Cement Interfaces: Current Understanding, Challenges, and Opportunities

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Abstract

Cement and concrete are rapidly growing in demand and pose many unresolved chemistry questions at particle interfaces, during hydration reactions, regarding the role of electrolytes and organic additives. Solutions through developing greener, more sustainable formulations are needed to reduce the high carbon footprint that amounts to 11% of global CO_2 emissions. Cement is a multi-phase material composed of calcium silicates, aluminates, and other mineral phases, produced from natural and low-cost industrial sources, which undergoes complex hydration reactions. This perspective highlights current research challenges and opportunities for new chemistry insight, including intriguing colloid and interface science problems that involve mineral surfaces, electrolytes, polymers, and hydration reactions. Specifically, we discuss (1) characteristics of cement phases, supplementary cementitious materials, and other constituents, (2) hydration reactions and the characterization by imaging and NMR spectroscopy, (3) the structure of hydrated cement phases including calcium-silicate-hydrates at different scales, (4) quantitative simulation techniques from the atomic scale to microscale kinetic models, as well as (5) the function of organic additives. Focusing on new directions, we explain the benefits of integrating knowledge from inorganic chemistry, acid-base chemistry, polymer chemistry, reaction mechanisms, and theory to describe mesoscale cement properties and bulk properties upon manufacturing.

1. Overview

The global construction industry comprises one of the largest and most influential markets in the world economy with annual spending of about \$10 trillion on construction-related goods and services and including a yearly cement production of over 4 billion tons. The last half-century of research efforts on concrete and cement have lead to remarkable results such as ultra-high-strength or self-compressing concrete due to augmented understanding of the composite materials, the utilization of admixtures, advances in concrete processing and construction technologies.[1] Emerging automated construction methods such as additive manufacturing (layer-by-layer 3D construction) further aim at improving the overall productivity of the cement industry, harnessing recent advances and producing more sustainable civil structures.[2]

The cement industry and related research efforts face two critical challenges in today's competing demand for more efficient utilization of spaces and a growing world population (Figure 1): (1) a high, unsustainable carbon footprint of cement production equal to 11% of global carbon emissions[3] and (2) limited understanding of the chemical reactions of various cement formulations due to the complexity of solid and liquid multi-phase media. [4, 5] The key to solve these challenges lies in understanding the chemistry at the interfaces, which still remains in the beginnings after about 100 years of research, and determines the assembly and properties of cement-based materials at larger scales.

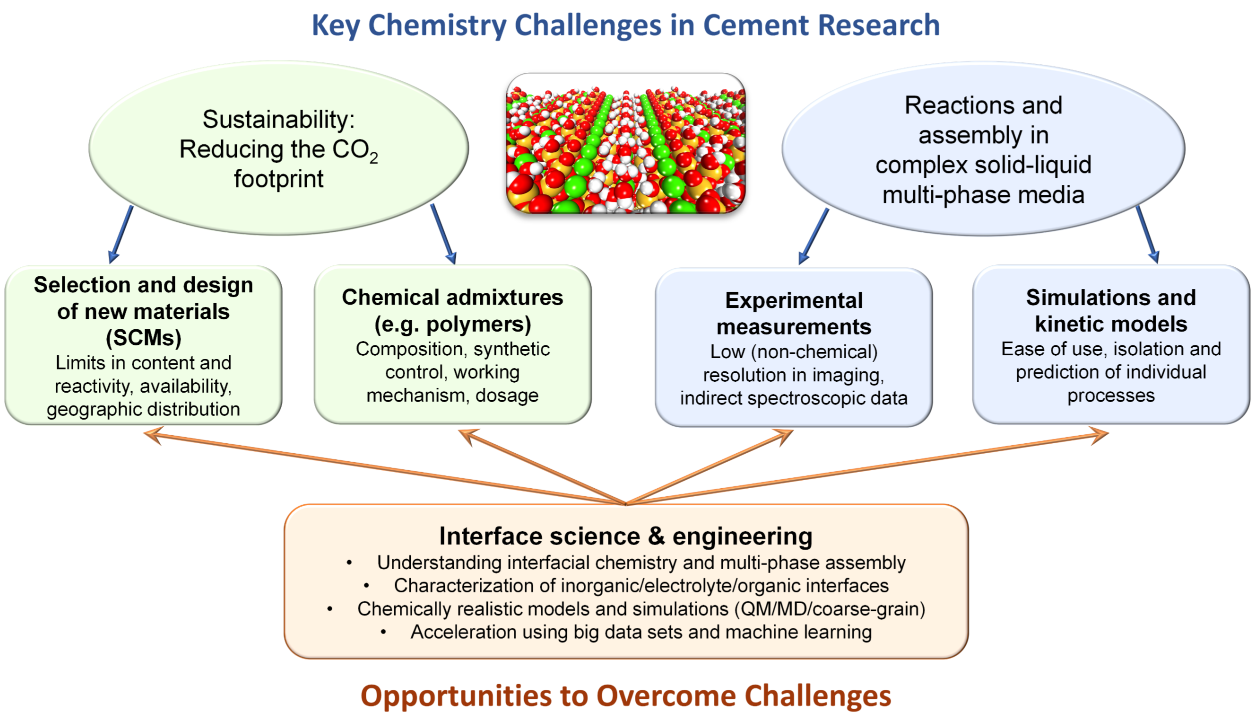
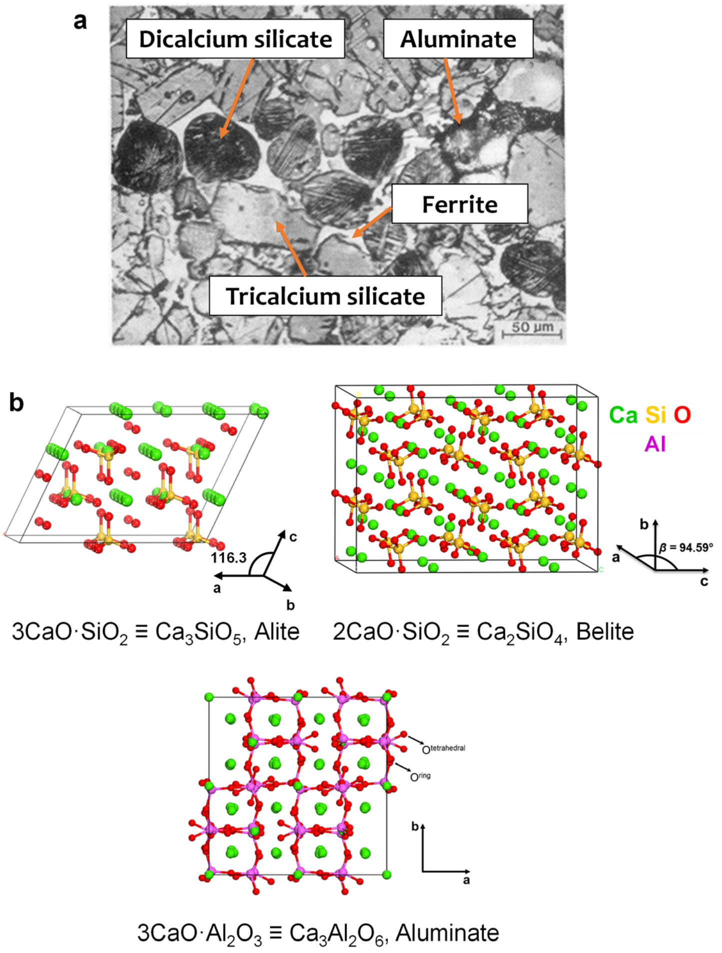


Figure 1. Key chemistry challenges and opportunities in cement research. Cement properties are dominated by interfaces, including interparticle forces, hydration reactions in interlayer spaces, modification of interfacial properties by admixtures (molecular and polymeric additives), and the assembly of the constituents across many orders of length scales. The image shows a perspective view of a calcium-silicate-hydrate surface. SCM = supplementary cementitious materials.

Cement and concrete can be considered the most widely used man-made material, and at the same time, remain one of the least comprehended manufactured materials. In the age of sophisticated instrumental analysis capabilities, molecular-scale control of chemistry, and structural control of advanced materials, there are yet no generally accepted answers regarding the structure, composition, and reaction kinetics of hydrated cement and concrete.[2, 6] The design and process technologies require more complete knowledge of chemical reactions and interactions between phases, particularly at the solid-liquid-organic interfaces, to better predict the macroscopic properties. The uncertainties may be resolved using new interdisciplinary approaches to interface science and engineering, including systematic efforts of synthesis and manufacturing, characterization and development of techniques to tackle complex interfacial chemistry problems, as well as by guidance using quantitative atomistic and multi-scale simulations (Figure 1).[7, 8]

The most widely used, ordinary Portland cement consists of 4 major inorganic phases, which include (in mass%) 50-70% of tricalcium silicate, $3\ CaO \cdot SiO_2$ (also called alite and abbreviated C_3S), 10-20% of dicalcium silicate, $2\ CaO \cdot SiO_2$ (also called belite and abbreviated C_2S), 5-10% tricalcium aluminate, $3\ CaO \cdot Al_2O_3$ (abbreviated C_3A), and 5-15% tetracalcium alumino ferrite, $4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (abbreviated C_4AF) (Figure 2). The production of these core compounds in cement incurs a high carbon footprint related to the use of limestone ($CaCO_3$) as the sole precursor for all Ca content. To produce ordinary Portland cement, limestone is heated together with an appropriate amount of clay minerals (aluminosilicates, shale) in a kiln at temperatures near 1450 °C. The electricity needed to operate the kiln as well as transportation add to the high carbon footprint of cement production.[9]



$3CaO{\cdot}SiO_2 \equiv Ca_3SiO_5$, Alite

$2CaO{\cdot}SiO_2 \equiv Ca_2SiO_4$, Belite

$3CaO{\cdot}Al_2O_3 \equiv Ca_3Al_2O_6$, Aluminate

Figure 2. Image of a cement clinker surface and the chemistry of the major constituting phases. (a) Image of a polished cement clinker surface (reflected light), indicating the constituting phases (from ref. [10]). The particle size is in the micrometer range. (b) 3D atomic structures of three of the major cement phases. Upon hydration, the aluminate particles and the surfaces of the silicate particles react with water. Aluminate ions and $Ca(OH)_2$ are formed, increasing the pH value to between 11 and 13. Calcium hydroxide and partially protonated silicate ions ($H_2SiO_4^{2-}$, $H_3SiO_4^{3-}$) form on the silicate particle surfaces. Then, partially protonated oligomeric silicate chains precipitate in the form of calcium-silicate-hydrate (C-S-H). The pore solution at the aqueous interfaces contains a variety of electrolytes and adsorbed organic additives that regulate the

fluidity, kinetics of the hydration reaction, and development of mechanical properties of cement and concrete over a duration of seconds to months.

To reduce the high carbon dioxide emissions related to cement production, supplementary cementitious materials (SCMs) and fillers with zero carbon footprint are used to dilute ordinary Portland cement.[3] SCMs need to be available in large quantity to fulfill the annual demand of 4 billion metric tons of cement and are usually cheap by-products of industrial processes, for example, slag, fly ash, and silica fume. Simultaneously, SCMs can change the reactions, setting times, and mechanical properties of concrete, requiring further investigations of reaction and multi-phase assembly mechanisms. In addition to SCMs, organic and inorganic additives can improve the characteristics and performance of concrete, leading to ecological savings by reducing the amount of concrete necessary.[6] The customization of organic and inorganic additives is also essential to retain key properties of cement and concrete fortified with SCMs. The two pathways, SCMS and organic/inorganic additives, improve sustainability. Thereby, understanding the molecular and atomic details of the interactions of SCMs and organic/inorganic additives with various cement phases, and of the modified interfacial hydration reactions is essential for rational guidance (Figure 1).[6]

2. Characteristics of Cement Blends, Constituents, and Current Performance

During more than a century of widespread use, Portland cement underwent only incremental changes in content and fineness of the particles to improve the strength of concrete. The raw materials are limestone and clay (shale), which are mixed in precise stoichiometry and progressively burnt to achieve a transformation into cement nodules called clinker. The resultant Portland cement clinker is composed of the two silicate phases alite (tricalcium silicate, C_3S) and belite (dicalcium silicate, C_3S), and the two aluminous phases tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) (Figure 2). Alite and belite form coarse crystals while the aluminous phases act as an interstitial phase bonding the silicate phases.[1] The clinker is co-ground with a certain amount of calcium sulfate, usually ~5% gypsum ($CaSO_4 \cdot 2\ H_2O$), which controls the rheology of hydrated cement, and hence the workability of concrete.

Several SCMs and filler materials have been tested to dilute clinker and decrease the CO_2 footprint of cement production.[3, 11] Pozzolanic SCMs consist of finely ground silica and alumina-containing compounds that can react with lime (CaO) or $Ca(OH)_2$ formed during cement hydration. Pozzolans increase the number of constituents and reactions at cement interfaces. The reactivity of pozzolanic SCMs with calcium species increases with amorphous silica content, fineness of the particles, and high lime concentration during hydration. In contrast, so-called filler materials are much less reactive, or non-reactive, such as pulverized limestone and silica.

Despite several limitations, blast-furnace slag, fly ash, natural pozzolan, vegetable ashes, silica fume, limestone and calcined clay are the most widely used clinker substitutes.[11] On the other hand, current clinker substitution averages only 20% by mass and mainly includes limestone, slag and fly-ash (Figure 3).[12] Cost, local availability, geographic distribution and predictable performance are key factors in partial clinker replacement. More than 90% of granulated slag is already utilized, and fly ash is challenging due to the heterogeneity of the chemical composition, such as carbon content and impurities. In addition to geographic variability, the use of natural pozzolans can necessitate a high water-to-cement ratio for processing and lead to workability problems. Likewise, vegetable ashes such as rice husk ash are considered a regional solution.[3, 13] Very little is known about the resulting structure of the modified interfaces and reactions to-date.

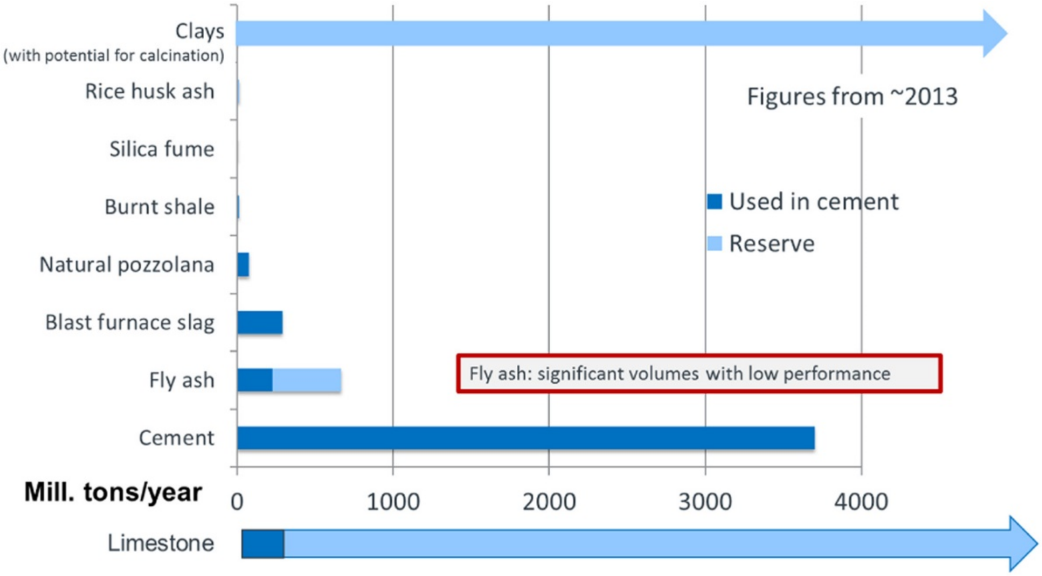


Figure 3. Availability of common supplementary cementitious materials (SCMs). Reproduced with permission from ref. [13].

The useful amount of pulverized limestone in blended cement is limited particularly due to dilution of mechanical properties of the resulting cement and concrete.[14] Amounts above 10% limestone (calcite) can dilute the paste and reduce the strength, even though the use of larger amounts in combination with other SCMs has been reported. Recent studies demonstrated that kaolinitic clays calcined at temperatures around 800°C contain a reactive aluminosilicate phase (metakaolin) that can successfully substitute clinker up to 30% along with 15% limestone.[15] The ternary blend of Portland cement, limestone, and calcined clay, LC^3-50, for example, offers a 50% reduction in clinker content and 30% less CO_2 emission than ordinary Portland cement.[12] Clinker substitution by SCMs has been so far the most promising strategy from a sustainability point of view as it reduces the CO_2 emission by using less clinker, recycles some industrial by-products, and increases the pozzolanic potential (reactivity with $Ca(OH)_2$) of the blended cement.[6] The known benefits, judicious selection and combination of SCMs in blended cements could lead to synergistic effects that allow increased substitution amounts while enhancing the mechanical properties and durability of concrete (the end-product). From a chemistry point of view, formulations remain largely empirical and benefit from better understanding of the interfacial processes from the scale of electronic structure and reactivity to the scale of particle size and the macroscale.

In addition to partial clinker substitution, alternative binder systems have also been explored to reduce CO_2 emissions. Despite their unique challenges, carbonation-hardening cements, calcium sulfoaluminate cement (ye'elimite or CSA), alkali-activated geopolymer cements and active belite offer the possibility of substantially decreasing the environmental cost of cementing materials.[2, 3, 16] The yet rarely commercially used CSA cement already offers up to 62% reduction in CO_2 emissions in addition to improved strength and rapid setting. On the other hand, fly ash-based geopolymer mixtures release 45% less CO_2 than average Portland cement and concrete mixtures.[14] These recent applications demonstrate that greener and more advantageous binder systems are possible and worth exploring in terms of interfacial chemistry.

In addition to the composition of the solid phases, the use of organic and inorganic admixtures is an intensely studied area in cement research because small additions (0.1-0.5%) can have significant impacts on the interfacial properties. Control over the bulk properties by modifying the interfacial characteristics of the C-S-H binder through the use of organic and inorganic additives is of great importance. Many chemical admixtures are effective at 0.1-0.5% by weight as they coat the particle surface and reduce particle agglomeration in the liquid media.[17] The admixtures act as water reducers, enabling a lower water-to-cement ratio for processing, and as retarders for cement hydration. Admixtures can likewise coat liquid surfaces at liquid-vapor interfaces to reduce shrinkage and air-entrance (air-entraining agents). Well-understood and purposeful utilization of admixtures can have a significant environmental impact, particularly when cement is blended with SCMs, which are less active in hydration reactions.

Water-reducing admixtures (superplasticizers), such as polycarboxylate ethers, reduce the carbon footprint of concrete structures by decreasing the water-to-cement ratio up to 30%.[6, 18] It is then possible to manufacture high-strength concrete with lower cement content. In addition to polymers, also inorganic additives can be beneficial. For example, the addition of 0.15% functionalized WS_2 to cement resulted in 80% improvement in strength and in inhibited crack propagation.[4] The efficiency of the admixtures, organic or inorganic/organic, is determined by the preferential adsorbed amount and assembly of the molecules or nanostructures on the chemically and morphologically varying phases and particle types in cement.

To reduce carbon emissions by a more significant amount than today, e.g., by 90%, a clear understanding of the chemistry of mineralogical components, the chemistry of surface-solution interfaces, and the reaction kinetics is required, which may lead to entirely new chemistries and applications.

3. Hydration Reactions and the Structure of Hydrated Cement at Different Scales

The hydration of ordinary Portland cement first leads to the dissolution of tricalcium aluminate (C_3A) within minutes, generates calcium hydroxide, and raises the pH value to a range between

11 and 13. This reaction is followed by the slower superficial hydration of tricalcium silicate (C_3S), the major component of ordinary Portland cement. This process takes several hours, involves a much-debated delay for about 3h, and generates further calcium hydroxide as well as calcium silicate hydrate gel (Figure 4a).[1, 4] The ferrite phase (C_4AF) hydrates at a similar rate as C_3S and is typically considered less influential due to the small contribution by weight (5 to 15%) and relative inertness of iron oxides and hydroxides. Dicalcium silicate (C_2S) hydrates very slowly over a period of 1-3 months and contributes to cement's strength development.

The hydration of calcium silicate particles (C_3S and C_2S) in ordinary Portland cement causes the formation of calcium-silicate-hydrate (C-S-H) gel on the particle surfaces (Figure 4b).[19] The reaction only occurs on the particle surface so that the core of the particles keeps the original composition. The resulting superficial C-S-H gel comprises about half of the binder in cement, the other half is calcium hydroxide (portlandite).[20] The transformation of the interstitial aluminous phases (C_3A, C_4AF) in the presence of calcium sulfate causes additional formation of ettringite and sulphoaluminate phases which remain somewhere part of hydrated cement.

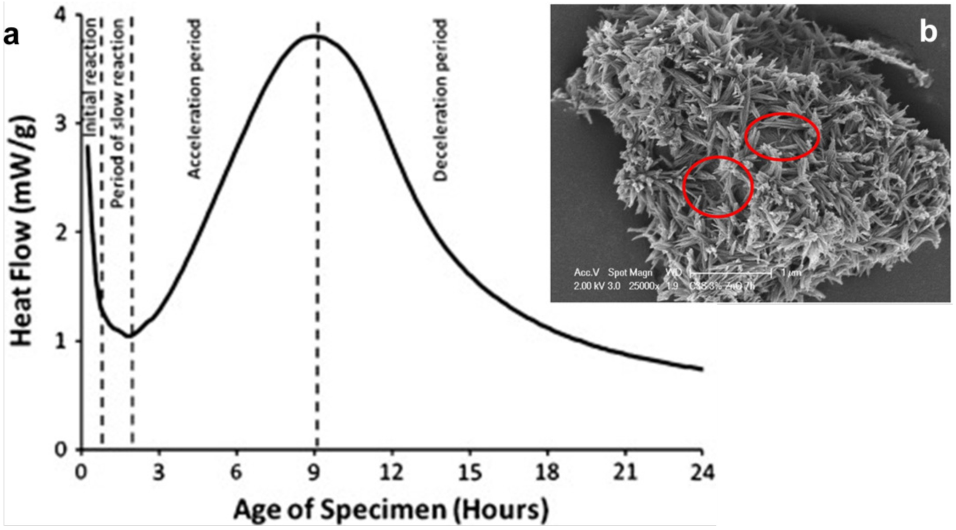


Figure 4. Hydration kinetics of the major cement phase alite (C_3S, Ca_3SiO_5) and formation of calcium-silicate-hydrate gel (C-S-H). (a) The rate of alite hydration is shown as a function of time by isothermal calorimetry measurements. The initial reaction largely represents the hydration energy of the particles. The acceleration period after several hours leads to the formation of calcium-silicate hydrate (C-S-H) and portlandite ($Ca(OH)_2$). Reproduced with permission from ref. [4]. (b) The image shows the growth of C-S-H needles on the surface of an alite grain during the main heat evolution peak. Red circles highlight the alite surface. C-S-H formation in cement (including all mineral phases) is influenced by additional factors. Reproduced with permission from ref. [19].

The hydration of cement is fundamentally a simultaneous dissolution-precipitation process that includes at least two solid phases, i.e., the initial anhydrous and the final hydrated phases, and a liquid phase (Figure 5).[5, 21] X-ray diffraction and ^{29}Si solid-state magnetic resonance (NMR) are the most common techniques to monitor the anhydrous components (alite, belite, and their admixtures) and the formation of C-S-H phases.[22] The role of the concentration of calcium ions and dissolved silicate ions in solution, as well as of the pH value on the formation of C-S-H gel have been investigated by many groups (Figure 5a-c).[5] Therefore, the impacts of these conditions on the C-S-H compositions are known. Broadly speaking, C-S-H can have Ca/Si ratios from 0.5 to 2.0, and several tobermorite minerals are regular model structures of C-S-H with Ca/Si ratios less than 1.0 (Figure 5d).

C-S-H gel at higher Ca/Si ratios has a non-crystalline, locally ordered structure and most of the macroscopic properties are determined by the processes at the interface with the pore solution and superplasticizers. C-S-H forms by precipitation of the ions present in the pore solution mainly due to the dissolution of anhydrous calcium silicates (alite, belite) and other soluble siliceous materials that could be present in blended cements such as silica fume, fly ash or slag.[4] The surface charge follows from the stoichiometry, in particular the Ca/Si ratio, protonation state, and overall charge neutrality (Ca/Si = 1 equals a linear continuous chain and Ca/Si = 2 equals fully broken, individual Ca_2SiO_4 units, and modifications can result from partial protonation). C-S-H with Ca/Si ratios above ~0.83 dissolves under flow conditions and the dissolution products can be conveniently monitored and indirectly quantified by ^{29}Si-NMR (Figure 5e).[23, 24] ^{29}Si-NMR studies confirm that the Ca/Si ratio is inversely related with the silicate chain length (Ca/Si and Q^2/Q^1 ratios in Figure 5e).

The closest crystalline models of C-S-H are tobermorite structures, e.g. tobermorite 14 Å, which consists of extended silicate chains interspersed by calcium ions with a Ca/Si ratio of 0.83 (Figure 5d).[18] The C-S-H structure at higher Ca/Si ratio can be considered as a defective tobermorite structure in which the silicate chains are cut at certain intervals, for example, including "Dreierketten" (3-mer) and other oligomers. C-S-H, like all other cement phases, is in contact with the pore solution that contains a variety of ions, for example, Na^+, K^+, Mg^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, SO_4^{2-}, and Cl^-.[25] Particularly at a low Ca/Si ratio, competition occurs between the Ca^{2+} ions and alkali cations or aluminum ions to balance the negative surface charge of protonated silicate species.[26] The resultant structure of C-S-H thus varies depending on the ratio and activity of these ions.

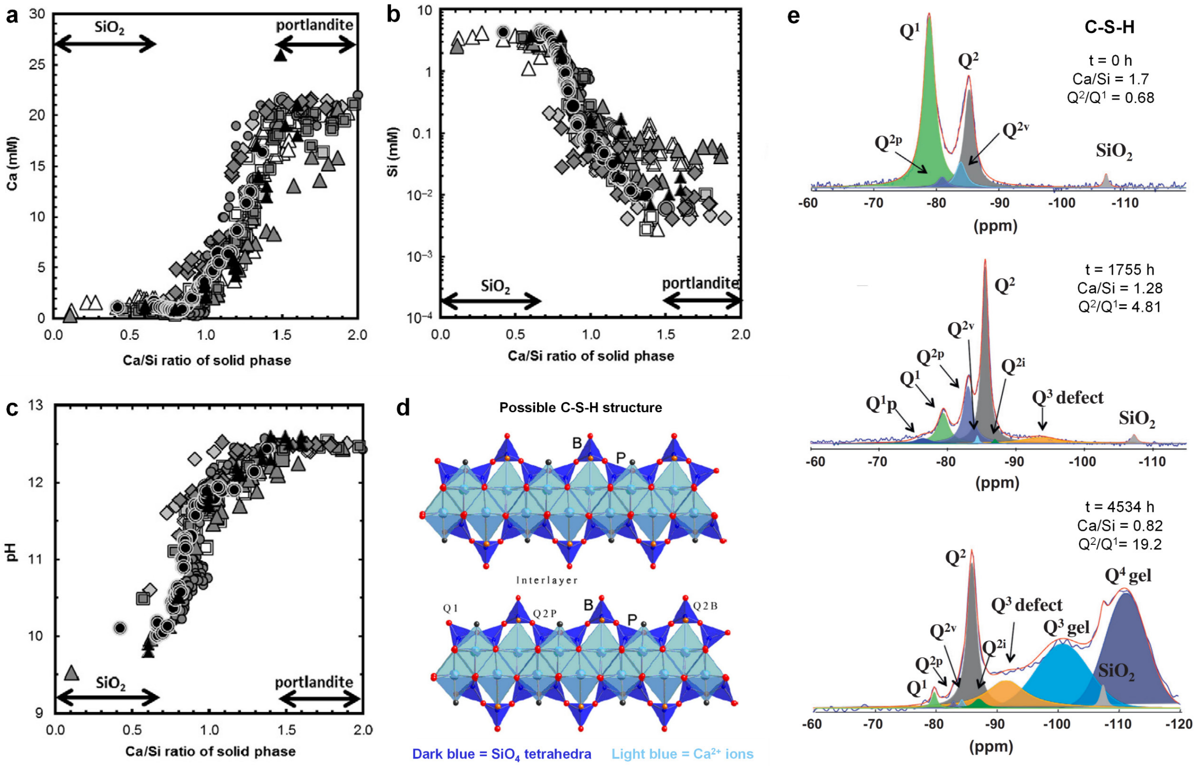


Figure 5. Hydration products of calcium silicates and characterization by ^{29}Si-NMR spectroscopy. (a-c) Relation between solid Ca/Si ratio of synthetic C-S-H, aqueous phase composition, and pH value in the absence of aluminate or alkali metal ions. The composition of C-S-H can cover a wide range of Ca/Si ratios, commonly 1.5 or slightly higher in hydrated Portland cement. Reproduced with permission from ref. [5]. (d) Possible C-S-H structure (tobermorite 14 Å), showing silicate chains and labels of silicate tetrahedra (B = bridging, P = pairing). The different environments of Si atoms identified by NMR are marked: Q^1 = end of chains (1 O-Si neighbor), Q^2 = middle of chains (2 O-Si neighbors). Reproduced with permission from ref. [5]. (e) Deconvolution of the ^{29}Si-NMR spectra of a C-S-H sample subjected to dissolution in flow-through experiments (initial composition: 67 wt% C-S-H, 33 wt% $Ca(OH)_2$, Ca/Si = 1.7 in the C-S-H phase). Different types of silica environments and their ratios are indicated. Reproduced with permission from ref. [24].

Even though the main steps of the hydration of ordinary Portland cement have been identified, the underlying mechanisms and chemical details are still being debated. Specifically, the first deceleration stage followed by the highly exothermic dissolution of alite is not fully understood (< 3 h in Figure 4a). Hypotheses to explain the delay of hydration until the end of this so-called induction period include a protective membrane layer and dissolution control.[4] From a chemistry perspective, we hypothesize that the initial pH value upon dissolution of Ca_3SiO_5 will reach extremely high local values (>15) as a result of the formation of hydroxide ions from oxide ions, conversion of CaO to portlandite, and protonation of SiO_4^{4-} ions ($Ca_3SiO_5 + 3\ H_2O \rightarrow Ca^{2+} + 4\ OH^- + H_2SiO_4^{2-}$). The very high local pH values are initially maintained by the significantly ionic, strong cohesive forces and may require time to decrease to below 13. Only at local pH values below 13, the condensation of $H_2SO_4^{2-}$ ions (pK > 16) and $H_3SO_4^-$ ions (pK ~13.2) into C-S-H oligomers with Q^2 environments can proceed (Figure 5). The process of formation of C-S-H thus involves the "corrosion" of many molecular layers on the C_3S (and C_2S) surface, and phase separation of calcium hydroxide, before the exothermic condensation reactions to C-S-H can occur. These steps might explain the slow rate and the delay/induction period. Recently, a phenomenological C-S-H needle model was proposed to explain the delay of the main heat evolution peak, assuming that the kinetics is described by the growth rate of C-S-H "needles" (Figure 4b).[19]

More investigations will be needed to ascertain these hypotheses, taking into account all factors affecting the C-S-H growth rate including the dynamics of the pore solution. The presence of silicates, sulfates and aluminates and their combined effect in the cement paste increase the level of complexity for understanding the underlying growth mechanisms. The difficulty of answering how tricalcium silicate reacts with water shows that it is still tortuous to isolate individual processes among competing interfacial reactions. The presence of clinker substitutes and admixtures in blended cements further complicates these challenges.[27] Nevertheless, chemical theory, insights from similar reactions (e.g. silica surface chemistry), and simulation can lead to supported hypotheses to be tested in experiments and validated by predictions of related properties.

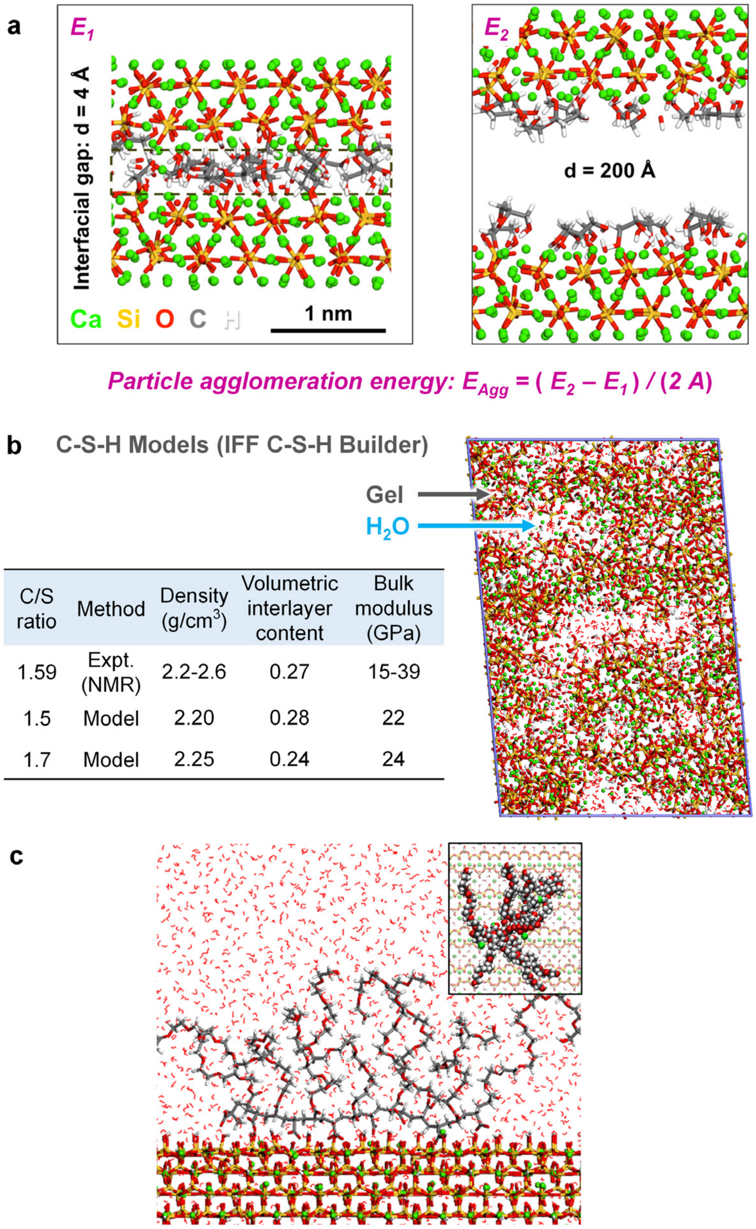
In summary, after decades of empirical research at different scales, we still face the need to comprehend the nano-scale and micro-scale chemical and physical processes at the particle interfaces that cause the formation of different morphologies, determine the strength, durability, and sustainability of cement-based structures.[28] The growth mechanism of C-S-H and the morphology are still being debated. Recent bio-inspired studies suggested that it is possible to stabilize the C-S-H particles and control the agglomeration via an increase in pH value or via control of the C-S-H/polymer ratio.[29] CSH/polymer composites could efficiently combine the stiffness of three-dimensionally ordered C-S-H mesocrystals (nanoplatelets) with the elasticity of polymers. It has been realized that calcium-silicate-hydrate (C-S-H) is the principal binder phase in cement that governs the behavior and engineering performance at the bulk scale. C-S-H can reach a high specific solid-liquid interfacial area of 80-280 m^2/g related to the irregular nanoscale stucture.[5] C-S-H thus encompasses a range of compositions and phases, including amorphous phases, nano-size crystals, and micro-size crystals (such as tobermorites, see also Section 4). The water-to-cement ratio (w/c ratio) for processing cement is linked to the type of C-S-H microstructures and associated characteristics of the resulting cement and concrete structures. When the water-to-cement ratio is low, amorphous C-S-H bulk structures dominate, and clusters of high order and local uniformity are rare. At high water-to-cement ratio, excess water and interlayer space supports the growth of regular crystals of portlandite, ettringite and aluminate along with regular crystals of C-S-H as seen in electron microscopy.[6] Due to the small size of the crystallites and often broad XRD patterns, experimental data remain limited.[30] The absence of long-range order and an intrinsic gel porosity of 26-28% with a characteristic size of 4-5 nm are known (see models in Section 4). Complete knowledge of the meso-structure and the impact of variability is essential to advance our understanding. To date, the Jennings model assumes a colloidal structure of discrete C-S-H nanoparticles, which are not linked,[31] and the Feldman-Sereda model assumes nanocrystalline regions with well-aligned C-S-H layers that could be interconnected.[32] In either case, there is consensus that C-S-H gel has reproducible thermodynamic behavior (Figure 5a-c) and the high specific surface area affects the key engineering properties of concrete structures.

4. Modeling and Simulation of Cement Interfaces and Hydration Reactions

Models and simulations have undergone rapid development in recent decades and become helpful to explain interfacial interactions, their role in hydration reactions, admixture design, and the approximate kinetics of cement hydration.

Several interatomic potentials (force fields) have been used for the simulation of cementitious system at the scale of all-atom resolution such as molecular dynamics. Available force fields include the Interface force field (IFF), CSH-FF, CementFF, CLAYFF, GULP, ReaxFF, and UFF. The CemFF database provides an online library of the parameters, input files for the reproducible calculation of key properties, and bench-marking data for side-by-side comparisons and user guidance.[8] Except for some FFs that entirely lack validation and interpretability (UFF, GULP), most FFs reproduce crystal structures well. IFF has the best property predictions across the spectrum of structures, energies such as cleavage, hydration, organic binding, and mechanical properties.[7] CSH-FF, CementFF, CLAYFF, and GULP perform reasonably well for mechanical properties but fail to reproduce surface and interfacial energies, lack interpretability of the parameters, and have been designed as niche force fields without compatibility with available force fields for polymers and solvents (over 100% deviations in binding energies common). The Interface force field (IFF) has been developed using consistent descriptions of chemical bonding in silicates and clay minerals.[7, 8, 33] The minerals are predominantly covalently bonded structures with significant atomic charges of +1.0 to +1.1e on Si atoms according to experimental electron deformation densities and theory. A quantitative representation of chemical bonding is essential to model interfacial interactions and reactions. Several force fields do not reproduce chemical bonding and lead to large errors in interfacial energies up to several 100% (e.g., CLAYFF with Si charges of +2.1e and early models by Catlow et al. with formal Si charges of +4.0e), and authors quite often try to hide away such limitations. Unbiased validation for molecular simulations usually includes lattice parameters, surface energies or hydration energies, and mechanical properties, and a full disclosure of the parameters including a discussion of interpretability and transferability. IFF typically reaches <0.5% deviation in lattice parameters, <10% deviation in surface and interfacial energies, and <10% deviation in mechanical properties. It covers C_3S, C_3A, tobermorites, C-S-H, other phases including ettringite, gypsum, silica, as well as interfaces with polymers and biomolecules via full compatibility with CHARMM, PCFF, AMBER, and other force fields (Figure 6).[7] The coverage is expanding to oxides and hydroxides.

Recent MD simulations have illustrated the magnitude of particle agglomeration energies of C_3S with and without organic surface modifiers (Figure 6a), and introduced C-S-H structural models that reproduce the density, volume fraction of water, and solid-water interfacial energies <10 mJ/m^2 (Figure 6b). The adsorption mechanism of polymeric admixtures such as methacrylic acid-polyethylene glycol methacrylate (MAA-PEGMA) copolymers of various grafting density of side chains and length of PEG side chains has been quantified on tobermorite 14 Å surfaces (Figure 6c).[18] Binding is mediated by ion-pairing interactions, whereby PEG avoids surface contact, and the polymer architecture leads to different surface contact time and binding free energies that range from 0 to -5 kcal per mol acrylate monomer. The interactions of polyelectrolytes with cement phases play a critical role to control workability (rheology), setting behavior, and contribute to the ultimate mechanical properties of concrete.[34] The organic modifiers reduce ionic particle-particle agglomeration energies, increase the fluidity, reduce the necessary water content for processing cement, and the amount of cement needed overall for high-strength construction. Better understanding of the chemistry and mineral polymer interactions will also support additive manufacturing of concrete, which requires careful selections of ink additives to reach optimum thixotropy for extrusion.[2]



C/S ratio	Method	Density (g/cm^3)	Volumetric interlayer content	Bulk modulus (GPa)
1.59	Expt. (NMR)	2.2-2.6	0.27	15-39
1.5	Model	2.20	0.28	22
1.7	Model	2.25	0.24	24

Figure 6. All-atom simulation of agglomeration energies of cement particle surfaces, C-S-H morphology, and polymer adsorption using IFF. (a) The agglomeration energy of organically modified C_3S surfaces (reproduced with permission from ref. [35]). (b) Atomistic C-S-H models with silicate gel and water domains (shown for Ca/Si ratio = 1.5). A multitude of morphologies compliant with experimental data can be built. (c) Adsorption of a polymethacrylate-co-PEG-

methacrylate polymer onto a tobermorite 14 Å (100) surface (top view in inset) (reproduced with permission from ref. [18]).

Atomistic simulation studies can also be used to explain kinetic aspects of cement hydration. A bottleneck have been the structural properties of the hydrated cement phases, particularly C-S-H gel (Figure 6b). Layered mineral analogs of C-S-H gel (tobermorite and jennite) were often used in ab-initio, Monte Carlo (MC) and MD simulations.[36, 37] Hereby, ^{29}Si NMR spectra studied by density functional theory have shown that tobermorite-based models of C-S-H gel agree better with experimental data than jennite-based models.[38] Ca ions in the interlayer spaces are not exchangeable and trapped by iono-covalent forces, leading to different behavior of inter-layer water molecules due to surrounding forces and nanoconfinement.[8, 18] Kinetic Monte-Carlo (KMC) studies could help to explain the dissolution and growth of minerals using relative variations in the saturation state of the solution and in pH, possibly providing clarifications of the complex kinetics of cement hydration including the induction period (Figure 4a). The strength of cohesive forces at the nano-scale correlates with bulk properties such as cohesion and durability.

At scales upward of 100 nm to millimeters, several kinetic models and simulations of cement hydration and structure development have been reported.[39] Early kinetic models such as single-particle models and nucleation and growth models aimed at reproducing the hydration kinetic. However, the models could not represent the kinetics including particle-particle interactions and the simultaneous multi-phase microstructure development. A hydration model with microstructural simulations was pioneered by Jennings and Johnson using a vector approach to cement hydration, followed by the HymoStruc Model. Nevertheless, the off-lattice models do not account for solution-phase chemistry and real transport phenomena. The CEMHYD3D digital hydration model uses a lattice-based approach leading to a 3D microstructure for ordinary Portland cement that includes the spatial distribution of hydration products, unhydrated cement, and capillary porosity (Figure 7a). A later implementation of the vector approach is the μic model, which can simulate the microstructural evolution of hydrating cement paste (Figure 7b). The μic models can be extensively customized, for example, to investigate the early hydration kinetics of alite, the distribution of hydration products, and the effect of particle size. Simulations require user-defined phases, phase distribution, placement, and plugins customized to simulate the overall effect of solution-phase transport phenomena. The μic platform can rapidly screen multiple scenarios for microstructure evolution with a particle size resolution of 0.1 μm if the user is in a position to provide accurate input data which depend on knowledge of the reaction mechanism. Alternatively, the HydratiCA simulation model overcomes kinetic limitations and the coarse lattice resolution (1 μm) of CEMHYD3D (Figure 7c). HydratiCA is a kinetic cellular automaton program to simulate multicomponent mass transport, including multiple heterogeneous and homogeneous reactions within 3D microstructures.[29] For detailed predictions of phase changes and microstructure development as a function of solution chemistry and temperature, HydratiCA also requires dependable input of thermodynamic variables and carries out intensive computations.[7, 8] Therefore, the micrometer-scale kinetic models require knowledge of structural data, thermochemical data, hydration mechanisms, and interfacial interactions from experiments, atomistic MD simulations, or reaction simulations (MD/DFT) at smaller scales (Figure 6).

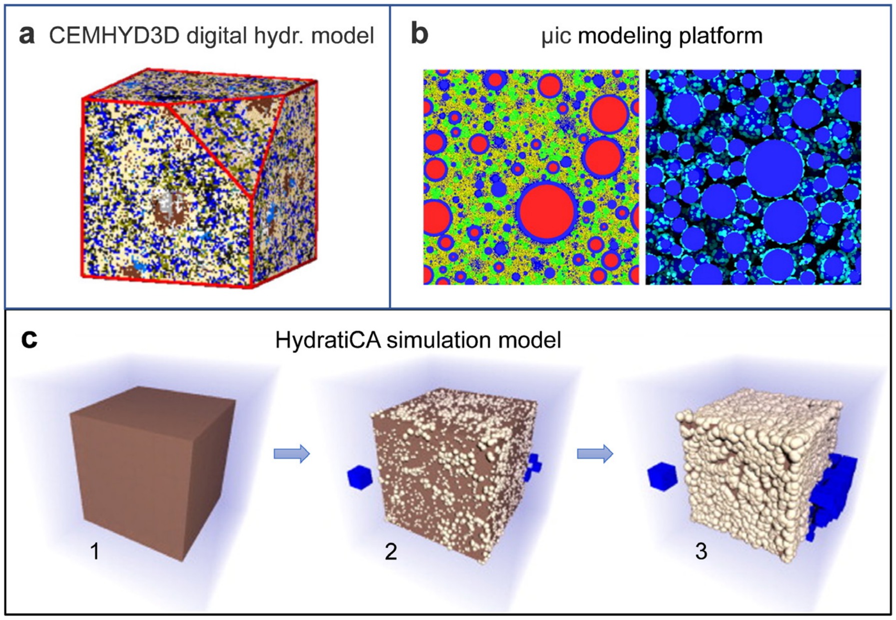


Figure 7. Kinetic models to simulate the hydration of cement. (a) Simulated microstructure of type I ordinary Portland cement paste hydrated for 14 days using CEMHYD3D. Reproduced with permission from ref. [29]. (b) Simulation of the microstructure with fine fillers and many particles (left) and controlled nucleation on the surface of particles (right) using the modeling platform μic. Reproduced with permission from ref. [29, 40]. (c) Microstructure of the hydration products on a single cubic particle of C_3S using HydratiCA simulations. (1) start of the simulation, (2) 3.5 h of hydration, corresponding to maximum hydration rate, and (3) 24 h of hydration. C_3S (brown), C–S–H (beige), and CH (blue). Aqueous solution is shown as a light blue cloud filling. Reproduced with permission from ref. [39].

Going forward, there are many opportunities to study agglomeration forces between particle surfaces of the same and of different phases, the dynamics of aqueous interlayer spaces, the dissolution of clinker, growth of hydrated cement phases, and the interaction of additives with the surfaces of all hydrous and anhydrous cement phases. The effect of clinker substitutes on the chemical composition, hydration kinetics, microstructure development, degradation, and reinforcement mechanisms of cement and concrete can also be better understood using the recent IFF capabilities for modeling multiphase systems (silicates, gypsum, clays, polymers etc).[7, 41] Large amounts of imaging, spectroscopy, and computational data provide opportunities for multi-modal data integration, discovery of new causal relationships in the composition-property spectrum with multiple phases, and machine learning of known properties that could accelerate traditional simulations. Specifically, high-quality molecular-scale MD data can be generated with moderate cost and linked to experimental observables for such purposes.

5. Opportunities and Future Directions

Advances in cement chemistry will likely align with the goals of reducing the global carbon emissions and add to interface science and engineering across scales. Solutions to the challenges will expand our knowledge of the fundamental inorganic chemical reaction mechanisms, organic-inorganic interfacial processes, hierarchical assembly, and a multitude of material performance parameters. Foremost, (1) fundamental advances in elucidating the chemistry of hydration and microstructure development in ordinary Portland cement are needed, including various C-S-H, calcium-aluminate-silicate-hydrate (C-A-S-H), and other possible phases. After 100 years, we still know no fully consistent mechanism. An increasing role can be played by advances in theory and simulation in combination with the integration of knowledge from adjacent disciplines such as sol-gel science, clay science, mineralogy, geochemistry, inorganic, and organic chemistry. (2) The exploration of supplementary cementitious materials (SCMs) such as metakaolin, calcined clays, fly ash, renewable polymers, and new materials additives is promising to create functional interfaces and favorable bulk material properties. Understanding the mechanisms of the hydration reactions across the composition space is a formidable challenge that can benefit other applications as well. (3) Another promising huge parameter space is constituted by the design and testing of new molecular, polymeric, and nanostructured additives. New formulations can build on existing technology such as polycarboxylate ethers, and a particular challenge is using polymers of well-defined composition and molecular weight to elucidate reproducible relationships with rheological properties of cement, the necessary water-to-cement-ratio, and amount of cement needed to obtain desired mechanical properties. (4) A major component of mechanistic studies are new insights into nucleation and crystal growth in interfacial spaces under a variety of electrolyte conditions (e.g. C-S-H). In addition, the role of agglomeration forces between regular and irregular particle surfaces, quantitative measures of interfacial tensions, adsorption energies, and capillary forces can add intriguing new science. The integration of high fidelity atomistic simulations (e.g. IFF) with advances in imaging, spectroscopy, calorimetric techniques, and chemical theory could transform the research field. (5) High throughput experimental data sets, big data from MD and calibrated coarse-grain simulations, can be utilized to detect new causal relationships using Bayesian approaches and accelerate property predictions using machine learning approaches. (6) Simulations at multiple scales are improving (QM/MD/coarse-grain/finite elements) and will be useful to complement and guide experiments. Increased reliability of models, accessibility of code, and user-friendly graphical user interfaces can lead to broader adoption and integration of these approaches. Uniform standards for validation need to be developed for unbiased comparisons and simulation scripts, e.g., as is in progress for CemFF, IFF, OpenKIM, and CHARMM-GUI. (7) Ultimately, precise discovery and engineering of the interfaces at the atomic scale can have unprecedented benefits to tune macroscopic properties. Key properties for cement and concrete include rheology/fluidity, setting time, porosity, mechanical properties, degradation resistance, and suitability for digital manufacturing (3D printing). Integrated theory and tested models that connect atomic-level heterogeneous structures and processes with macroscopic engineering properties could enable a revolution in cement and concrete design.

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References

1. Taylor, H. F. W., *Cement Chemistry*. Academic Press, London: 1997.
2. Biernacki, J. J.; Bullard, J. W.; Sant, G.; Brown, K.; Glasser, F. P.; Jones, S.; Ley, T.; Livingston, R.; Nicoleau, L.; Olek, J.; Sanchez, F.; Shahsavari, R.; Stutzman, P. E.; Sobolev, K.; Prater, T., Cements in the 21st Century: Challenges, Perspectives, and Opportunities. *J. Am. Ceram. Soc.* **2017,** *100*, 2746-2773.
3. Scrivener, K. L.; John, V. M.; Gartner, E. M.; Environment, U. N., Eco-efficient Cements: Potential Economically Viable Solutions for a Low-CO2 Cement-Based Materials Industry. *Cem. Concr. Res.* **2018,** *114*, 2-26.
4. Bullard, J. W.; Jennings, H. M.; Livingston, R. A.; Nonat, A.; Scherer, G. W.; Schweitzer, J. S.; Scrivener, K. L.; Thomas, J. J., Mechanisms of Cement Hydration. *Cem. Concr. Res.* **2011,** *41*, 1208-1223.
5. Lothenbach, B.; Nonat, A., Calcium Silicate Hydrates: Solid and Liquid Phase Composition. *Cem. Concr. Res.* **2015,** *78*, 57-70.
6. Aitcin, P. C.; Flatt, R. J., *Science and Technology of Concrete Admixtures*. 1st ed.; Woodhead Publishing: Amsterdam, 2015.
7. Heinz, H.; Lin, T.-J.; Mishra, R. K.; Emami, F. S., Thermodynamically Consistent Force Fields for the Assembly of Inorganic, Organic, and Biological Nanostructures: The INTERFACE Force Field. *Langmuir* **2013,** *29*, 1754-1765.
8. Mishra, R. K.; Mohamed, A. K.; Geissbühler, D.; Manzano, H.; Jamil, T.; Shahsavari, R.; Kalinichev, A. G.; Galmarini, S.; Tao, L.; Heinz, H.; Pellenq, R.; Van Duin, A. C.; Parker, S. C.; Flatt, R. J.; Bowen, P., CEMFF: A Force Field Database for Cementitious Materials Including Validations, Applications and Opportunities. *Cem. Concr. Res.* **2017,** *102*, 68-89.
9. Mishra, R. K.; Weibel, M.; Muller, T.; Heinz, H.; Flatt, R. J., Energy-effective Grinding of Inorganic Solids Using Organic Additives. *Chimia* **2017,** *71*, 451-460.
10. Bresson, A., Influence de la Minéralogie sur le Comportement des Mortiers de Ciment au Jeune Âge. *Thesis Université Laval (Canada)* **2006**, https://www.collectionscanada.gc.ca/obj/s4/f2/dsk3/QQLA/TC-QQLA-23642.pdf.

11. Malhotra, V. M., Global Warming, and Role of Supplementary Cementing Materials and Superplasticisers in Reducing Greenhouse Gas Emissions from the Manufacturing of Portland Cement. *Int. J. Struct. Eng.* **2010,** *1*, 116-130.
12. Skibsted, J.; Snellings, R., Reactivity of Supplementary Cementitious Materials (SCMs) in Cement Blends. *Cem. Concr. Res.* **2019,** *124*, 105799.
13. Scrivener, K.; Martirena, F.; Bishnoi, S.; Maity, S., Calcined Clay Limestone Cements (LC3). *Cem. Concr. Res.* **2018,** *114*, 49-56.
14. Provis, J. L.; Palomo, A.; Shi, C. J., Advances in Understanding Alkali-Activated Materials. *Cem. Concr. Res.* **2015,** *78*, 110-125.
15. Scrivener, K.; Avet, F.; Maraghechi, H.; Zunino, F.; Ston, J.; Hanpongpun, W.; Favier, A., Impacting Factors and Properties of Limestone Calcined Clay Cements (LC3). *Green Materials* **2019,** *7*, 3-14.
16. Zajac, M.; Lechevallier, A.; Durdzinski, P.; Bullerjahn, F.; Skibsted, J.; Ben Haha, M., CO2 Mineralisation of Portland Cement: Towards Understanding the Mechanisms of Enforced Carbonation. *J. CO2 Utilization* **2020,** *38*, 398-415.
17. Heinz, H.; Pramanik, C.; Heinz, O.; Ding, Y.; Mishra, R. K.; Marchon, D.; Flatt, R. J.; Estrela-Lopis, I.; Llop, J.; Moya, S.; Ziolo, R. F., Nanoparticle Decoration with Surfactants: Molecular Interactions, Assembly, and Applications. *Surf. Sci. Rep.* **2017,** *72*, 1-58.
18. Jamil, T.; Javadi, A.; Heinz, H., Mechanism of Molecular Interaction of Acrylate-Polyethylene Glycol Acrylate Copolymers with Calcium Silicate Hydrate Surfaces. *Green Chem.* **2020,** *22*, 1577-1593.
19. Scrivener, K.; Ouzia, A.; Juilland, P.; Mohamed, A. K., Advances in Understanding Cement Hydration Mechanisms. *Cem. Concr. Res.* **2019,** *124*, 105823.
20. Rodriguez-Navarro, C.; Ruiz-Agudo, E.; Ortega-Huertas, M.; Hansen, E., Nanostructure and Irreversible Colloidal Behavior of Ca(OH)(2): Implications in Cultural Heritage Conservation. *Langmuir* **2005,** *21*, 10948-10957.
21. Garrault, S.; Nonat, A., Hydrated Layer Formation on Tricalcium and Dicalcium Silicate Surfaces: Experimental Study and Numerical Simulations. *Langmuir* **2001,** *17*, 8131-8138.
22. Skibsted, J.; Hall, C., Characterization of Cement Minerals, Cements and their Reaction Products at the Atomic and Nano Scale. *Cem. Concr. Res.* **2008,** *38*, 205-225.
23. Scrivener, K. L.; Kirkpatrick, R. J., Innovation in Use and Research on Cementitious Material. *Cem. Concr. Res.* **2008,** *38*, 128-136.
24. Trapote-Barreira, A.; Cama, J.; Soler, J. M., Dissolution Kinetics of C-S-H Gel: Flow-through Experiments. *Phys. Chem. Earth* **2014,** *70-71*, 17-31.
25. Jonsson, B.; Nonat, A.; Labbez, C.; Cabane, B.; Wennerstrom, H., Controlling the Cohesion of Cement Paste. *Langmuir* **2005,** *21*, 9211-9221.
26. Myers, R. J.; Bernal, S. A.; San Nicolas, R.; Provis, J. L., Generalized Structural Description of Calcium-Sodium Aluminosilicate Hydrate Gels: The Cross-Linked Substituted Tobermorite Model. *Langmuir* **2013,** *29*, 5294-5306.
27. Myers, R. J.; Geng, G. Q.; Li, J. Q.; Rodriguez, E. D.; Ha, J. Y.; Kidkhunthod, P.; Sposito, G.; Lammers, L. N.; Kirchheim, A. P.; Monteiro, P. J. M., Role of Adsorption Phenomena in Cubic Tricalcium Aluminate Dissolution. *Langmuir* **2017,** *33*, 45-55.
28. Picker, A.; Nicoleau, L.; Burghard, Z.; Bill, J.; Zlotnikov, I.; Labbez, C.; Nonat, A.; Colfen, H., Mesocrystalline Calcium Silicate Hydrate: A Bioinspired Route Toward Elastic Concrete Materials. *Sci. Adv.* **2017,** *3*, e1701216.
29. Thomas, J. J.; Biernacki, J. J.; Bullard, J. W.; Bishnoi, S.; Dolado, J. S.; Scherer, G. W.; Luttge, A., Modeling and Simulation of Cement Hydration Kinetics and Microstructure Development. *Cem. Concr. Res.* **2011,** *41*, 1257-1278.

30. Roosz, C.; Gaboreau, S.; Grangeon, S.; Pret, D.; Montouillout, V.; Maubec, N.; Ory, S.; Blanc, P.; Vieillard, P.; Henocq, P., Distribution of Water in Synthetic Calcium Silicate Hydrates. *Langmuir* **2016,** *32*, 6794-6805.

31. Jennings, H. M., A Model for the Microstructure of Calcium Silicate Hydrate in Cement Paste. *Cem. Concr. Res.* **2000,** *30*, 101-116.

32. Feldman, R. F.; Sereda, P. J., A Model for Hydrated Portland Cement Paste as Deduced from Sorption-Length Change and Mechanical Properties. *Matériaux et Construction* **1968,** *1*, 509-520.

33. Heinz, H.; Suter, U. W., Atomic Charges for Classical Simulations of Polar Systems. *J. Phys. Chem. B* **2004,** *108*, 18341-18352.

34. Flatt, R. J.; Schober, I.; Raphael, E.; Plassard, C.; Lesniewska, E., Conformation of Adsorbed Comb Copolymer Dispersants. *Langmuir* **2009,** *25*, 845-855.

35. Mishra, R. K.; Flatt, R. J.; Heinz, H., Force Field for Tricalcium Silicate and Insight into Nanoscale Properties: Cleavage, Initial Hydration, and Adsorption of Organic Molecules. *J. Phys. Chem. C* **2013,** *117*, 10417-10432.

36. Bonnaud, P. A.; Ji, Q.; Coasne, B.; Pellenq, R. J. M.; Van Vliet, K. J., Thermodynamics of Water Confined in Porous Calcium-Silicate-Hydrates. *Langmuir* **2012,** *28*, 11422-11432.

37. Honorio, T., Monte Carlo Molecular Modeling of Temperature and Pressure Effects on the Interactions between Crystalline Calcium Silicate Hydrate Layers. *Langmuir* **2019,** *35*, 3907-3916.

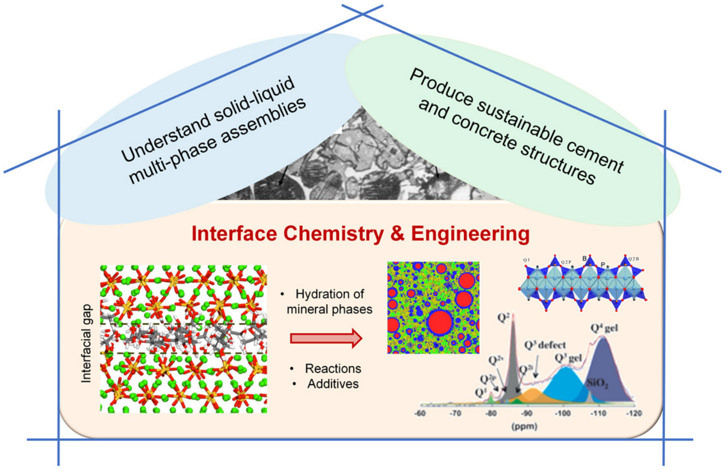
38. Dolado, J. S.; van Breugel, K., Recent Advances in Modeling for Cementitious Materials. *Cem. Concr. Res.* **2011,** *41*, 711-726.

39. Bullard, J. W.; Scherer, G. W.; Thomas, J. J., Time Dependent Driving Forces and the Kinetics of Tricalcium Silicate Hydration. *Cem. Concr. Res.* **2015,** *74*, 26-34.

40. Bishnoi, S.; Scrivener, K. L., mu ic: A New Platform for Modelling the Hydration of Cements. *Cem. Concr. Res.* **2009,** *39*, 266-274.

41. Rejmak, P.; Dolado, J. S.; Stott, M. J.; Ayuela, A., Si-29 NMR in Cement: A Theoretical Study on Calcium Silicate Hydrates. *J. Phys. Chem. C* **2012,** *116*, 9755-9761.

Table of Contents Graphic



Biographical sketches

Ozge Heinz received her BA in Chemical Engineering from Izmir Institute of Technology in 2002, graduating with departmental honors. After earning her MS in Chemical Engineering, she moved to the Materials Science and Engineering program at Sabancı University in Istanbul, where her Ph.D. research focused on nanoparticle synthesis and their use in polyurethane-based nanocomposites. Ozge joined the Nanostructure Polymer Lab at the University of Colorado Boulder for post-doctoral work on reverse-osmosis membranes. Currently, she is pursuing studies on the force field parameters for aqueous ions and model development for cement minerals at the Interface Lab at CU Boulder.

Hendrik Heinz obtained his M.S. degree in chemistry in 2000 and a Ph.D. degree in Materials Science and Engineering in 2003 from ETH Zurich. Following postdoctoral work at the Air Force Research Laboratory, he became a faculty member in Polymer Engineering at the University of Akron, Ohio, and later in Chemical and Biological Engineering at the University of Colorado at Boulder. His research focuses on the simulation of biomaterials and nanomaterials from atoms to the microscale, including catalysts, biomineralization, hydrogels, inorganic/polymer hybrid materials, and corrosion in high accuracy and speed. He develops the Interface force field and a surface model database for the simulation of compounds across the periodic table and explores data science and machine learning approaches to predict reactivity and materials designs. He serves as a Senior Editor for Langmuir.