica flour additions and proper curing conditions) can entail a 37% reduction of material volume and associated CO₂ emissions for compressive members, not counting further reductions achieved by diluting cement's calcium clinker with silica or other cement substitutes. However, in this speculation it is important to note that other microstructural features such as porosity contribute strongly to the macroscale stiffness and strength, so realization of this potential will require optimization of porosity and other features of concrete beyond the properties of nanoscale C-S-H particles.

What are the remaining gaps?

- Relation between nano, meso, and macroscale physical and mechanical properties: CSHub Phase I focused largely on the nanoscale C-S-H and nanoscale clinker reactivity. Particularly in terms of mechanical properties, our CSHub experiments have shown repeatedly that the stiffness and hardness of the nanoscale C-S-H has no strong correlation with the macroscale engineering stiffness and hardness of the cement paste. Rather, the macroscale properties are governed much more strongly by (1) porosity at various length scales; and (2) cohesion at interfaces between phases. Thus, there are many remaining gaps in terms of the role of porosity and control of porosity, rather than continued emphasis on C-S-H alone. Making C-S-H stiffer or harder will not necessarily make cement paste or concrete stiffer or harder. Mesoscale simulations are a step in this direction, and require a coarser description of particle interactions and the role of electrolyte within these pores.

- Creep and aging are two significant items to be investigated in the characterization of C-S-H.

Subtopic b: Mesotexture of C-S-H

What was accomplished in the project?

- For the first time, we modeled and examined the meso-scale structure (micron scale) of C-S-H by building up from atomistic scale simulations. Cement setting and cohesion are governed by the precipitation and growth of calcium-silicate-hydrate through a complex evolution of microstructure. A colloidal model to describe nucleation, packing, and rigidity of calcium-silicate-hydrate aggregates was proposed at the meso-scale. This model is based on atomistic results for C-S-H. Polydispersity and particle size dependent cohesion strength combine to produce a spectrum of packing fractions and of corresponding elastic properties that were tested against nano-indentation experiments (see **Fig. 10**).
- The potentials of effective interaction that we developed are able to include a few features obtained from experiments and molecular scale simulations of C-S-H (e.g. the polydispersity and the strain at rupture). We have showed here that accounting for the interfacial zone at the “contact” points between the nanoparticles is key to obtaining elastic constants and hardness values for model gels that agree well with the results from nano-indentation experiments.

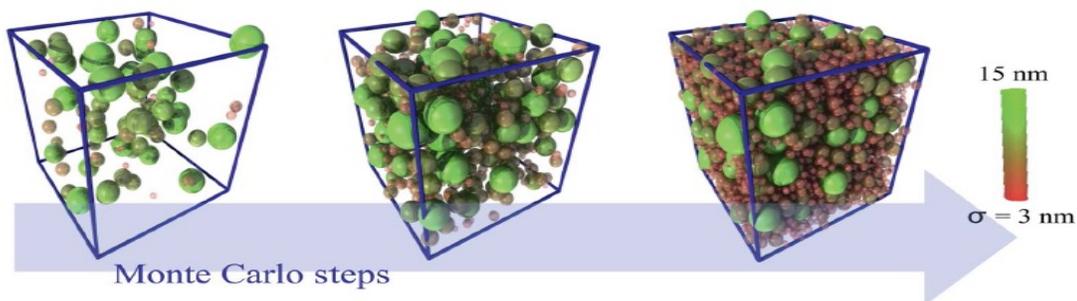


Fig. 10: Snapshots from a simulation to generate a model C-S-H structure extracting particles from a reservoir with polydispersity of 0.38. The color code indicates the particle size that, in our model, is indicative also of the strength of cohesion. Due to space filling, as the simulation advances the small particles increase in number compared to the large ones.

- We use a Monte Carlo space-filling algorithm to generate the model colloidal structures, followed by relaxation to zero stress. The algorithm is based on random insertion of polydisperse particles into a simulation box, and on minimization of the total interaction energy. This protocol has the advantage of producing systems with high packing fractions, in the range of those measured experimentally by nano-indentation on the C-S-H gel (see **Fig. 10**). We found that the resulting distributions of particle sizes (and hence structural heterogeneities) are consistent with small angle neutron scattering and water adsorption experiments.

- We have investigated the accumulation of irreversible processes in the mechanical response, by relaxing our configurations from different levels of applied strain, back to zero shear stress. The results show that once yielding is triggered, the accumulation of irreversible strain is similar for all the model systems irrespective of their polydispersity. Nevertheless, the amount of irreversibility quantified by the decrease of total interaction energy during the shear tests is remarkably smaller in the highly polydisperse systems. We have shown that the mechanisms of accumulation of irreversible deformations (“plastic rearrangements”) are discrete events, whose signature is an abrupt drop of shear stresses and pressure, accompanied by large non-affine displacements of the particles.
- By monitoring the non-affine displacements of subsets of particles within certain ranges of sizes, we have shown that small particles undergo larger non-affine displacement during a plastic event, i.e. they play a primary role in the accumulation of irreversible deformations. By contrast, large particles behave as inclusions that hardly move and that need to be “excluded” by the motion of the rest of the system in order for yielding to occur.

What are the remaining gaps?

- Creep of mesoscale texture remains to be investigated.
- The above mesoscale model did not use an experimentally measured or computationally predicted description of the interaction forces between the particles. Instead, a simple mathematical description was used, while we computed such interactions in a related CSHub project. Such forces are key to the resulting mesoscale and macroscale properties of pastes and concrete. Particle interactions can be efficiently and accurately described by potentials of mean force (PMF). We developed a method to construct such PMFs, in direct response to Phase I needs in mesoscale modeling, and reported PMFs for one physical scenario (low humidity and volume fraction). The current PMF can now be utilized to refine the model, compare with predictions, and motivate the construction of PMFs for other conditions and compositions of interest.

Subtopic c: Nanotexture of CASH / Hg-C-S-H / Sr-C-S-H

What was accomplished in the project?

Nanotexture of CASH: Incorporation of aluminum in the molecular building blocks of C-S-H entails structural and chemo-mechanical consequences. These alterations can be measured through solid-state nuclear magnetic resonance (NMR) experiments. By conducting a wide spectrum of atomistic simulation methods on thousands of aluminum-containing molecular CASH structures, an overall molecular approach for determination of CASH nanostructure is presented. Through detailed analysis of different order parameters, it is found that aluminum can exhibit a tetra-/penta-/octahedral behavior which is fully consistent with the recent NMR observations. This corresponds to the formation of a class of complex three-dimensional alumino-silicate skeletons with partial healing effect in the CASH nanostructure potentially increasing durability and strength of hydration products.

- We have identified two ways for substituting aluminum in layered C-S-H: the aluminum-silicon substitution which is common in aluminosilicate minerals and the calcium-aluminum substitution. More precisely, the silicon-aluminum substitution is favored in bridging sites of silica chains only (excluding all ending sites) whereas the calcium to aluminum substitution leads to the diffusion of aluminum atoms to vacant silica tetrahedral sites. This concerns only the interlayer calcium content (the intralayer calcium species cannot be substituted by aluminum). The consequence of interlayer calcium ions substitutions by aluminum is a healing process that allows the lengthening of silica chains and cross-linkages between layers leading to improved mechanical properties that impact CASH durability.
- In case of aluminum-calcium substitution, study of the penta-/octahedral order parameter revealed that the aluminum can have penta-/octahedral coordination because of the nearby arrangement of water molecules which is fully consistent with the most recent solid state NMR data available. We explored the variation of mechanical observables by increasing aluminum content in CASH model structures of varying calcium to silicon ratio.
- Finally, deformation of C-S-Hs and CASHs of different chemical formula in a multi-scale fashion unravels the effect of chemical composition on the strength and kinematics of deformation in this particular type of composites: we paved the first steps toward the application of the multi-scale Cauchy-Born theory for the nanotexture of cementitious materials. In particular we were able to identify a localized shear deformation within the solid layers.

Nanotexture of Hg-C-S-H: There is an ongoing debate as to whether coal fly-ashes should be regulated as hazardous materials. Due to the mixture of calcium and aluminum it contains, fly ash is an excellent candidate to partially replace portland cement, and thus a viable economical and ecological solution to a waste disposal issue for the power industry. Fly ash, however, is known to contain naturally occurring trace concentrations of mercury and other heavy metals, which raises important environmental concerns. From a concrete science perspective, it is thus important to pin down the way mercury is locked into C-S-H, when cement blended with fly ash reacts with water to form cement hydrates. The key question to be addressed is how the incorporation of mercury in C-S-H affects its long-term structural and chemo-mechanical stability. Answering this question is critical to balance effective use of materials with environmental concerns, with high economical and ecological pay-offs for industry and society at large.

- We have chosen a bottom-up approach that starts at the electron and atomic scale of cement hydrates with calcium-mercury (Ca-Hg) substitutions. Based on first principles of ion coordination, mercury in the ionic Hg^{2+} electronic state is recognized to substitute for calcium atoms in the C-S-H molecular structure. Energy minimization of a large range of molecular structures with varying mercury concentration confirms the stability of this mercury adsorption, and provides a means to probe the mechanical properties of molecular structures at fundamental scales.
- The key finding of this research is that a stable C-S-H structure is maintained for a Ca-Hg substitution of up to 10% (in number of atoms) compared to normal C-S-H. In particular, below 2% of substitution, the

mechanical properties are unaffected by the mercury adsorption. Above 2%, there is a degradation in elastic properties of the Hg-containing compounds, which reaches 30% for the highest, still stable configuration. To fully recap the benefits of higher strength and durability of concrete with high fly ash concentrations, it may turn out beneficial to limit the mercury content in fly ashes for concrete.

Nanotexture of ^{90}Sr -C-S-H: Cementitious materials have been applied to ultimate disposal of radioactive materials in geological repositories. We investigated by means of atomistic simulations the encapsulation of strontium-90, an important radionuclide, in C-S-H and its crystalline analog, the 9 Å-tobermorite. Strontium was shown to energetically favor substituting for calcium in the interlayer sites in C-S-H and 9 Å-tobermorite with the trend more pronounced in the latter. The integrity of the silicate chains in both cementitious waste forms were not affected by strontium substitution within the time span of molecular dynamics simulation. Finally, we observed a limited degradation of the mechanical properties in the strontium-containing cementitious waste form with the increasing strontium concentration. These results suggest that cement hydrate is a good candidate for immobilizing radioactive strontium.

Topic 4.3: Water within particles, water between particles, predictive water isotherms, water in pores under applied load

Subtopic a: Water sorption hysteresis, transport, and drying shrinkage

What was accomplished in the project?

We developed a simple model of water sorption that

- Explains the mechanism of hysteresis (the ink-bottle effect in the porous network), and hence enables the pore size distribution to be obtained from the adsorption isotherm.
- Allows the sorbed water to be divided into different contributions (particularly separating interlayer and gel pore water).
- Defines a new parameter f , which is a measure of how well gel pores are exposed to the vapor, and hence a measure of the capillary porosity even when capillary pores are not filled at the highest humidities.
- Includes cavitation, avoiding the possibility of confusion from the bump around 40%.
- Can explain experimental data, not just for water in cement, but for other materials (e.g. dental enamel, carbon nanotubes) and sorbates (e.g. nitrogen).
- Gives results that behave in a reasonable way (e.g. implies higher capillary porosity for higher water to cement ratio).

We have also outlined how the pores in cement can be divided into categories by size, and how the water in these different pores influences shrinkage.

- Some of the shrinkage comes from Laplace pressure in the gel pores and from surface tension.
- An additional contribution, and most of the hysteresis in shrinkage, comes from the removal and reinsertion of interlayer water, the water molecules that are located between silicate-rich layers of C-S-H.

We have developed a model identifying the transport mechanisms of water in cement.

- Existing models postulate an empirical humidity-dependent water diffusivity, without any explanation of the mechanisms involved
- Our theory shows that the dominant mechanism of water transport is vapor adsorption/desorption at low relative humidity and vaporous diffusion through the liquid filled pores at moderate relative humidity.
- The theory agrees with a set of experimental results measuring the adsorbed mass versus time after a humidity change.

What are the remaining gaps?

We are in the process of completing publications on our phase I results. We have submitted our main paper explaining water sorption hysteresis, and nearly ready to submit a paper on drying shrinkage, identifying two mechanisms depending on different pore sizes. This summer we plan to submit a third paper on the theory of water transport in concrete.

There are several open questions for transport:

- Does the model explain variation between different samples?
- The model was tested for 100 micron powder. Do different mechanisms (e.g. the role of cracks) become important for larger scales?
- Is transport of a bulk liquid (controlled by immersion) very different from that when the humidity is controlled?

We have looked at reversible shrinkage: irreversible is next. In particular, what is the effect of load, water content (static and varying), and the interaction between these?

Subtopic b: Water within particles, water between particles, predictive water isotherms

What was accomplished in the project?

Water in C-S-H particles: In this work, we show how substrate composition affects chemo-physical properties of water in ultraconfined hydrophilic media. This is achieved by performing molecular dynamics simulation on a set

of 150 realistic models with different compositions of calcium and silicon contents (see **Fig. 11**). It is demonstrated that the substrate chemistry directly affects the structural properties of water molecules.

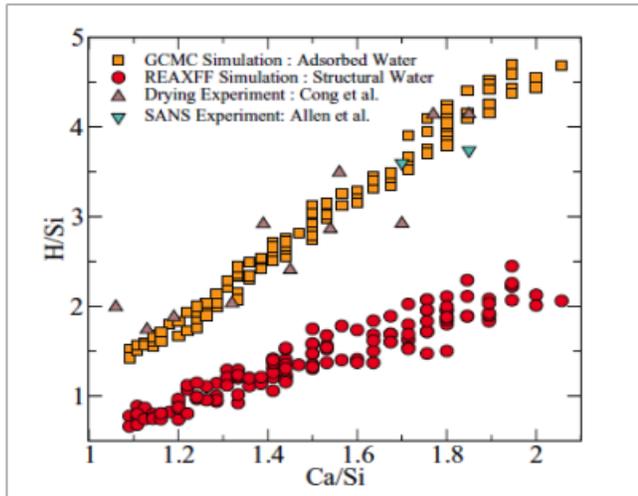


Fig. 11: State of hydrogen in C–S–H nanotexture as a function of stoichiometry. The total hydrogen content calculated via a combination of grand canonical Monte Carlo and molecular dynamics simulations based on REAXFF potential compared to drying experiment of Cong and Kirkpatrick and Small Angle Neutron Scattering (SANS) experiment of Allen et al.

- The motion of confined water shows a multi-stage dynamics which is characteristic of supercooled liquids and glassy phases. Inhomogeneity in that dynamics is used to differentiate between mobile and immobile water molecules.
- Furthermore, it is shown that the mobility of water molecules is extremely reduced and composition-dependent. Similar to the pressure-driven self-diffusivity anomaly observed in bulk water, we report the first study on composition-driven diffusion anomaly, the self-diffusivity increases with increasing confined water density in C-S-H. Such anomalous behavior is explained by the decrease in the typical activation energy required for a water molecule to escape its dynamical cage.
- Computational simulations of water within C-S-H particles (intragranular water) and between C-S-H particles (intergranular water) was studied extensively at the atomistic scale, via Grand Canonical Monte Carlo (GCMC, to produce the C-S-H structure at a specific temperature and humidity) and via Molecular Dynamics simulations (MD, to quantify thermodynamic, structural, and mechanical properties of the resulting C-S-H assemblies).
- The specific computational model of water that best predicted the structure and properties of C-S-H reported in experiments was identified through a detailed survey of several explicit water models. We showed that Single Point Charge (SPC) water models can accurately describe key properties and lowest computational cost for MD simulations (**Fig. 12**).

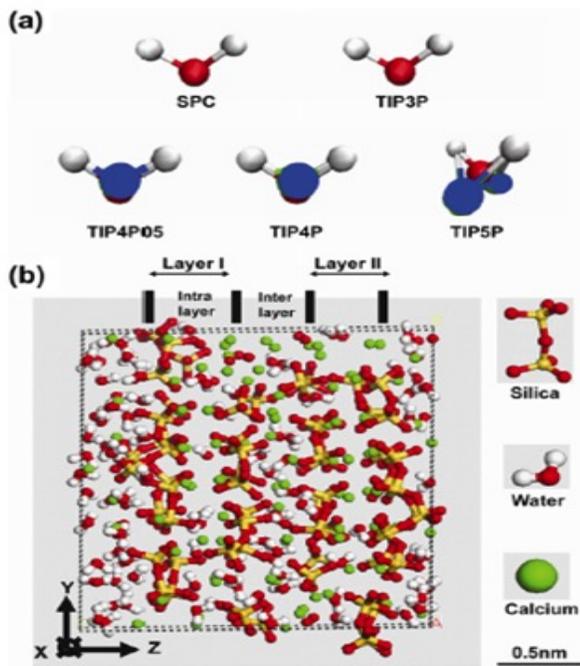


Fig. 12: Classical molecular dynamics simulations were used to identify the explicit water model (a) best suited for structural and mechanical simulations of C-S-H dynamics (b). TIP5P and SPC water models provided reasonable fidelity with available experimental data, and SPC was more computationally efficient.

- We then used this optimized computational model to quantify the structure and properties of the water confined within C-S-H, specifically to demonstrate whether this water behaved as “liquid water” or was so confined within the nanoscale interlayer and intralayer spaces that its physical and thermodynamic properties are a distinct, liquid-crystal-like phase. Our simulations showed that the confined water is in fact a distinct phase.
- How does the mechanical stiffness and strength of a C-S-H nanoparticle change with the amount of water inside C-S-H? The answer helps to predict how concrete structures will respond to changes in humidity and temperature (e.g., due to weather or extreme environments). Such fundamental studies of water content on C-S-H properties also establish a link between the chemistry and the resulting mechanical performance of packed C-S-H nanoparticles. The number of water molecules within our molecular structure of typical C-S-H was varied via statistical mechanics. This Monte Carlo approach effectively simulates a wide range of temperatures and humidities. Mechanical properties of the resulting C-S-H phases, such as elastic moduli and shear strength, were determined by Ji via molecular simulations that deform the nanoscale phase (**Fig. 13**).

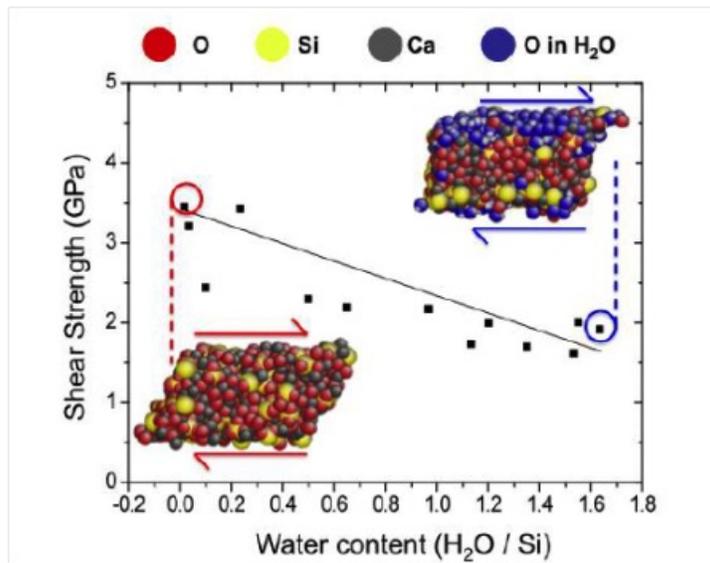


Fig. 13: As the intra-particle water content of C-S-H is changed, its shear strength changes concurrently. Atomistic simulation results indicate that a reduction of H_2O/Si from typical ratios of 1.7 to ratios of 0.2, would increase shear strength of C-S-H nanoparticles by 75%.

- This molecular model shows that the properties of C-S-H depend directly on the intra-particle water content of C-S-H. In particular, the density of C-S-H nanoparticles corresponds directly to water content. Correspondingly, the stiffness and strength of the C-S-H nanoparticles vary directly with water content (see **Fig. 13**). C-S-H can double in strength if the water content is decreased from levels typical of hardened cement pastes.

Water in-between C-S-H particles: The microstructure of cement paste forms by precipitation of products, the most important and abundant of which is C-S-H. Recent approaches to characterizing this microstructure have included models with disordered mesoporous networks that have various pore size distributions, and the comparison of these models to experimental gas sorption isotherms. Although the hysteresis in cement paste adsorption/desorption isotherms were first observed decades ago, no models have been able to quantitatively predict those isotherms and be consistent with mechanical properties. Our approach incorporates the mesoscale and permits verification of the model through direct comparisons with experimental data.

- The water content within C-S-H at very low humidities or high temperatures is difficult to obtain experimentally, and thus we computed it via GCMC and calculated the resulting mechanical properties of C-S-H grains and C-S-H within cement pastes via MD. We showed that water leaves the interlayer regions of C-S-H as humidity is lowered or temperature is raised, but essentially never leaves the intralayer silicate regions. These findings agreed reasonably well with NMR measurements of silicate Q_i , and also formed the basis for a new model of water transport across various scales by which we can understand isotherms and macroscale shrinkage. Prior to these simulations, the actual location of water within C-S-H and the relative humidity at which it would leave the structure were only speculated.
- The thermodynamic and mechanical properties of C-S-H due to this confined water within the calcium-silicate-hydrate pores at various length scales was then computed. Water within such pores plays a

crucial role in damage processes in cement pastes. We calculated the properties of C-S-H as a function of relative humidity (RH), via GCMC simulations (Fig. 14). These results showed that pores of 0.1 to 1 nm within C-S-H regions are completely filled with water for RH > 20%. These simulations also demonstrated that cohesion with C-S-H is attributable chiefly to the calcium ions, and that this cohesion is diminished at very low humidity or high temperatures. These results were key in understanding previous empirical predictions of C-S-H loss of mechanical stiffness and hardness after sustained exposure to high temperatures including fire.

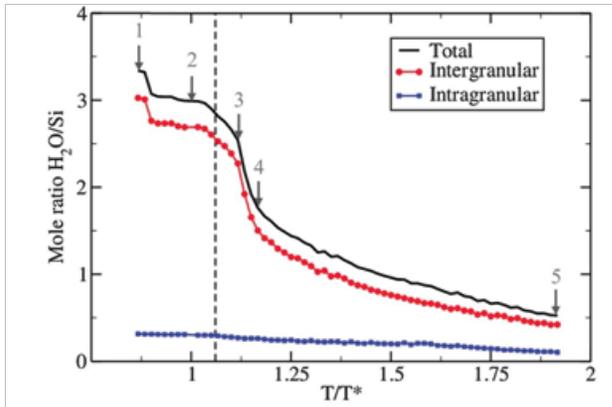


Fig. 14: Atomistic simulations show water molecules leaving the C-S-H intergranular space with increasing temperature, whereas water never leaves the intragranular space at temperatures well above the bulk-water evaporation or sublimation temperatures.

- We conducted a theoretical study of adsorption/desorption hysteresis by combining the mean-field (thermodynamic) density functional theory (DFT) with a coarse-grained lattice-gas model of C-S-H microstructures (Fig. 15). To achieve this goal, a model of C-S-H microstructure is combined with a model of gas/liquid adsorption in a porous structure, which is capable of predicting sorption isotherms.

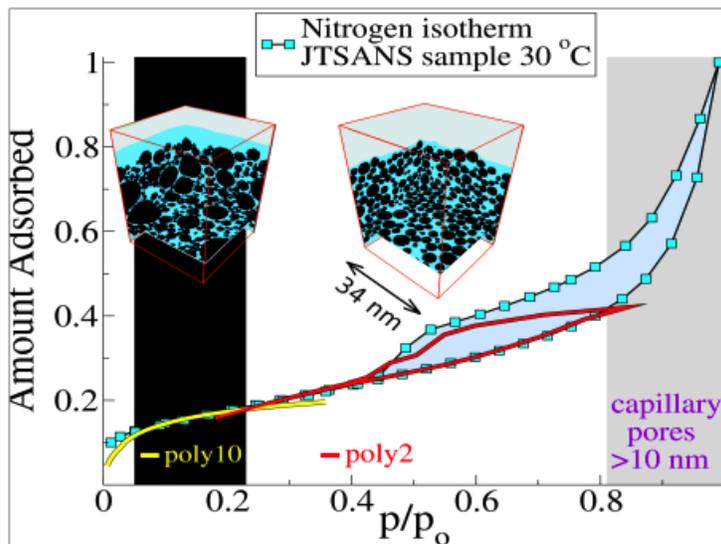


Fig. 15: Comparison of experimental nitrogen sorption isotherm [exp. data from Thomas, Schlumberger Doll Research] with the theoretical results obtained using model C-S-H microstructures.

- We explored heterogeneous microstructures in terms of local densities and packing fractions that were generated via Grand Canonical Monte Carlo simulations of aggregation of nano-sized C-S-H grains with diameters ranging between 1 and 10 nm. We show that the combination of DFT with a simple lattice-gas model of the polydisperse C-S-H grains can reproduce major features of the experimental sorption isotherms (see **Fig. 15**). We identify three distinct regions in the adsorption/desorption curve: sorption at relative pressures below $0.25 P/P_0$ is characterized by the highly polydisperse C-S-H grains with high density (packing fraction 75%) and narrow pores; sorption between 0.25 and $0.80 P/P_0$ occurs in the less dispersed granular material with low density (packing fraction 66%) and wide range of pore size distribution; and above $0.80 P/P_0$ the major contribution is due to the capillary pores whose distribution can be determined from the classic Kelvin equation.
- We found that the adsorbed water has to be divided into different contribution regions (particularly separating water within C-S-H interlayers and water within larger gel pores). In this theoretical approach we have introduced a new parameter f , which is a measure of how well gel pores are exposed to the vapor, and hence a measure of the capillary porosity even when capillary pores are not filled at the highest humidities. It includes cavitation, avoiding the possibility of confusion from the bump around 40%. Our results that behave in a reasonable way (e.g. implies higher capillary porosity for higher water to cement ratio). We have also outlined how the pores in cement paste can be divided into categories by size, and how the water in these different pores influences shrinkage. Some of the shrinkage comes from Laplace pressure in the gel pores and from surface tension. An additional contribution, and most of the hysteresis in shrinkage, comes from the removal and reinsertion of interlayer water.
- In addition, we have developed a model identifying the transport mechanisms of water in cement. Existing models postulate an empirical humidity-dependent water diffusivity, without any explanation of the mechanisms involved. Our theory shows that the dominant mechanism of water transport is vapor adsorption/desorption at low relative humidity and vaporous diffusion through the liquid filled pores at moderate relative humidity. The theory agrees with a set of experimental results measuring the adsorbed mass versus time after a humidity change.

What are the remaining gaps?

- Does the model explain variation between different samples?
- The model was tested for 100 micron powders. Do different mechanisms (e.g. the role of cracks) become important for larger scales?
- Is transport of a bulk liquid (controlled by immersion) very different from that when the humidity is controlled?
- We have looked at reversible shrinkage: irreversible is next. In particular, what is the effect of load, water content (static and varying), and the interaction between these?

- Electrolyte (water and ions) plays a key role in initial reactivity and also in the mechanical properties of hardened cement pastes and concrete. In Phase I, we developed new computational tools at the atomistic, meso, and macroscales to predict effects of *water* (no ions) on pressure within pores, on lab-based isotherm experiments, and on macroscale shrinkage. However, remaining gaps include explicit consideration of how ions (calcium, silicon, and others that may be impurities in the water) will alter these effects. To address the complexity of the *electrolyte*, new computational advances and new experiments for in situ measurement of water content and mechanical stability must be utilized.

Topic 5.3: Modulus of particles, strength of particles, cohesion, friction, creep, drying shrinkage, toughness at micron scale, multiscale predictions

Subtopic a: Aging, fracture resistance, creep, drying shrinkage

What was accomplished in the project?

Aging: The aging of concrete is of critical importance for the industry as well as the research community. The aging process can impact performance characteristics such as creep and shrinkage and may be important in chemical reactions related to durability. In order to reduce the aging of concrete, and especially of its binding phase C-S-H, the composition of the latter might be optimized, e.g. via addition of silica fume, although a thorough understanding of the general relation between composition and aging properties is still lacking. To study the aging of C-S-H, we used tools from glass science. Indeed, designing high-performance glass, such as Gorilla Glass® from Corning® Inc., requires a careful optimization of the composition, which is not feasible by systematic brute force experiments or simulations of every possible mixture.

- This has led to the introduction of a predictive tool: the topological constraint theory, or rigidity theory. This theory relies on an enumeration of the constraints (radial two body and angular three body) between the atoms in the network, and is largely inspired by the study of mechanical truss stability. When the number of constraints per atom, n_c , is less than 3 (being the number of degrees of freedom per atom), the network is said to be flexible. On the contrary, when $n_c > 3$, the network is stressed-rigid and is locked by its high connectivity. An optimal "isostatic" state is achieved when $n_c = 3$. In the latter case, molecular networks show some remarkable properties such as a space-filling tendency, a maximum of toughness and very weak aging phenomena. Based on molecular dynamics simulations, we applied this simple but powerful theory to C-S-H samples characterized by different compositions with Ca/Si from 1 to 2 (covering the whole experimental range).
- We found that C-S-H shows a rigidity transition, being flexible at high Ca/Si ratio (typical of ordinary portland cement), stressed-rigid at low Ca/Si ratio and optimally isostatic around Ca/Si=1.5 (see **Fig. 16**). The latter demonstrated a space-filling tendency at the nanoscale similar to what is observed in glasses. The analysis of the constraints created by each atomic species allows predicting the rigidity status of any composition of C-S-H as well as the existence of a family of isostatic compositions that are likely to be

the most durable. This is the first time that rigidity theory has been applied to such a complex material. Importing glass science tools to C-S-H brings new ideas to predict the effect of composition on cement paste aging. The use of cementitious materials that provide the predicted optimal compositions of C-S-H could lead to more durable concrete. More generally, this highlights the fact that increasing the amount of silica in cement is another means for producing green sustainable concrete.

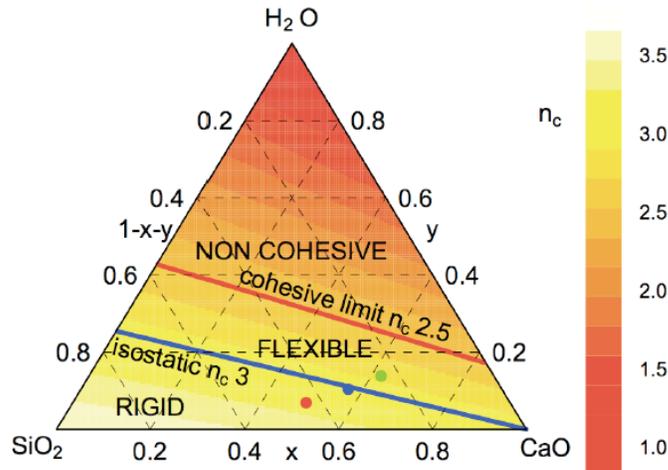


Fig. 16: Rigidity phase diagram of C-S-H with respect to its composition. The blue line indicates the durable isostatic compositions family.

While structural and mechanical properties correlate well with C/S, the cross correlation between all three defect attributes reveals a toughness extremum (maximum) at C/S=1.5, analogous to identifying optimum network connectivity in glass rheology and transport.

Fracture at the nanoscale: From an engineering perspective, predicting and controlling fracture properties offer new opportunities to improve concrete structures' reliability and clinker's / raw materials' grinding. At the atomic scale, crack propagation results of complex atomic rearrangements at the crack tip whereas, at the macroscopic scale, one refers to the simplified notions of toughness and ductility. A fine understanding requires an approach at the atomic scale that can capture in detail the role of chemistry and nanotexture. An approach at the atomic scale can capture the fracture properties of the elementary constituents and their interface that would be very challenging with conventional experiments.

- We developed a methodology to estimate fracture properties: we propagate cracks in mode I at the nano-scale by stretching the system, and we use a thermodynamic integration, valid for any material behavior, to derive the fracture properties of bulk materials and their interfaces.
- An increased resistance to fracture would improve cement's longevity, making it even more sustainable. We compute by molecular dynamics the fracture toughness of all C-S-H spanning the range of possible compositions, $1 < C/S < 2$. The fracture toughness of C-S-H grains is maximal for isostatic composition at a Ca/Si molar ratio around 1.5 (see Fig. 17).

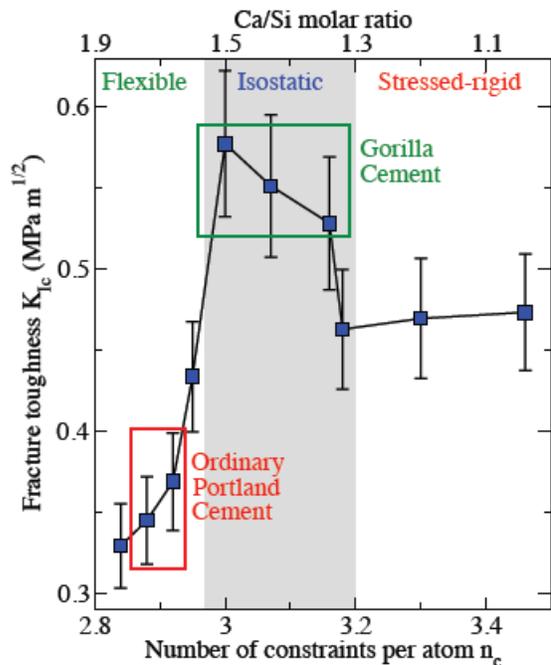


Fig. 17: Computed fracture toughness of C-S-H as a function of composition / number of constraints

- This state of rigidity appears to be optimal. Indeed, stressed-rigid systems are completely locked by the high number of constraints and, consequently, tend to break in a brittle way. On the contrary, thanks to their internal degrees of freedom, flexible systems can deform and show some ductility, but their surface energy is low. Isostatic materials are able to deform and feature relatively high surface energy. Hence, we predict that decreasing the Ca/Si of C-S-H from 1.7 — typical for ordinary portland cement — to 1.5 would increase its toughness by 70%, thus allowing using less material without compromising performance. Decreasing the relative amount of calcium in cement can be achieved by replacing clinker with silica-rich byproduct materials such as fly ash. Tougher and greener, this “Gorilla cement” would help improve the sustainability of our built environment.

What are the remaining gaps?

- Fracture at the mesoscale remains an open question.

Subtopic b: High temperature

- The mechanical properties of C-S-H were also quantified upon exposure of a hardened cement pastes to high temperatures approaching 500°C, in collaboration with and co-sponsorship by the U.S. Army Corps of Engineers. We again employed instrumented nano-indentation and wavelength dispersive spectroscopy to show that the composition and stiffness of C-S-H were not significantly affected by high temperatures. In contrast, the volume fraction of C-S-H formed was strongly affected by addition of reinforcement fibers within the matrix (as is used in UltraHigh Performance Concrete, UHPC, like Ductal®, Lafarge).
- The mechanical properties of C-S-H as a function of exposure to high temperatures were predicted from GCMC and MD simulations. In other words, these simulations showed the atomic structure and mechanical properties of C-S-H at conditions well beyond the initial model (PNAS 2009), where water content is altered by changes in humidity or temperature. We simulated C-S-H over a wide range of temperatures. These results showed that water content within C-S-H grains decreased with increasing relative temperature up to $T/T^* = 2$ (where T^* is the transition temperature at which the bulk liquid and gas are in equilibrium for a given pressure), and that C-S-H grains densified with attendant increases in heat capacity, stiffness, and hardness (see **Fig. 18**).

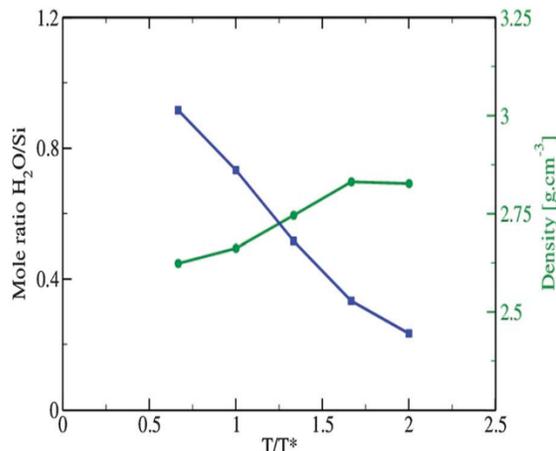


Fig. 18: Computed water content decreases (left axis) and density increases (right axis) for C-S-H as temperature increases.

Although intragranular cohesion increased monotonically with increasing relative temperature over this range, intergranular cohesion increased up to a relative temperature of $T/T^* = 1.1$ and then decreased at higher relative temperatures. This finding suggests a rationale for the decreased mechanical performance of cement paste and concrete at high relative temperatures, and supports previous claims (by Jagannathan et al. 2014 discussed above, and by DeJong and Ulm under different high-temperature exposures in 2007) of peak hardness in C-S-H at an intermediate relative temperature between 1 and 2.61. Further, these atomistic simulations (**Fig. 19**) underscore the important role of confined water in modulating the structure and properties of C-S-H upon exposure to extreme thermal environments.

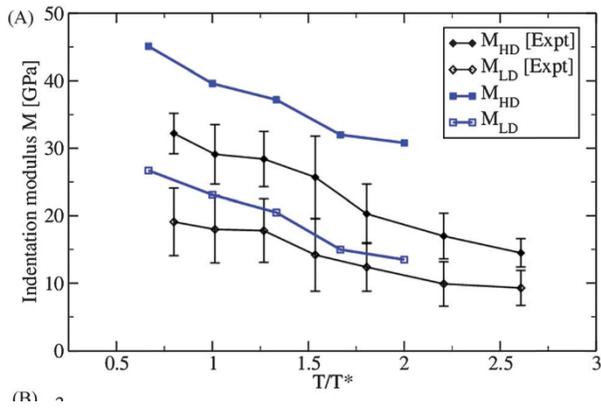


Fig. 19: The computed elastic modulus of low density and high density C-S-H (MLD and MHD, respectively) agree well with that measured experimentally, who quantified this stiffness via indentation after samples were exposed to high temperatures. Computations showed that reduced stiffness with increased temperature is due to reduced cohesion among the C-S-H grains.

APPENDIX – PEER-REVIEWED PUBLICATIONS

This is a listing of peer-reviewed publications on cement and concrete published by the MIT PIs during Phase I of the CSHub. While not all publications are on research directly funded by the CSHub, they are included here in order to contextualize the CSHub research and chronicle the evolution of the topics during Phase I. This appendix includes a total of 72 papers published in peer-reviewed journals as of September 2014.

2014

Title: Combinatorial molecular optimization of cement hydrates

Author(s): Abdolhosseini Qomi MJ, Krakowiak KJ, Bauchy M., Stewart KL, Shahsavari R, Jagannathan D, Brommer DB, Baronnet A, Buehler MJ, Yip S, Ulm FJ, Van Vliet KJ & Pellenq RJM

Source: NATURE COMMUNICATIONS, DOI: 10.1038/ncomms5960, **Published:** SEPT 24 2014

Title: Nanoscale Structure of Cement: Viewpoint of Rigidity Theory

Author(s): Bauchy, M; Qomi Abdolhosseini, MJ; Bichara, C; Ulm, FJ; Pellenq, RJM

Source: JOURNAL OF PHYSICAL CHEMISTRY C **Volume:** 118 **Issue:** 23 **Pages:** 12485-12493 **DOI:** 10.1021/jp502550z **Published:** JUN 12 2014

Title: Order and disorder in calcium-silicate-hydrate

Author(s): Bauchy, M; Qomi, Abdolhosseini Qomi, MJ ; Ulm, FJ; Pellenq, RJM

Source: JOURNAL OF CHEMICAL PHYSICS **Volume:** 140 **Issue:** 21 **Article Number:** 214503 **DOI:** 10.1063/1.4878656 **Published:** JUN 7 2014

Title: Atomic-scale modelling of elastic and failure properties of clays

Author(s): Hantal, G; Brochard, L; Laubie, H; Ebrahimi, D; Pellenq, RJM; Ulm, FJ; Coasne, B

Source: MOLECULAR PHYSICS **Volume:** 112 **Issue:** 9-10 **Pages:** 1294-1305 **DOI:** 10.1080/00268976.2014.897393 **Published:** MAY 19 2014

Title: An improved technique for characterizing the fracture toughness via scratch test experiments

Author(s): Akono, AT; UlmSHS, FJ

Source: WEAR **Volume:** 313 **Issue:** 1-2 **Pages:** 117-124 **DOI:** 10.1016/j.wear.2014.02.015 **Published:** MAY 15 2014

Title: Flugge's Conjecture: Dissipation- versus Deflection-Induced Pavement-Vehicle Interactions

Author(s): Louhghalam, A; Akbarian, M; Ulm, FJ

Source: JOURNAL OF ENGINEERING MECHANICS **Volume:** 140 **Issue:** 8 **Article Number:** 04014053 **DOI:** 10.1061/(ASCE)EM.1943-7889.0000754 **Published:** AUG 2014

Title: Stimuli-Responsive Cement-Reinforced Rubber

Author(s): Musso, S; Robisson, A; Maheshwar, S; Ulm, FJ

Source: ACS APPLIED MATERIALS & INTERFACES **Volume:** 6 **Issue:** 9 **Pages:** 6962-6968 **DOI:** 10.1021/am500774k **Published:** MAY 14 2014

Title: Elastic Properties of Swelling Clay Particles at Finite Temperature upon Hydration

Author(s): Carrier, B; Vandamme, M; Pellenq, RJM; Van Damme, H

Source: JOURNAL OF PHYSICAL CHEMISTRY C **Volume:** 118 **Issue:** 17 **Pages:** 8933-8943 **DOI:** 10.1021/jp412160e **Published:** MAY 1 2014

Title: Mesoscale properties of clay aggregates from potential of mean force representation of interactions between nanoplatelets

Author(s): Ebrahimi, D; Whittle, AJ; Pellenq, RJM

Source: JOURNAL OF CHEMICAL PHYSICS **Volume:** 140 **Issue:** 15 **Article Number:** 154309 **DOI:** 10.1063/1.4870932 **Published:** APR 21 2014

Title: Chemoelastic Fracture Mechanics Model for Cement Sheath Integrity

Author(s): Ardakani, SM; Ulm, FJ

Source: JOURNAL OF ENGINEERING MECHANICS **Volume:** 140 **Issue:** 4 **Article Number:** 04013009 **DOI:** 10.1061/(ASCE)EM.1943-7889.0000690 **Published:** APR 2014

Title: A Reaction Zone Hypothesis for the Effects of Particle Size and Water- to Cement Ratio on the Early Hydration Kinetics of C3S

Author(s): Masoero, E; Thomas, JJ; Jennings, HM

Source: JOURNAL OF THE AMERICAN CERAMIC SOCIETY **Volume:** 97 **Issue:** 3 **Pages:** 967-975 **DOI:** 10.1111/jace.12713 **Published:** MAR 2014

Title: Anomalous composition-dependent dynamics of nanoconfined water in the interlayer of disordered calcium-silicates

Author(s): Qomi, MJA; Bauchy, M; Ulm, FJ; Pellenq, RJM

Source: JOURNAL OF CHEMICAL PHYSICS **Volume:** 140 **Issue:** 5 **Article Number:** 054515 **DOI:** 10.1063/1.4864118 **Published:** FEB 7 2014

Title: Poro-chemo-fracture-mechanics ... bottom-up: Application to risk of fracture design of oil and gas cement sheath at early ages

Author(s): Ulm, FJ; Abuhaikal, M; Petersen, T; Pellenq, RJM

Edited by: Bicanic N; Mang H; Meschke G; DeBorst R

Source: COMPUTATIONAL MODELLING OF CONCRETE STRUCTURES, VOL 1 **Pages:** 61-71 **Published:** 2014

Title: Modelling cement at fundamental scales: From atoms to engineering strength and durability

Author(s): Masoero, E; Jennings, HM; Ulm, FJ; Del Gado, E; Manzano, H; Pellenq, RJM; Yip, S

Edited by: Bicanic N; Mang H; Meschke G; DeBorst R

Source: COMPUTATIONAL MODELLING OF CONCRETE STRUCTURES, VOL 1 **Pages:** 139-148 **Published:** 2014

Title: Is cement a glassy material?

Author(s): Bauchy, M; Abdolhosseini Qomi MJ; Pellenq, RJM; Ulm, FJ

Edited by: Bicanic N; Mang H; Meschke G; DeBorst R

Source: COMPUTATIONAL MODELLING OF CONCRETE STRUCTURES, VOL 1 **Pages:** 169-176 **Published:** 2014

Title: Pavement infrastructures footprint: The impact of pavement properties on vehicle fuel consumption

Author(s): Louhghalam, A; Akbarian, M; Ulm, FJ

Edited by: Bicanic N; Mang H; Meschke G; DeBorst R

Source: COMPUTATIONAL MODELLING OF CONCRETE STRUCTURES, VOL 2 **Pages:** 1051-1058 **Published:** 2014

Title: Docking Sr-90 radionuclide in cement: An atomistic modeling study

Author(s): Youssef, M; Pellenq, RJM; Yildiz, B

Source: PHYSICS AND CHEMISTRY OF THE EARTH **Volume:** 70-71 **Pages:** 39-44 **DOI:** 10.1016/j.pce.2013.11.007 **Published:** 2014

Title: Controlling local packing and growth in calcium-silicate-hydrate gels

Author(s): Ioannidou, K; Pellenq, RJM; Del Gado, E

Source: SOFT MATTER **Volume:** 10 **Issue:** 8 **Pages:** 1121-1133 **DOI:** 10.1039/c3sm52232f **Published:** 2014

Title: Simultaneous assessment of phase chemistry, phase abundance and bulk chemistry with statistical electron probe micro-analyses: Application to cement clinkers

Author(s): Wilson, W; Krakowiak, KJ; Ulm, FJ

Source: CEMENT AND CONCRETE RESEARCH **Volume:** 55 **Pages:** 35-48 **DOI:** 10.1016/j.cemconres.2013.09.013 **Published:** JAN 2014

Title: Nano-scale mechanics of colloidal C-S-H gels

Author(s): Masoero, E; Del Gado, E; Pellenq, RJM; Yip, S; Ulm, FJ

Source: SOFT MATTER **Volume:** 10 **Issue:** 3 **Pages:** 491-499 **DOI:** 10.1039/c3sm51815a **Published:** 2014

2013

Title: Nanoindentation investigation of creep properties of calcium silicate hydrates

Author(s): Vandamme, M; Ulm, FJ

Source: CEMENT AND CONCRETE RESEARCH **Volume:** 52 **Pages:** 38-52 **DOI:** 10.1016/j.cemconres.2013.05.006 **Published:** OCT 2013

Title: Reactive elastomeric composites: When rubber meets cement

Author(s): Robisson, A; Maheshwari, S; Musso, S; Thomas, JJ; Auzerais, FM; Han, DZ; Qu, M; Ulm, FJ

Source: COMPOSITES SCIENCE AND TECHNOLOGY **Volume:** 75 **Pages:** 77-83 **DOI:** 10.1016/j.compscitech.2012.11.012 **Published:** FEB 11 2013

Title: Shear deformations in calcium silicate hydrates

Author(s): Manzano, H; Masoero, E; Lopez-Arbeloa, I; Jennings, HM

Source: SOFT MATTER **Volume:** 9 **Issue:** 30 **Pages:** 7333-7341 **DOI:** 10.1039/c3sm50442e **Published:** 2013

Title: Effects of elevated temperature on the structure and properties of calcium-silicate-hydrate gels: the role of confined water

Author(s): Bonnaud, PA; Ji, Q; Van Vliet, KJ

Source: SOFT MATTER **Volume:** 9 **Issue:** 28 **Pages:** 6418 **DOI:** 10.1039/c3sm50975c **Published:** 2013

2012

Title: Nanoscale Elastic Properties of Montmorillonite upon Water Adsorption

Author(s): Ebrahimi, D; Pellenq, RJM; Whittle, AJ

Source: LANGMUIR **Volume:** 28 **Issue:** 49 **Pages:** 16855-16863 **DOI:** 10.1021/la302997g **Published:** DEC 11 2012

Title: Nanostructure and Nanomechanics of Cement: Polydisperse Colloidal Packing

Author(s): Masoero, E; Del Gado, E; Pellenq, RJM; Ulm, FJ; Yip, S

Source: PHYSICAL REVIEW LETTERS **Volume:** 109 **Issue:** 15 **Article Number:** 155503 **DOI:** 10.1103/PhysRevLett.109.155503 **Published:** OCT 10 2012

Title: Theory of sorption hysteresis in nanoporous solids: Part I Snap-through instabilities

Author(s): Bazant, ZP; Bazant, MZ

Source: JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS **Volume:** 60 **Issue:** 9 **Pages:** 1644-1659 **DOI:** 10.1016/j.jmps.2012.04.014 **Published:** SEP 2012

Title: Theory of sorption hysteresis in nanoporous solids: Part II Molecular condensation

Author(s): Bazant, MZ; Bazant, ZP

Source: JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS **Volume:** 60 **Issue:** 9 **Pages:** 1660-1675 **DOI:** 10.1016/j.jmps.2012.04.015 **Published:** SEP 2012

Title: Thermodynamics of Water Confined in Porous Calcium-Silicate-Hydrates

Author(s): Bonnaud, PA; Ji, Q; Coasne, B; Pellenq, RJM; Van Vliet, KJ

Source: LANGMUIR **Volume:** 28 **Issue:** 31 **Pages:** 11422-11432 **DOI:** 10.1021/la301738p **Published:** AUG 7 2012

Title: Concrete Innovation Potential: From Atoms to Green Infrastructure

Author(s): Ulm, FJ

Source: BETON- UND STAHLBETONBAU **Volume:** 107 **Issue:** 8 **Pages:** 504-U79 **DOI:** 10.1002/best.201200020 **Published:** AUG 2012

Title: Understanding and Controlling the Reactivity of the Calcium Silicate phases from First Principles

Author(s): Durgun, E; Manzano, H; Pellenq, RJM; Grossman, JC

Source: CHEMISTRY OF MATERIALS **Volume:** 24 **Issue:** 7 **Pages:** 1262-1267 **DOI:** 10.1021/cm203127m **Published:** APR 10 2012

Title: Set in stone? A perspective on the concrete sustainability challenge

Author(s): Van Vliet, K; Pellenq, R; Buehler, MJ; Grossman, JC; Jennings, H; Ulm, FJ; Yip, S

Source: MRS BULLETIN **Volume:** 37 **Issue:** 4 **Pages:** 395-402 **DOI:** 10.1557/mrs.2012.55 **Published:** APR 2012

Title: Poromechanics of microporous media

Author(s): Brochard, L (; Vandamme, M; Pellenq, RJM

Source: JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS **Volume:** 60 **Issue:** 4 **Pages:** 606-622 **DOI:** 10.1016/j.jmps.2012.01.001 **Published:** APR 2012

Title: Evidence on the Dual Nature of Aluminum in the Calcium-Silicate-Hydrates Based on Atomistic Simulations

Author(s): Abdolhosseini Qomi, MJA; Ulm, FJ; Pellenq, RJM

Source: JOURNAL OF THE AMERICAN CERAMIC SOCIETY **Volume:** 95 **Issue:** 3 **Pages:** 1128-1137 **DOI:** 10.1111/j.1551-2916.2011.05058.x **Published:** MAR 2012

Title: Nano-Engineering of Concrete

Author(s): Ulm, FJ

Source: ARABIAN JOURNAL FOR SCIENCE AND ENGINEERING **Volume:** 37 **Issue:** 2 **Pages:** 481-488 **DOI:** 10.1007/s13369-012-0181-x **Published:** MAR 2012

Title: Scratch hardness-strength solutions for cohesive-frictional materials

Author(s): Bard, R; Ulm, FJ

Source: INTERNATIONAL JOURNAL FOR NUMERICAL AND ANALYTICAL METHODS IN GEOMECHANICS **Volume:** 36 **Issue:** 3 **Pages:** 307-326 **DOI:** 10.1002/nag.1008 **Published:** FEB 25 2012

Title: Confined Water Dissociation in Microporous Defective Silicates: Mechanism, Dipole Distribution, and Impact on Substrate Properties

Author(s): Manzano, H; Moeini, S; Marinelli, F; van Duin, ACT; Ulm, FJ; Pellenq, RJM

Source: JOURNAL OF THE AMERICAN CHEMICAL SOCIETY **Volume:** 134 **Issue:** 4 **Pages:** 2208-2215 **DOI:** 10.1021/ja209152n **Published:** FEB 1 2012

Title: Density and water content of nanoscale solid C-S-H formed in alkali-activated slag (AAS) paste and implications for chemical shrinkage

Author(s): Thomas, JJ; Allen, AJ; Jennings, HM

Source: CEMENT AND CONCRETE RESEARCH **Volume:** 42 **Issue:** 2 **Pages:** 377-383 **DOI:** 10.1016/j.cemconres.2011.11.003 **Published:** FEB 2012

Title: Comparison of computational water models for simulation of calcium-silicate-hydrate

Author(s): Ji, Q; Pellenq, RJM; Van Vliet, KJ

Source: COMPUTATIONAL MATERIALS SCIENCE **Volume:** 53 **Issue:** 1 **Pages:** 234-240 **DOI:** 10.1016/j.commatsci.2011.08.024 **Published:** FEB 2012

Title: Mechanistic Approach to Pavement-Vehicle Interaction and Its Impact on Life-Cycle Assessment

Author(s): Akbarian, M; Moeini-Ardakani, SS; Ulm, FJ; Nazzal, M

Source: TRANSPORTATION RESEARCH RECORD **Issue:** 2306 **Pages:** 171-179 **DOI:** 10.3141/2306-20 **Published:** 2012

Title: Development of Frangible Concrete to Reduce Blast-Related Casualties

Author(s): O'Neil, EF; Shen, WG; Jennings, HM; Thomas, JJ; Cummins, T

Source: ACI MATERIALS JOURNAL **Volume:** 109 **Issue:** 1 **Pages:** 31-40 **Published:** JAN-FEB 2012

2011

Title: Mechanisms of cement hydration

Author(s): Bullard, JW; Jennings, HM; Livingston, RA; Nonat, A; Scherer, GW; Schweitzer, JS; Scrivener, KL; Thomas, JJ

Source: CEMENT AND CONCRETE RESEARCH **Volume:** 41 **Issue:** 12 **Special Issue:** SI **Pages:** 1208-1223 **DOI:** 10.1016/j.cemconres.2010.09.011 **Published:** DEC 2011

Title: The scratch test for strength and fracture toughness determination of oil well cements cured at high temperature and pressure

Author(s): Ulm, FJ; James, S

Source: CEMENT AND CONCRETE RESEARCH **Volume:** 41 **Issue:** 9 **Pages:** 942-946 **DOI:** 10.1016/j.cemconres.2011.04.014 **Published:** SEP 2011

Title: Time scale bridging in atomistic simulation of slow dynamics: viscous relaxation and defect activation

Author(s): Kushima, A; Eapen, J; Li, J; Yip, S; Zhu, T

Source: EUROPEAN PHYSICAL JOURNAL B **Volume:** 82 **Issue:** 3-4 **Pages:** 271-293 **DOI:** 10.1140/epjb/e2011-20075-4 **Published:** AUG 2011

Title: A nanoscale numerical model of calcium silicate hydrate

Author(s): Fonseca, PC; Jennings, HM; Andrade, JE

Source: MECHANICS OF MATERIALS **Volume:** 43 **Issue:** 8 **Pages:** 408-419 **DOI:** 10.1016/j.mechmat.2011.05.004 **Published:** AUG 2011

Title: Influence of nucleation seeding on the hydration kinetics and compressive strength of alkali activated slag paste

Author(s): Hubler, MH; Thomas, JJ; Jennings, HM

Source: CEMENT AND CONCRETE RESEARCH **Volume:** 41 **Issue:** 8 **Pages:** 842-846 **DOI:** 10.1016/j.cemconres.2011.04.002 **Published:** AUG 2011

Title: Impact of Chemical Impurities on the Crystalline Cement Clinker Phases Determined by Atomistic Simulations

Author(s): Manzano, H; Durgun, E; Qomi; Abdolhosseini Qomi MJA; Ulm, FJ; Pellenq, RJM; Grossman, JC

Source: CRYSTAL GROWTH & DESIGN **Volume:** 11 **Issue:** 7 **Pages:** 2964-2972 **DOI:** 10.1021/cg200212c **Published:** JUL 2011

Title: From electrons to infrastructure: Engineering concrete from the bottom up

Author(s): Jennings, HM; Bullard, JW

Source: CEMENT AND CONCRETE RESEARCH **Volume:** 41 **Issue:** 7 **Special Issue:** SI **Pages:** 727-735 **DOI:** 10.1016/j.cemconres.2011.03.025 **Published:** JUL 2011

Title: Unified nano-mechanics based probabilistic theory of quasibrittle and brittle structures: I. Strength, static crack growth, lifetime and scaling

Author(s): Le, JL; Bazant, ZP; Bazant, MZ

Source: JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS **Volume:** 59 **Issue:** 7 **Pages:** 1291-1321 **DOI:**

10.1016/j.jmps.2011.03.002 **Published:** JUL 2011

Title: Scratching as a Fracture Process: From Butter to Steel

Author(s): Akono, AT; Reis, PM; Ulm, FJ

Source: PHYSICAL REVIEW LETTERS **Volume:** 106 **Issue:** 20 **Article Number:** 204302 **DOI:** 10.1103/PhysRevLett.106.204302 **Published:** MAY 20 2011

Title: The sorption behavior of Cs (+) ion on clay minerals and zeolite in radioactive waste management: sorption kinetics and thermodynamics

Author(s): Yildiz, B; Erten, HN; Kis, M

Source: JOURNAL OF RADIOANALYTICAL AND NUCLEAR CHEMISTRY **Volume:** 288 **Issue:** 2 **Pages:** 475-483 **DOI:** 10.1007/s10967-011-0990-5 **Published:** MAY 2011

Title: Glassy Nature of Water in an Ultraconfining Disordered Material: The Case of Calcium-Silicate-Hydrate

Author(s): Youssef, M; Pellenq, RJM; Yildiz, B

Source: JOURNAL OF THE AMERICAN CHEMICAL SOCIETY **Volume:** 133 **Issue:** 8 **Pages:** 2499-2510 **DOI:** 10.1021/ja107003a **Published:** MAR 2 2011

Title: Scratch test model for the determination of fracture toughness

Author(s): Akono, AT; Ulm, FJ

Source: ENGINEERING FRACTURE MECHANICS **Volume:** 78 **Issue:** 2 **Pages:** 334-342 **DOI:** 10.1016/j.engfracmech.2010.09.017 **Published:** JAN 2011

Title: Empirical force fields for complex hydrated calcio-silicate layered materials

Author(s): Shahsavari, R; Pellenq, RJM; Ulm, FJ

Source: PHYSICAL CHEMISTRY CHEMICAL PHYSICS **Volume:** 13 **Issue:** 3 **Pages:** 1002-1011 **DOI:** 10.1039/c0cp00516a **Published:** 2011

2010

Title: The effect of drying on early-age morphology of C-S-H as observed in environmental SEM

Author(s): Fonseca, PC; Jennings, HM

Source: CEMENT AND CONCRETE RESEARCH **Volume:** 40 **Issue:** 12 **Pages:** 1673-1680 **DOI:** 10.1016/j.cemconres.2010.08.007 **Published:** DEC 2010

Title: Roughness of fracture surfaces and compressive strength of hydrated cement pastes

Author(s): Ficker, T; Martisek, D; Jennings, HM

Source: CEMENT AND CONCRETE RESEARCH **Volume:** 40 **Issue:** 6 **Pages:** 947-955 **DOI:** 10.1016/j.cemconres.2010.02.002 **Published:** JUN 2010

Title: Relationships between Composition and Density of Tobermorite, Jennite, and Nanoscale CaO-SiO₂-H₂O

Author(s): Thomas, JJ; Jennings, HM; Allen, AJ

Source: JOURNAL OF PHYSICAL CHEMISTRY C **Volume:** 114 **Issue:** 17 **Pages:** 7594-7601 **DOI:** 10.1021/jp910733x **Published:** MAY 6 2010

Title: A Coupled Nanoindentation/SEM-EDS Study on Low Water/Cement Ratio Portland Cement Paste: Evidence for C-S-H/Ca(OH)(2) Nanocomposites

Author(s): Chen, JJ; Sorelli, L; Vandamme, M; Ulm, FJ; Chanvillard, G

Source: JOURNAL OF THE AMERICAN CERAMIC SOCIETY **Volume:** 93 **Issue:** 5 **Pages:** 1484-1493 **DOI:** 10.1111/j.1551-2916.2009.03599.x **Published:** MAY 2010

Title: Nanogranular packing of C-S-H at substoichiometric conditions

Author(s): Vandamme, M; Ulm, FJ; Fonollosa, P

Source: CEMENT AND CONCRETE RESEARCH **Volume:** 40 **Issue:** 1 **Pages:** 14-26 **DOI:** 10.1016/j.cemconres.2009.09.017 **Published:** JAN 2010

Title: Does microstructure matter for statistical nanoindentation techniques?

Author(s): Ulm, FJ; Vandamme, M; Jennings, HM; Vanzo, J; Bentivegna, M; Krakowiak, KJ; Constantinides, G; Bobko, CP; Van Vliet, KJ

Source: CEMENT & CONCRETE COMPOSITES **Volume:** 32 **Issue:** 1 **Pages:** 92-99 **DOI:** 10.1016/j.cemconcomp.2009.08.007 **Published:** JAN 2010

2009

Title: Hydration Kinetics and Microstructure Development of Normal and CaCl₂-Accelerated Tricalcium Silicate Pastes

Author(s): Thomas, JJ; Allen, AJ; Jennings, HM

Source: JOURNAL OF PHYSICAL CHEMISTRY C **Volume:** 113 **Issue:** 46 **Pages:** 19836-19844 **DOI:** 10.1021/jp907078u **Published:** NOV 19 2009

Title: First-Principles Study of Elastic Constants and Interlayer Interactions of Complex Hydrated Oxides: Case Study of Tobermorite and Jennite

Author(s): Shahsavari, R; Buehler, MJ; Pellenq, RJM; Ulm, FJ

Source: JOURNAL OF THE AMERICAN CERAMIC SOCIETY **Volume:** 92 **Issue:** 10 **Pages:** 2323-2330 **DOI:** 10.1111/j.1551-2916.2009.03199.x **Published:** OCT 2009

Title: A realistic molecular model of cement hydrates

Author(s): Pellenq, RJM; Kushima, A; Shahsavari, R; Van Vliet, KJ; Buehler, MJ; Yip, S; Ulm, FJ

Source: PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES OF THE UNITED STATES OF AMERICA **Volume:** 106 **Issue:** 38 **Pages:** 16102-16107 **DOI:** 10.1073/pnas.0902180106 **Published:** SEP 22 2009

Title: Nanogranular origin of concrete creep

Author(s): Vandamme, M; Ulm, FJ

Source: PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES OF THE UNITED STATES OF AMERICA **Volume:** 106 **Issue:** 26 **Pages:** 10552-10557 **DOI:** 10.1073/pnas.0901033106 **Published:** JUN 30 2009

Title: Influence of Nucleation Seeding on the Hydration Mechanisms of Tricalcium Silicate and Cement

Author(s): Thomas, JJ; Jennings, HM; Chen, JJ

Source: JOURNAL OF PHYSICAL CHEMISTRY C **Volume:** 113 **Issue:** 11 **Pages:** 4327-4334 **DOI:** 10.1021/jp809811w **Published:** MAR 19 2009

Title: Nanoindentation analysis as a two-dimensional tool for mapping the mechanical properties of complex surfaces

Author(s): Randall, NX; Vandamme, M; Ulm, FJ

Source: JOURNAL OF MATERIALS RESEARCH **Volume:** 24 **Issue:** 3 **Pages:** 679-690 **DOI:** 10.1557/JMR.2009.0149 **Published:** MAR 2009

Title: A constitutive model for drying of a partially saturated porous material

Author(s): Vlahinic, I; Jennings, HM; Thomas, JJ

Source: MECHANICS OF MATERIALS **Volume:** 41 **Issue:** 3 **Pages:** 319-328 **DOI:** 10.1016/j.mechmat.2008.10.011 **Published:** MAR 2009

Title: The Colloid/Nanogranular Nature of Cement Paste and Properties

Author(s): Jennings, H

Edited by: Bittnar Z; Bartos PJM; Nemecek J; Smilauer V; Zeman J

Source: NANOTECHNOLOGY IN CONSTRUCTION 3, PROCEEDINGS **Pages:** 27-36 **DOI:** 10.1007/978-3-642-00980-8_3 **Published:** 2009

Title: Probing Nano-structure of C-S-H by Micro-mechanics Based Indentation Techniques

Author(s): Ulm, FJ; Vandamme, M

Edited by: Bittnar Z; Bartos PJM; Nemecek J; Smilauer V; Zeman J

Source: NANOTECHNOLOGY IN CONSTRUCTION 3, PROCEEDINGS **Pages:** 43-53 **DOI:** 10.1007/978-3-642-00980-8_5 **Published:** 2009

Title: The Nanogranular Nature of Hydrated Porous Materials: Concrete, Shale and Bone

Author(s): Ulm, FJ

Edited by: Ling HI; Smyth A; Betti R

Source: PORO-MECHANICS IV **Pages:** 57-68 **Published:** 2009

Conference Title: 4th Biot Conference on Poromechanics

Title: Nano-Porosity as the Governing Parameter of Creep of Calcium-Silicate-Hydrates

Author(s): Vandamme, M; Ulm, FJ

Edited by: Ling HI; Smyth A; Betti R

Source: PORO-MECHANICS IV **Pages:** 746-751 **Published:** 2009

Conference Title: 4th Biot Conference on Poromechanics

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