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Hierarchical multiscale modeling for predicting the physicochemical characteristics of construction materials: A review

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Abstract. The growing demands for sustainable and high-performance construction materials necessitate a deep understanding of their physicochemical properties by that of these heterogeneities. This paper presents a comprehensive review of the state-of-the-art hierarchical multiscale modeling approach aimed at predicting the intricate physicochemical characteristics of construction materials. Emphasizing the heterogeneity inherent in these materials, the review briefly introduces single-scale analyses, including the ab initio method, molecular dynamics, and micromechanics, through a scale-bridging technique. Herein, the limitations of these models are also overviewed by that of effectively scale-bridging methods of length or time scales. The hierarchical multiscale model demonstrates these physicochemical properties considering chemical reactions, material defects from nano to macro scale, microscopic properties, and their influence on macroscopic events. Thereby, hierarchical multiscale modeling can facilitate the efficient design and development of next-generation construction.

Keywords: cement mortar; concrete; homogenization; multiscale modeling; physicochemical characteristics

1. Introduction

Early construction-materials research has focused on improving the mechanical characteristics of strength, durability, weight reduction, and relevant performances (Nayak *et al.* 2013, Haeri *et al.* 2019). After a few decades, recent advancements in the development of next-generation construction materials, which consider either the brutal environmental concern or multi-features (e.g., self-healing, self-heating, and electromagnetic shielding), have been studied (Gamal *et al.* 2017, Nasr *et al.* 2020). Many of the researchers have attempted to explore either the physical interaction between cement hydrate and reinforcements (reinforcement particles, fibers, plastics, and carbon-based materials) or the chemical interaction under various environmental conditions (temperature, humidity, and reactive ions of CO_2^-, Cl^-, or SO_4^{2-} concentrations causing ion-exchange in-between the cement hydrates and ions) for predicting the physicochemical performance (Cheung *et al.* 2011, Seo *et al.* 2021). From a material perspective, the retroaction of the corresponding interactions on the physical properties at the micro/macro scale is attributed to the mineral transformation of cement hydrates occurring at the nanoscale, thereby contributing to the complexity of the model development due to those of the scale problems (Mustafa *et al.* 2019, Alyousef *et al.* 2020). In this regard, to address these scale problems, a hierarchical multi-scale model has been introduced in the analytical framework of construction materials.

The hierarchical multi-scale modeling framework integrates single-scale analysis covering the nano-, micro-, and macro-scales to simulate physical and/or chemical phenomena (Mustafa *et al.* 2019). At the nanoscale, various techniques such as *ab initio*, density functional theory, Monte Carlo simulation, and molecular dynamics (MD) simulation have been employed to investigate hydration mechanisms, mineral transformation, leaching of Ca ions, diffusion of chloride and sulfate ions, carbon capture, nucleation immobilization, and mechanical properties of single-crystal hydrates or unhydrated products (Horstemeyer 2009, Kanoute *et al.* 2009, Ma and Li 2013). Moving to the micro/macroscale, micromechanics-based homogenization technique and finite element method (FEM) have been applied to address physical problems related to pore affinity, microcrack evolution, and the interfacial transition zone (ITZ) (Yang *et al.* 2012, Dimitrienko *et al.* 2015, Dickson *et al.* 2017, Chen *et al.* 2019). The integration of these single-scale analyses into the hierarchical multi-scale framework enables a multi-physics-based exploration of the physicochemical characteristics of construction materials by merging phenomena across the nano-, micro-, macro-scales

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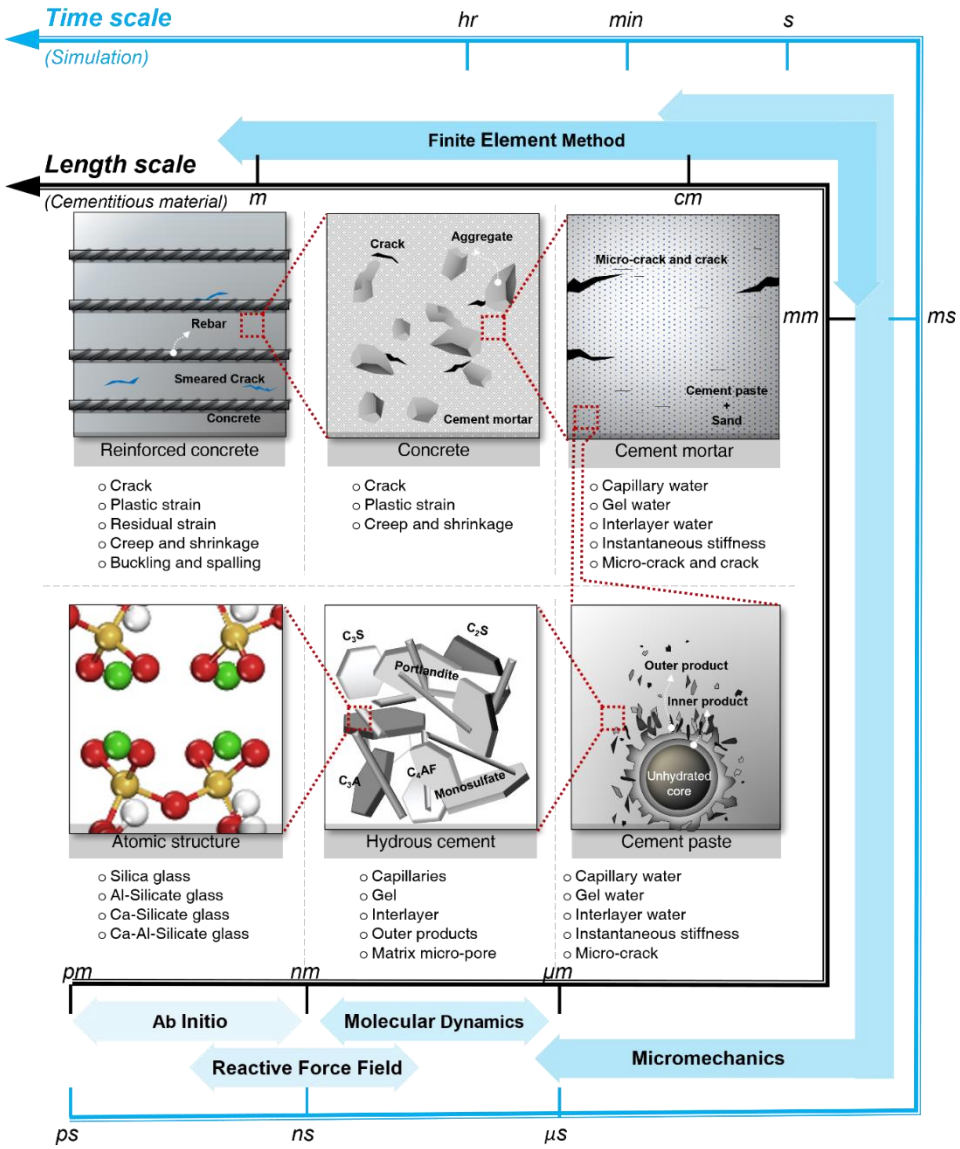

Fig. 1 Schematic of the multiscale modeling scheme corresponding to the length and time scale in which both indicate the inherent phenomenon of the building materials

phenomena.

Recent advancements in the development of hierarchical multi-scale modeling have been introduced by employing machine learning, multivariable models, and multi-expression programming (Salih *et al.* 2020, Emad *et al.* 2021, Piro *et al.* 2021, Salih *et al.* 2021, Emad *et al.* 2022, Piro *et al.* 2022, Ahmed *et al.* 2022, Abdalla and Salih, 2022, Jaf *et al.* 2023, Isleem *et al.* 2023). These methodologies have been integral in exploring the physicochemical characteristics of construction materials, reflecting a paradigm shift from conventional mechanical-centric analyses. Pioneering studies, such as those investigating the impact of silicon dioxide (SiO_2) and calcium oxide (CaO) in fly ash on the compressive strength of green concrete, underscore the growing emphasis of machine learning on their prediction (Jaf *et al.* 2023). Metamodel techniques have been employed to estimate the compressive strength of Ultra-High-Performance Fiber-Reinforced Concrete (UHPFRC) under various mix proportions and curing conditions (Emad *et al.* 2022). Systematic multiscale models have provided insights into the effects of high-volume fly ash on the maximum compression stress of cement-based mortar, accounting for different water/cement ratios and curing times (Abdalla and Salih 2022).

This present review aims to provide a comprehensive overview of the state-of-the-art in hierarchical multi-scale modeling for predicting the physicochemical characteristics of construction materials. The characteristics of cementitious materials are introduced, encompassing the experimental assessments of mineral composition, microstructure, and mechanical properties. Moreover, the review delves into the application of single-scale analyses at varying scales, emphasizing the critical role of hierarchical multi-scale modeling in refining predictions and advancing the current understanding of next-generation construction material models as shown in Fig. 1.

Fig. 2 Feedstocks of (a) Portland cement, (b) CSA, (c) Slag and (d) Silica fume

2. Characteristics of cementitious materials

Cement production involves the extraction of lime (CaO) from limestone ($CaCO_3$) via calcination, and the extracted lime is then combined with silicon oxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3) (Gadayev *et al.* 1999). The subsequent steps include smelting the mixture into clinker and then grinding it (Gadayev *et al.* 1999). Cement clinker, composed of alite ($3CaO{\cdot}SiO_2$), belite ($2CaO{\cdot}SiO_2$), aluminate ($3CaO{\cdot}Al_2O_3$), ferrite ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$), and gypsum ($CaSO_4{\cdot}0.5H_2O$), is mixed with water, sand, and aggregates to produce cement paste, mortar, and concrete, respectively (Ludwig *et al.* 2015).

In cement, hydrates are formed when water molecules react with unhydrated products, namely cement clinker (Scrivener *et al.* 2018). The hydrates include portlandite and calcium silicate hydrate (C-S-H), formed by the reaction of alite and belite with water, and ettringite and monosurfate, formed by the reaction of aluminate, ferrite, gypsum, and water (Xie *et al.* 2011, Scrivener *et al.* 2018). Variations in the characteristics of cementitious material are attributed to mineral compositions and alterations caused by factors such as water-to-binder ratio, cement particle size, fineness, temperature, and humidity, which contribute to the degree of hydration. Moreover, alternative binders such as calcium sulfoaluminate, calcium aluminate cement, magnesium-based cement, phosphate cement, and alkali-activated cement, or industrial by-products like slag and silica fume powders, can be employed, leading to enhancements in the performance of cementitious materials. The raw materials of Portland cement, calcium sulfoaluminate, slag, and silica fume are shown in Fig. 2.

The experimental assessments for estimating the mineral compositions of building materials can be performed using X-ray diffraction, thermogravimetry, nuclear magnetic resonance, energy-dispersive X-ray spectroscopy, and Rietveld analysis (Haile *et al.* 2019, Zhang *et al.* 2021). Moreover, the microstructure evolution associated with porosity can be analyzed using mercury intrusion porosimetry and computed tomography, and nanoindentation can be utilized for estimating the mechanical properties of hydrates at the nanoscale (Constantinides *et al.* 2003, Lu *et al.* 2006, Zeng *et al.* 2016, Fladr *et al.* 2019).

3. Theoretical background of multiscale modeling

The physical responses of materials via continuum mechanics have been addressed based upon the classical mechanics theory of elasticity, elastoplasticity, plasticity, and damage (Coultrup *et al.* 1970). Moreover, chemical phenomena can be more accurately predicted through thermodynamics, MD, and quantum mechanics (Qi *et al.* 2021). However, a single-scale analysis, which has a limitation of length and time, cannot precisely analyze the physicochemical properties of construction materials due to the different lengths of hydrates, unhydrated products, sand, and aggregates (Bensattalah *et al.* 2019). Herein, the mechanical properties of construction materials are changed by that to the mineral transformation of the hydrates over their service life (Scrivener *et al.* 2018). Thus, hierarchical multiscale modeling has attracted attention in the analysis of building materials in an attempt to solve the problems of physicochemical characteristics at various scales integrating their phenomena (Chan *et al.* 2010, Wu *et al.* 2011).

Meanwhile, multiscale models can be specified into the top-down or bottom-up approaches (Li and Wang 2018). In top-down approaches, continuum mechanics are used for solving nanoscale mechanical problems, whereas in bottom-up approaches, statistical averaging, simplified lattice dynamics, or scale-bridging method can be utilized for the macroscopic unit analysis of the coarse-grained model used in molecular unit analysis (Li and Wang 2018). Furthermore, multiscale modeling for the prediction of the physicochemical properties of construction materials based on microscopic chemical reactions can be classified into coexistent multiscale modeling (Maekawa 2008), which substitutes the information on a small scale (nano or micro level) into a relatively large scale (micro or macro level), and hierarchical multiscale modeling, which takes the scale-dependent results of *ab initio* methods, MD, micromechanics, FEM.

Coexistent multiscale modeling has, however, uncertainty in the process of extending units of time and length (Andreoni *et al.* 2020), on the contrary, hierarchical multiscale modeling has the disadvantage that the upper governing equations cannot be reached until the computation of a specific group of units is completed (Liu *et al.* 2004, Ellis *et al.* 2017, Göbel *et al.* 2018, Yang *et al.* 2019). In response to their limitations, various scale-bridging techniques, which extend or reduce the units of length or time, are used in the simulation of the multiscale models to achieve more efficient analysis (Liu *et al.* 2004, Ellis *et al.* 2017). Compared with coexistent multiscale modeling, hierarchical multiscale modeling has the advantage of being applicable to construction materials in a wider variety of environments (Ellis *et al.* 2017, Göbel *et al.* 2018) and has developed rapidly in recent years in

conjunction with scale-bridging techniques. This article briefly introduces an overview of representative theories for each unit constituting hierarchical multiscale modeling and describes the application of specialized multiscale methods in construction materials.

3.1 Ab initio method

The *ab initio* method based on quantum chemistry is considered to be the most accurate method for predicting molecular structures pertaining to various physical properties and chemical reactions, as it involves computing electron correlations without using empirical constants (Bartlett *et al.* 2005). The *ab initio* method identifies, through fully theoretical calculation, the entire process information, ranging from molecular migration, bonding, arrangement, and breaking to readjustment (Bartlett *et al.* 2005).

The *ab initio* method is used in the examination of construction materials for quantifying the reaction of specific hydrates or for simulating the persistent binding and unbinding of water molecules during the curing process, as well as for visualizing the changes in calcium, aluminum, chloride, and sulfate ions during the migration of internal water molecules (Gmira *et al.* 2004, Pegado *et al.* 2014, Mutisya *et al.* 2021). Other studies investigated the high-temperature stability of calcite crystals (Lardge *et al.* 2009), the reaction of portlandite with carbon dioxide (Mutisya *et al.* 2021), and the reactivity of calcium and magnesium-based hydrates according to the carbon-dioxide concentration (Chaka 2018, 2019) based on *ab initio* calculations (Lardge *et al.* 2009, Chaka 2019, Mutisva *et al.* 2021).

Using *ab initio* calculations, the hydrate formation mechanism can be considered theoretically under various environmental conditions (Bartlett *et al.* 2005). However, as the number of atoms for analysis increases, the computational cost increases geometrically, and it becomes difficult to identify diverse defects (Chaka 2018, 2019, Mutisya *et al.* 2021). Note that *ab initio* has a limitation considering various environmental factors to hydrates due to the high computational cost (Chaka 2018, 2019, Mutisya *et al.* 2021).

3.2 Molecular dynamics

MD is a branch of classical mechanics that provides information about atomic or molecular motion (Sprik *et al.* 1996). MD is based on statistical averaging techniques (i.e., the virial stress equation) (Sprik *et al.* 1996). MD can determine mechanical properties using a potential function that incorporates both theoretical and empirical variables applicable to metallic, silicon, carbon, and clay systems (Plimpton 1995, Sprik *et al.* 1996). The clay force field (ClayFF) and reactive force field (ReaxFF) have been applied to the analysis of construction materials (Shahsavari *et al.* 2011, Qomi *et al.* 2014, Senftle *et al.* 2016, Mutisya *et al.* 2017). Otherwise, numerous other force fields of CementFF, cohesive-friction force field (C-S-HFF), and interface force field (IFF), which modify the empirical variables in potential function specialized for the analysis of construction materials, have been proposed (Freeman *et al.* 2007, Mishra, *et al.* 2017, 2021).

ClayFF containing atomic information on the Coulomb, van der Waals, and bonded interactions is given as Eq. (1), as proposed by Cygan *et al.* (2004)

$$E_{\text{total}} = E_{\text{Coul}} + E_{\text{VDW}} + E_{\text{bond stretch}} + E_{\text{angle bond}} \quad (1)$$

where E_{Coul} and E_{VDW} are the coulombic and van der Waals energies, respectively, and $E_{\text{bond stretch}}$ and $E_{\text{angle bond}}$ are the bond stretch energy of the hydroxyl bond (e.g., O-H bond) and angle bend energy of the vibrational behavior of hydroxyl groups, respectively. In addition, the mass, bond angle, and bond strength of atomic structures for hydrates or un-hydrates are included in this model, including calcium, silicate, aluminum, magnesium, iron, lithium, sodium, cesium, and chloride ions.

ReaxFF includes atomic information regarding the breakage and formation of bonds, over- and under-coordination, bending according to the bonding angles, bond distortion, van der Waals force, and localized energy terms, as well as charge energy models (Duin *et al.* 2001). Reaxff is given as Eq. (2), as proposed by Duin *et al.* 2001

$$E_{\text{total}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{Coul}} + E_{\text{VDW}} \quad (2)$$

where E_{bond}, E_{over}, E_{under}, E_{val}, E_{pen}, and E_{tors} are the bond, atom over-/undercoordination, valence angle, penalty, torsion angles, conjugated system, coulomb interactions, and nonbonded van der Waals interactions energies, respectively. In this forcefield, the concept of bond order between a pair of atoms can be incorporated into the initially determined intermolecular bond information to represent the chemical bond formation and breaking behavior at the localized energy term in real time (Duin *et al.* 2001, Shchygol *et al.* 2019, Liu *et al.* 2012). The parameters in the ReaxFF are determined by the simulation at quantum mechanics (Duin *et al.* 2001). Thus, chemical reactions and state transitions of cement hydrates can be accurately simulated based on reaxff (Shchygol *et al.* 2019).

In MD simulation, empirical constants are applied to the mechanical properties of diverse atomic and molecular structures, independent ion diffusion, and molecular binding and breaking analyses, which have lower computational costs than *ab initio* calculations (Plimpton 1995, Cygan *et al.* 2004, Shchygol *et al.* 2019).

3.3 Micromechanical homogenization theory

Micromechanical homogenization involves homogenizing both the inserted reinforcement and the matrix to determine the effective properties of the composite (Mori *et al.* 1973, Lee *et al.* 2020, Patnaik *et al.* 2020). The constitutive equations of the homogenized material are derived using the representative volume element (RVE) framework (Mori *et al.* 1973). Here, the eigenstrain, which is defined for the analysis of micromechanical homogenization, represents the independent behavior of the reinforced material within the known matrix, and it is combined with Eshelby's tensor according to the shape of the reinforcement to represent the

overall behavior of the composite material (Eshelby 1957, 1961, Mura 2013).

Based on the effective medium approach, the self-consistent method homogenizes an infinite matrix medium and reinforcements with an assumption of a perfect bond between the matrix and reinforcements. However, if the volume fraction of reinforcements exceeds 40% or the volume fraction of voids in the reinforced composites exceeds 50%, the elastic moduli are overestimated to infinity (Huang *et al.* 1994). For resolving this issue, the generalized self-consistent scheme (GSCS) was proposed. The GSCS uses an energy-averaging method, and it provides more accurate analysis results, even with a high volume fraction of reinforcements (Lurie *et al.* 2018).

Based on the effective field approach, the Mori-Tanaka (MT) method takes into account the interfacial coupling between the matrix and reinforcements, including the interfacial imperfection. Numerous studies have demonstrated its high accuracy in predicting the effective elastic moduli and mechanical responses of the composites containing inhomogeneous reinforcements by that of a closed-form solution (Ju *et al.* 1994, Aboudi *et al.* 2013, Lee *et al.* 2018). However, the principle of the interaction among the reinforced materials considered in the MT method can increase the error of the analysis results when local deformation occurs (Ma *et al.* 2014). To minimize the error, it has been suggested that the volume fraction of the reinforcing material should be ≤20% (Doghri *et al.* 2003, Lee *et al.* 2020). Furthermore, the ensemble volume averaging method has been actively studied to accurately simulate the effective behavior, interfacial damage, and microfractures of composites containing multiphase reinforcements (Lee *et al.* 2008, Lee *et al.* 2010, Yang *et al.* 2014, Yang *et al.* 2019).

In the perspective of homogenization theory, the micromechanical homogenization theory can be applied to solve such problems as in the multi-layer, multi-level, and multi-phase, thereby potentially simulating the physicochemical properties of building materials (Zhou and Ju 2021, Bang *et al.* 2022, Kil *et al.* 2023). Moreover, the effective material properties can also be implemented into the upper scale simulation scheme based on FEM with the subroutine tool of user-defined material properties.

3.4 Finite element method

The FEM estimates approximate values utilizing numerical analysis for solving the differential equations by dividing a complex domain into a mesh with boundary conditions (Zienkiewicz *et al.* 1977). Thus, the solution space of the differential equation is approximated, in contrast to the approximation of the differential equation using the finite difference method (Zienkiewicz *et al.* 1997). A finite element analysis (FEA) is a widely used numerical analysis method based on the FEM (Chan *et al.* 2010). The analysis is based on energy principles, such as virtual force and energy conservation laws (Chan *et al.* 2010). As a general rule, closed-form analysis problems can be visualized using FEA (Zienkiewicz *et al.* 1997, Yang *et al.* 2017). Upon the hierarchical multiscale modeling, the

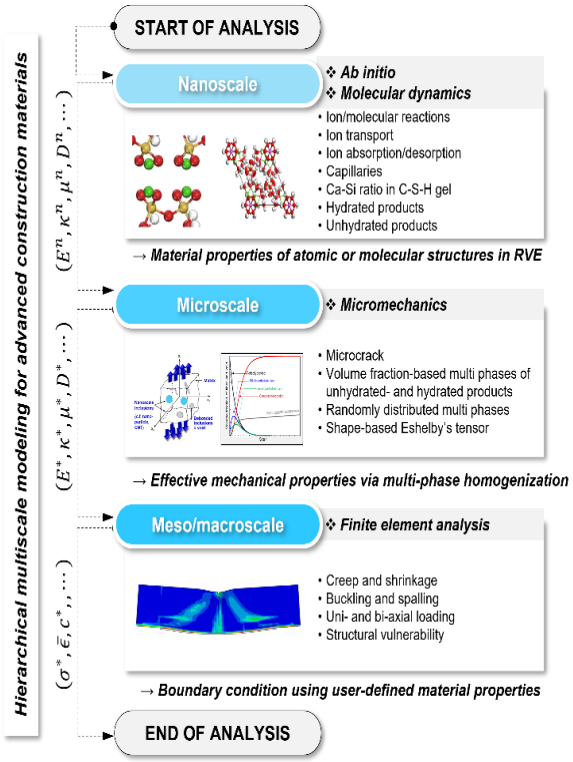

Fig. 3 Analytical framework for the hierarchical multiscale modeling scheme using *ab initio*, molecular dynamics, micromechanics, and finite element analysis

developed constitutive model for advanced building materials can be implemented into a subroutine of user-defined material analysis in commercial FEA software.

The FEM is useful for the analysis of large structures with complex geometries, and it is employed in many different fields, e.g., mechanics, fluid dynamics, thermal dynamics, electronics, biodynamics as well as aerospace, construction, shipbuilding, and nuclear (Zienkiewicz *et al.* 1997, Chan *et al.* 2010, Yu *et al.* 2012, Bakhshi *et al.* 2019, Shakouri, 2021). As a disadvantage, the level of confidence in the analysis results is determined by the decision-maker if analysis results are not verified with experimental results (Zienkiewicz *et al.* 1997, Chan *et al.* 2010, Lee *et al.* 2018).

4. Multiscale modeling refined for building-material analysis

The hierarchical multiscale modeling scheme can be constructed via the coupled effective properties from the viewpoints of the similarity dimension such as the effective stiffness tensor or effective diffusivity, as both determined by single-scale modeling. In this perspective, *ab initio* and/or MD simulations are used to simulate hydration, ion exchange, mineral transformation, and corresponding atomic structures at a stable time. Upon this scheme, the effective stiffness tensor or effective diffusivity of the corresponding atomic structures can be determined in the RVE. Furthermore, micromechanical homogenization theory is applied to homogenize these RVE, considering the

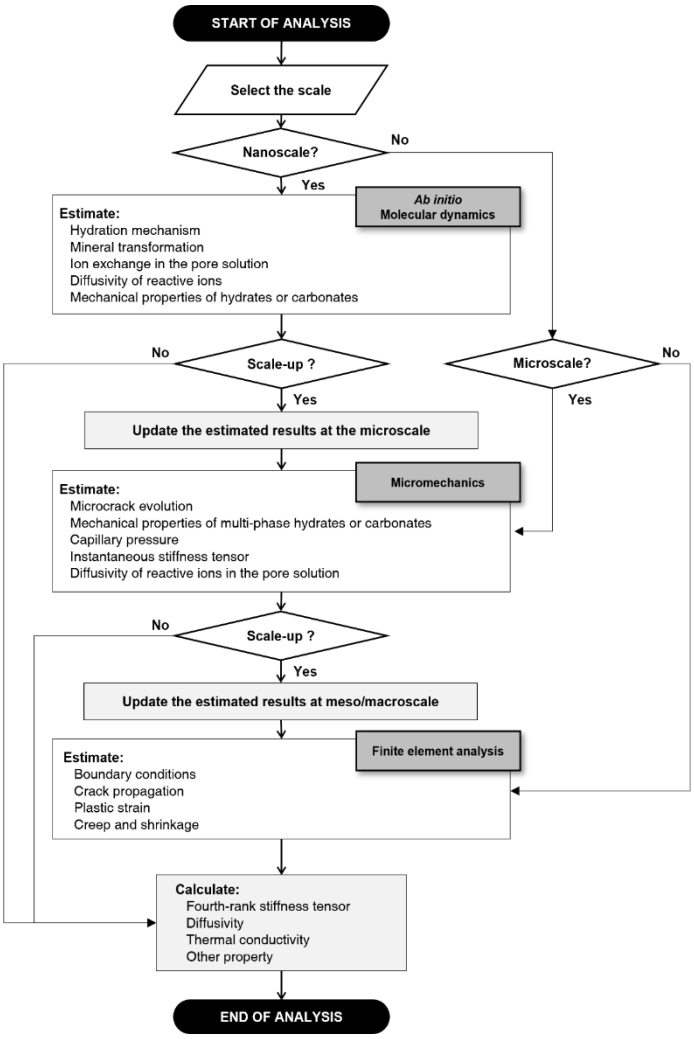

Fig. 4 Flowchart of the hierarchical multiscale modeling scheme

Table 1 Lattice parameters of calcium silica, carbonate, and hydrates

Chemical phase	Space group	Lattice parameters						Ref.
		a (Å)	*b* (Å)	*c* (Å)	*α* (Å)	*β* (Å)	*γ* (Å)	
Alite M3	cm	33.1078(6)	7.0355(1)	18.5211(4)	-	94.137	-	Ángeles *et al.* (2002)
Aluminate	Pa3	15.263(3)	-	-	-	-	-	Mondal *et al.* (1975)
Belite β	P21/n	5.48(2)	6.76(2)	9.28(2)	-	94.33	-	Midgley (1952)
Calcite	R-3c	4.991	-	17.062	-	-	-	Ma *et al.* (2010)
Ettringite	P31c	1.1229(1)	-	2.1478(3)	-	-	-	Goetz-Neunhoeffer *et al.* (2006)
Gypsum	I2/a	5.670(2)	15.201(2)	6.533(2)	-	6.533	-	Cole *et al.* (1974)
Jennite	P-I	10.576(2)	7.265(2)	10.931(3)	101.30	96.98	109.65	Bonaccorsi *et al.* (2004)
Portlandite	P-3m1	3.620	3.620	4.934	-	-	-	Ricci *et al.* (2021)
Tobermorite 11Å	B11m	6.735(2)	7.385(1)	22.487(4)	-	-	123.25(1)	Merlino *et al.* (2001)
Tobermorite 14Å	B11b	6.735(2)	7.425(2)	27.987(5)	-	-	123.25(1)	Bonaccorsi *et al.* (2005)

microscale phenomena as shown in Fig. 1. The coupled effective properties that exhibit inherent phenomena at the nano and microscale can be implemented into the FEA, considering meso- and macro-scale problems (Yang *et al.* 2019). Fig. 3 shows an analytical framework for the hierarchical multiscale modeling scheme using *ab initio*, MD, micromechanics, and FEA. Fig. 4 illustrates the flowchart of the hierarchical multiscale modeling scheme.

For *ab initio* and MD simulations of building materials, lattice parameters of calcium silica, carbonate, and hydrates are tabulated in Table 1. Furthermore, factors contributing to the physical behavior, chemical reactions, and

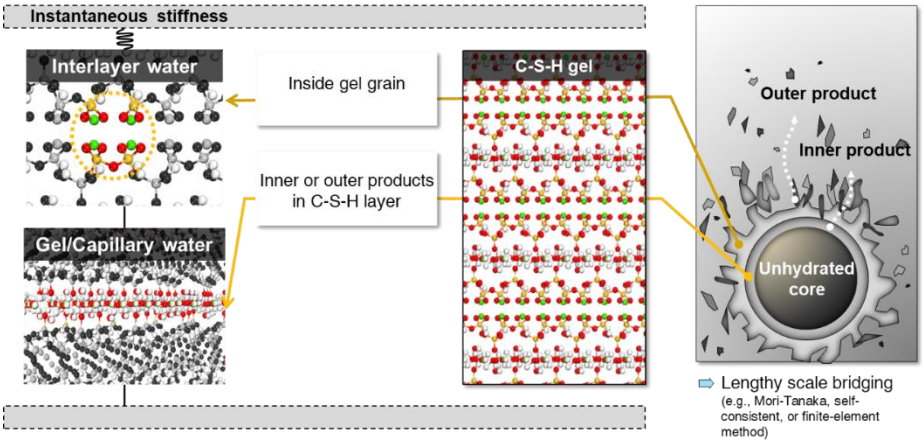

Fig. 5 Schematic of physical analysis of building materials via multiscale modeling (Red, white, green, and yellow represent oxygen, hydrogen, calcium, and silicon, respectively.)

physicochemical characteristics of construction materials are the environmental conditions (e.g., temperature, humidity, CO_2, Cl^-, or SO_4^{2-} concentrations in the pore solution) and material characteristics (e.g., microstructure, mineral composition, degree of hydration of clinker). Thus, to evaluate the corresponding factors, it is necessary to precisely establish the hierarchical multiscale modeling that can mimic reality (Sun *et al.* 2013). The following section briefly introduces a case study of the hierarchical multiscale model to the study of the physical behaviors, chemical reactions, and physicochemical properties of construction materials under various environmental conditions.

4.1 Physical-behavior analysis of building materials via multiscale modeling

The hierarchical multiscale modeling should consider the dimensions for coupling each single-scale analysis (Shin *et al.* 2016). Coupling of the dimension can be categorized into length and time integration methods (Choi *et al.* 2012). Length-dimensional integration methods have been applied using micromechanical homogenization techniques or the FEM with continuum mechanics (Choi *et al.* 2012, Lee *et al.* 2020). In the case of time-dimensional integration methods, the units of sub-models that discretize time intervals have been amplified (Chopard *et al.* 2018).

Fig. 5 describes the analyses of the physical behavior and the governing principles, respectively. In multiscale physical-behavior analysis of construction materials, the nanoscale (e.g., hydrates and unhydrated products) can be expanded by using the coefficient independent of time and length in the theory of subordinate scale and repeating stepwise expansion or by assuming that the energies derived from each scale are identical according to the law of energy conservation (Meakawa 2008, Haile *et al.* 2019, Qin *et al.* 2019, Kim *et al.* 2022). In terms of the bottom-up approach, MD results can be viewed as sub-events and evaluated using techniques such as the FEM or homogenization (Meakawa 2008, Haile *et al.* 2019, Zhang *et al.* 2021).

Palkovic *et al*. (2020) calculated the defects due to the presence of water molecules between C-S-H gel layers via MD simulation, and MD simulation results is incorporated into FEA using homogenization techniques to predict the localized elastic modulus. ClayFF, which is a numerically defined correlation between the interlaminar shear force and friction, was used to obtain more accurate results in MD simulation (Palkovic *et al.* 2020). By using MD and FEA, local internal friction coefficients were collected and applied to the Mohr-Coulomb model to provide a criterion for the failure of C-S-H gel layers (Palkovic *et al.* 2020).

Göbel *et al*. (2017) quantitatively characterized the degree of hydration of the major hydrates with the Bernard hydrate formation model (Bernard *et al.* 2003). The corresponding model is constructed through the MT method to the multiphase-classified hydrates for calculating the elastic modulus according to the aging period. In this model, Monte Carlo techniques were used to recalibrate the uncertainty in the coupling of the length scale to improve predictive accuracy (Göbel *et al.* 2017).

Haile *et al*. (2019) conducted a hierarchical multiscale analysis of ultrahigh-performance concrete (UHPC) composed of cement paste, silica sand, steel fibers, and aggregates using a micromechanical homogenization technique and MD. Haile *et al*. (2019) used MD simulation to determine the mechanical properties of the hydrates, gel pores, and portlandite in UHPC. The effective mechanical properties of UHPC, considering fiber size and type, show good agreement with the experimental results (Haile *et al.* 2019).

Unger and Eckardt (2011) investigated the numerical prediction of the coupled damage modeling for the building materials at the macro- and meso-scale using the micromechanical constitutive damage modeling and FEM in the multiscale framework. The micromechanical constitutive modeling considers the microcrack and ITZ, and the proposed model is implemented into the FEM for modeling the aggregate in the concrete. Their multiscale modeling confirmed variations in the mechanical responses of the concrete by that of microcrack evolution surrounding ITZ. According to the analysis results, the effect of crack opening on the mechanical responses beyond the elastic region can be negligible.

Hierarchical multiscale modeling is used to determine the physical behaviors of building materials by transferring

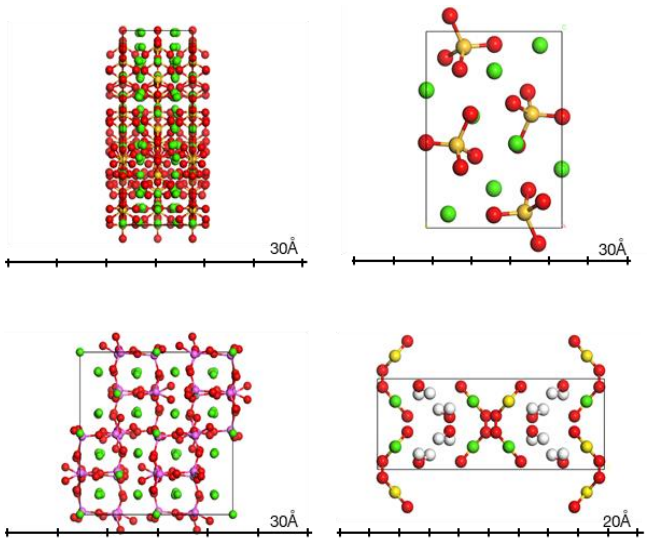

Fig. 6 Representative unhydrated products of (a) Alite M3, (b) Belite β, (c) Aluminate and (d) Gypsum with the lattice plane of (100) (Red, white, green, and yellow represent oxygen, hydrogen, calcium, and silicon, respectively.)

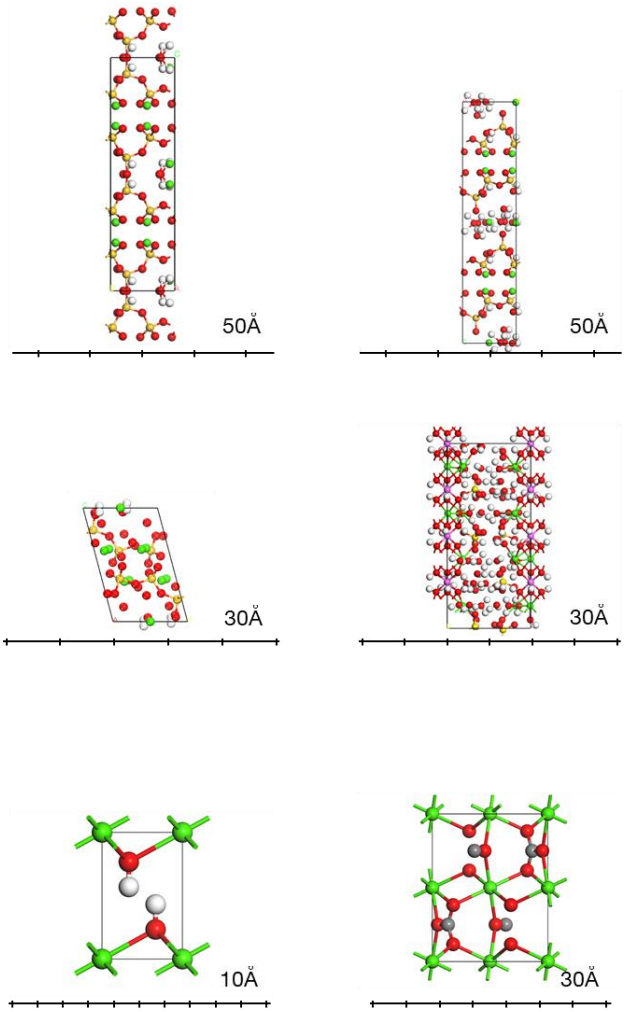

Fig. 7 Representative hydrated products of (a) Tobermorite 11Å, (b) Tobermorite 14Å, (c) Jennite, (d) Ettringite, (e) Portlandite and (f) Calcite with the lattice plane of (100) (Red, white, green, and yellow represent oxygen, hydrogen, calcium, and silicon, respectively.)

the specific phenomena and properties embodied in a single theory for each unit to the upper units via scale-bridging techniques (Meakawa 2008). Thus, analytical results based on the hierarchical multiscale modeling can be derived that consider the different environmental conditions of building materials (Haile *et al.* 2019, Deng *et al.* 2021, Zhang *et al.* 2021).

4.2 Chemical analysis of building materials via multiscale modeling

The chemical-reaction analysis of construction materials should adequately account for hydration mechanisms, ion exchange, and mineral transformations through the time-dependent formation, deformation, and decomposition of hydrates or unhydrated products (Masoero 2018). Moreover, molecular structures of the hydrate or unhydrated products and atomic structure transformation by ions reaction under aging conditions should be well defined to systematically perform the chemical analysis (Bernard *et al.* 2003, Pan *et al.* 2010, Göbel *et al.* 2017). This chapter includes the analyses of chemical reaction phenomena, such as the correlation between charge transfer and ionic bonding (Pan *et al.* 2010), state transitions of nuclear immobilization coupled with CO_2 capture (Han *et al.* 2016), and hydrate formation modeling (Arayro *et al.* 2018, Yildiz *et al.* 2022) in building materials. Figs. 6 and 7 show representative molecular structures of unhydrated and hydrated products of cement, respectively. More diverse visual perspectives on the unhydrated and hydrated molecular structures depicted in Figs. 6 and 7 are elaborately provided in the Appendix.

Pan *et al*. (2010) investigated the adsorption coefficients of chloride ions onto the C-S-H gel and portlandite via MD coupled with the Coulomb electrostatic force field and Lennard-Jones potential field. Following the derivation of the coefficients, they were applied to the dispersion equation to perform a macroscopic analysis. The results of C-S-H gel indicated that when the silicon-oxygen (Si-O) molecular bond, which has approximately 20%-30% higher energy than the calcium-oxygen (Ca-O) molecular bond, undergoes substitution of the silicon-hydroxide (Si-OH) bond to the silicon-oxygen molecule, the surface on the C-S-H gel was covered with a negative charge (Kirkpatrick *et al.* 2001). Consequently, chlorine ions were strongly adsorbed on the surface of portlandite via hydrogen bonding, however, the C-S-H gel exhibited very low chlorine adsorption performance with a surface covered with negative electrons (Pan *et al.* 2010). However, in the macroscopic analysis, the migration of chloride ions was physically bonded by the capillary pressure in the nanopores of the C-S-H gel, and the C-S-H gel had outstanding adsorption performance (Pan *et al.* 2010).

Han *et al*. (2016) used a three-dimensional scanner to measure the change in the microstructure of construction materials and determine the depth of CO_2 penetration into concrete, as well as cracks in the construction material. Based on the experimental outcomes of CO_2 penetration into concrete, the carbonation modeling is then implemented into the FEM considering the carbonation rate, moisture content flow, heat transfer, CO_2 flow, equivalent hydration period, and calcite precipitation nearby ITZ. The

Table 2 Kinematic chemo-physics and mechanical sub-events for cementitious materials (Meakawa 2008)

Sub-event	Governing principle	Scale (m)
Cement heat hydration and thermal conduction	Thermal conservation	10^{-6}-10^{-4}
Pore structure formation and moisture equilibrium/transport	Water mass conservation	10^{-10}-10^{-6}
Free/bound chloride equilibrium and chloride ion transport	Chloride ion conservation	10^{-8}-10^{-6}
Carbonation and dissolved carbon dioxide migration	CO_2/$Ca(OH)_2$ mass conservation	10^{-9}-10^{-6}
Corrosion of steel and dissolved oxygen transport	O_2/proton conservation	10^{-9}-10^{-6}
Calcium ion leaching from $Ca(OH)_2$ and transport	Ca^{++} ion and $Ca(OH)_2$ conservation	10^{-9}-10^{-6}
Chrome dissolution and migration	Cr ion mass conservation	10^{-9}-10^{-6}
Macro-damage evolution and momentum conservation	Static/dynamic equilibrium	10^{-3}-10^{-0}

results of a series of numerical investigations based on the carbonation model confirmed the stability of concrete exposed to a high concentration of CO_2, as the calcite precipitation can reduce the porosity due to its high volumetric change, in spite of the existence of the aggregate and ITZ (Han *et al.* 2016).

Arayro *et al*. (2018) investigated the immobilization mechanism of cesium ions in water molecular hierarchies coexisting in C-S-H. The classical MD technique cannot simulate atom adsorption, then, a Monte Carlo procedure was used in conjunction with the molecular dynamic simulation to simulate the chemical reactions of cesium ions (Arayro *et al.* 2018). In the simulation results, the C-S-H gel physically collected cesium ions through the capillary pressure of nanopores, and the chemisorption based on ion exchange with calcium ions was confirmed (Arayro *et al.* 2018).

By analyzing the chemical reactions of construction materials, more accurate an d systematic results can be achieved through multi-scale modeling, which can simulate the adsorption and the binding and breaking of hydrate molecules (Königsberger *et al.* 2016, Masoero 2018, He *et al.* 2020). Table 2 shows the kinematic chemo-physics and mechanical sub-events for building materials.

4.3 Physicochemical analysis of building materials via multiscale modeling

The inherent physicochemical phenomena of building materials are of paramount importance in the analytical framework predicting their correlations. Many of the researchers have endeavored to reasonably define the systemic interactions between chemical reactions and the corresponding mechanical degradation of building materials under harsh environments. This chapter presents the physicochemical properties under external harsh environments that provoke the mechanical degradation of building materials. Additionally, these phenomena take into account the modified transport laws, ion penetration through the depth direction, and ion reactions between the solid phase and dissolved ions in the pore solution.

Seigneur *et al*. (2022) presented a physicochemical and hydration kinetics-based hierarchical multiscale model to study the mineralogical evolutions of cementitious materials. Their simulation revealed the degradation of the cementitious matrix due to the progressive crack evolution after accelerated carbonation. The analysis results are noteworthy as the microscopic scheme built with multiphase transport and geochemical mechanisms revealed the evolution of porosity, water evaporation, and effective transport properties along with crack evolution. Consequently, the simulated results obtained from the degradation mechanism induced by the gaseous migration of CO_2 reacted with unhydrated products and C-S-H gel, as well as the existence of non-uniform carbonation profiles due to preexisting microcracks.

Zhou and Ju (2021) proposed a chemo-micromechanical damage modeling for concrete under sulfate attack. The multi-layer homogenization technique in a micromechanical framework considered the further chemical reaction of ettringite-induced damage as a cracked layer. Based on the multi-layer micromechanics, the damaged layers under sulfate attack were divided into the internal corrosion layer, damaged concrete layer with microcracks, and external intact layer. From these damage mechanisms, the constitutive model incorporated the progressive damage mechanism of local cracking and the corresponding expansion by ettringite formation under sulfate attack. As a result of the prediction, the accumulation of corrosion products critically degrades the effective mechanical properties due to the increase of expansion pressure and the damaged layer with microcracks.

Stora *et al*. (2009) explored the chemo-mechanical damage behavior of leached cementitious materials via a micromechanical framework. The chemo-transport-mechanical damage model built with multi-scale homogenization can predict the degradation of the elastic properties and the effective diffusivity with the microcrack formation under leaching. Moreover, this chemo-transport-mechanical damage model can be devoted to observing the crack density through the depth direction under pure water leaching on building materials. This simulation was confronted with experimental data of mineral compositions via the depth direction under pure water leaching. This simulation result shows a straightforward correlation between the dissolution of hydrated phases and the degradation of the mechanical properties in a systemic manner.

The hierarchical multiscale modeling is noteworthy in that the mineral transformation-induced damage mechanism of the building materials under harsh environments can be simulated from the viewpoint of macroscopic analysis as in

the degradation of the mechanical properties and formation of crack/microcrack (Stora *et al.* 2009, Zhou and Ju 2021).

5. Conclusions

This paper reviewed a comprehensive review of the state-of-the-art hierarchical multiscale modeling approach aimed at predicting the intricate physicochemical characteristics of construction materials. By integrating single-scale analyses—from atomistic *ab initio* methods to macroscopic FEM—through advanced scale-bridging techniques, this exploration unveils a modeling framework for predicting the heterogeneous nature of these materials. This approach, with its capacity for accurate electronic analyses, incorporation of experimental dynamics, and consideration of structural elements, emerges as a robust tool. The key findings derived in this study can be summarized below.

1. As a method for simulating the hydration mechanism, mineral transformation, and ion exchange in the pore solution, *ab initio* or MD based on reaxff can be highlighted, offering accurate electronic relationship calculations, whereas the classical MD (e.g., clayff, CementFF, C-S-HFF, and IFF) can offer the information of the mechanical responses of hydrates and diffusivities of reactive ions (e.g., CO_2^-, Cl^-, or SO_4^{2-}) by that of higher accuracy than MD based on reaxff.
2. For the hierarchical multiscale modeling of construction materials, scale-bridging techniques of the homogenization theory and the Monte-Carlo method are used in coupling the single-scale analysis.
3. Hierarchical multiscale modeling can complete the simulation considering the effects of such phenomena as hydration mechanisms and material defects on the physicochemical properties of construction materials.
4. While hierarchical multiscale modeling holds promise for predicting the physicochemical properties of construction materials, its accuracy is hindered by challenges related to bridging length or time scales.

Hierarchical multiscale modeling faces challenges posed by effectively scale-bridging methods of length or time scales. The time- and length-scale bridging methods are rigorously constrained by the coupling method from nano to macroscale in which similarity dimension (i.e., stress, stiffness tensor, diffusivity, etc.) and the dimensionless values (i.e., strain, volume/weight fraction in RVE, degree of hydration, etc.) both are the perspectives of the coupling single scale method for hierarchical multiscale modeling. Especially, reviewed scale bridging method of the homogenization theory in the micromechanical framework has a significant assumption that the strain field of the multi-phases should be uniformly stressed. In terms of the corresponding assumption, the effective mechanical properties can be correct when the phases are isotropic and homogeneous. It is expected that the physical, chemical, and physicochemical properties of various construction materials can be predicted more accurately when the corresponding limitations can be overcome. However, its effectiveness can highlight this model to predict the physicochemical properties of building materials. Moreover, achieving similarity along with dimensionless values such as stress, stiffness tensor, and diffusivity in RVE holds the potential to facilitate the efficient design and development of next-generation construction. Overcoming these limitations will contribute to the development of the materials precisely.

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Appendix. 3D-coordinate of unhydrated and hydrated products

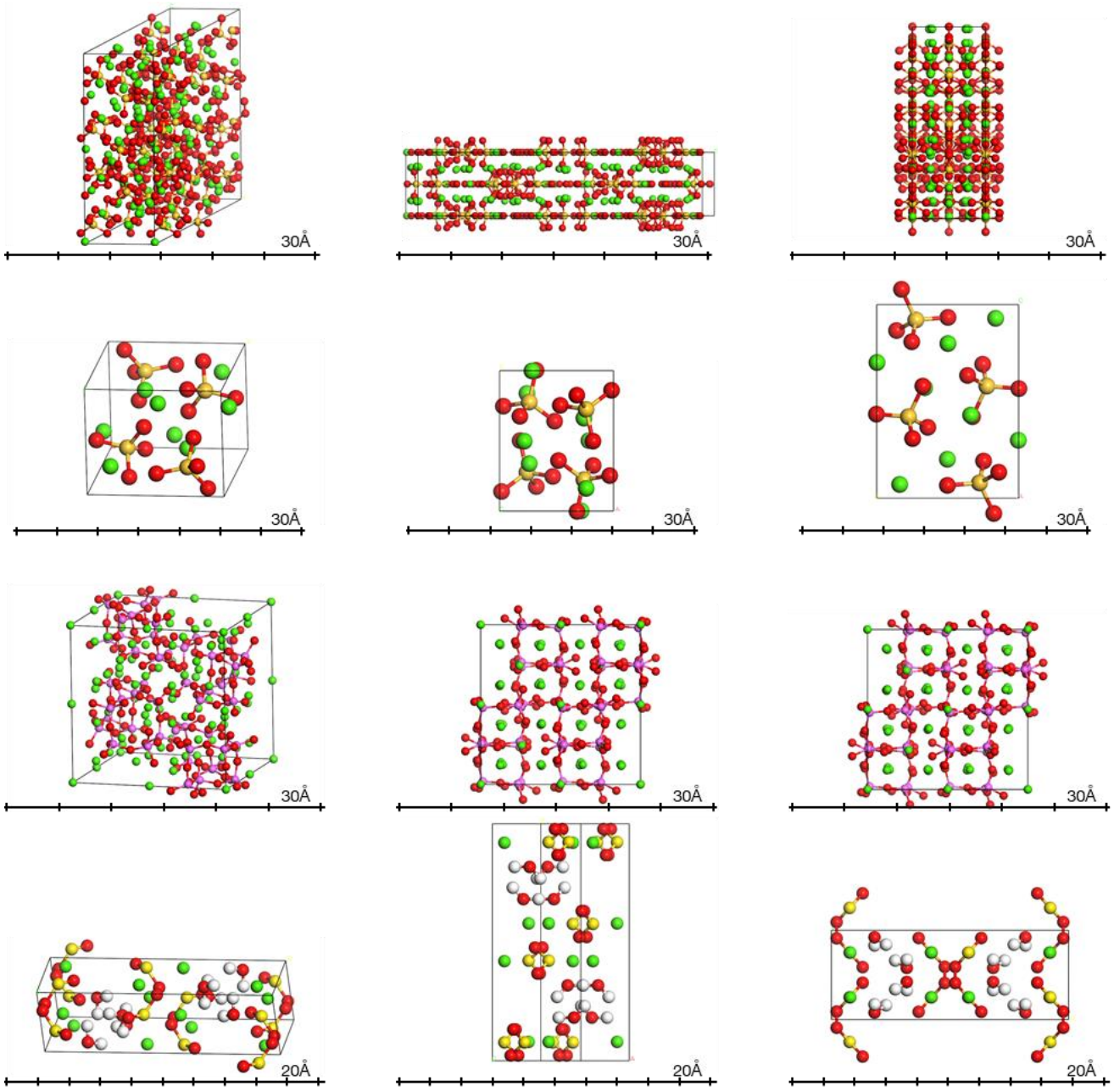

Fig. A1 3D-coordinate of (a) Alite M3, (b) Belite β, (c) Aluminate and (d) Gypsum in which the corresponding lattice planes of the molecular structures sequentially figured as (101), (001), and (100), respectively. Given that lattice parameters of alite M3, belite β, aluminate, and gypsum are monoclinic-B, monoclinic-B, cubic, and monoclinic-B, respectively. Red, white, green, and yellow represent oxygen, hydrogen, calcium, and silicon, respectively.

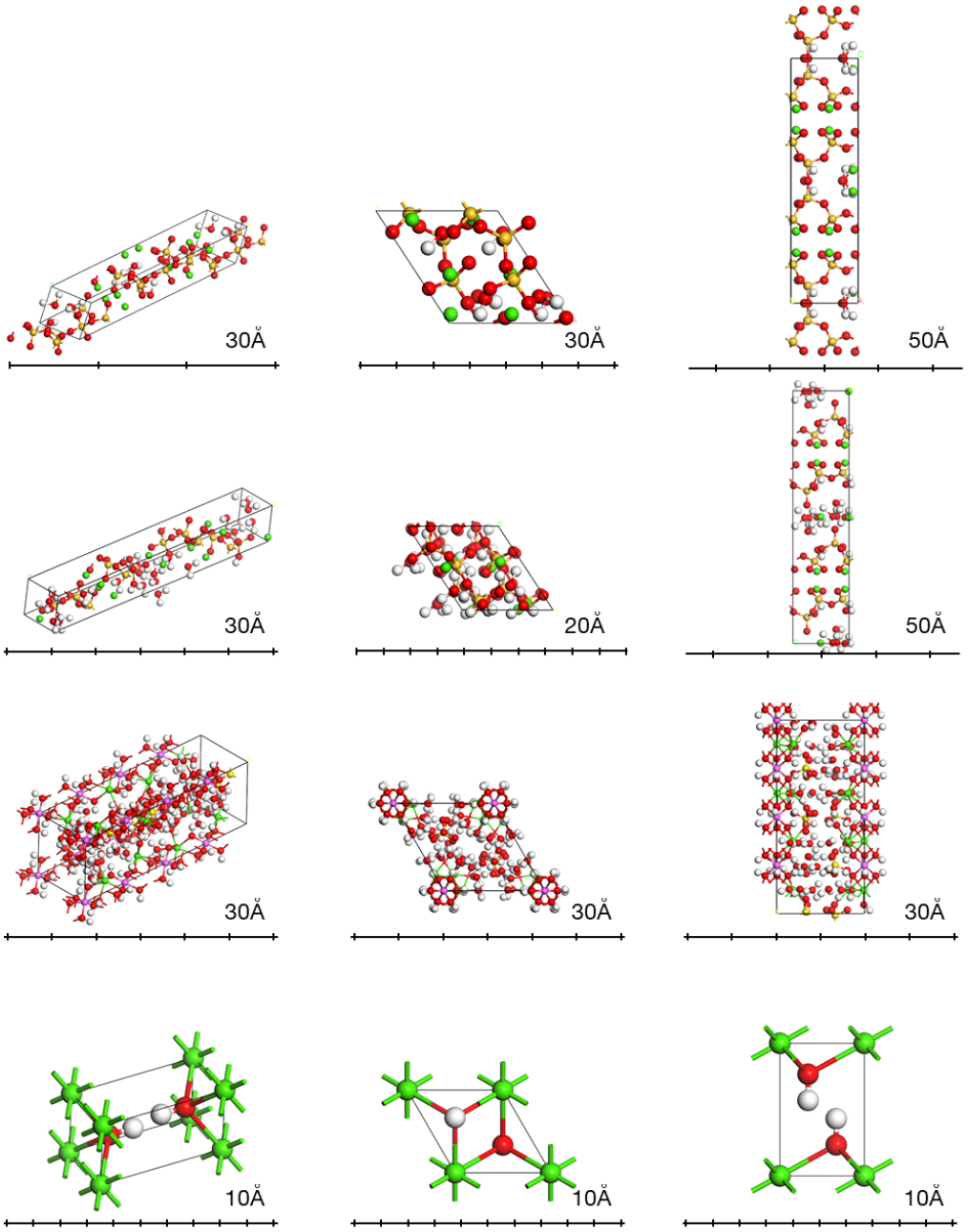

Fig. A2 3D-coordinate of (a) Tobermorite 11Å, (b) Tobermorite 14Å, (c) Ettringite, (d) Portlandite and (e) Calcite in which the corresponding lattice planes of the molecular structures sequentially figured as (101), (001), and (100), respectively. Given that lattice parameters of tobermorite 11Å, tobermorite 14Å, ettringite, portlandite, and calcite are monoclinic-C, monoclinic-C, hexagonal, triclinic, and triclinic, respectively. Red, white, green, and yellow represent oxygen, hydrogen, calcium, and silicon, respectively.