

¹ Development of a ReaxFF Reactive Force Field for Ettringite and ² Study of its Mechanical Failure Modes from Reactive Dynamics ³ Simulations

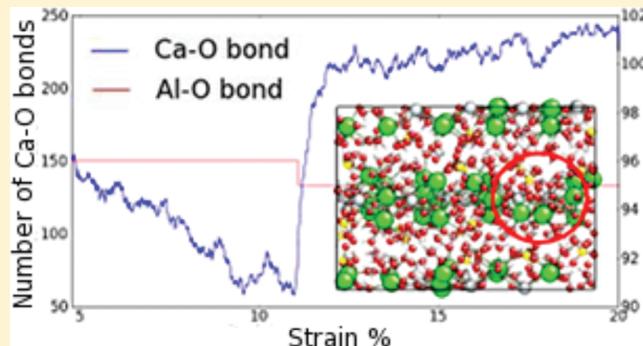
⁴ Lianchi Liu,[†] Andres Jaramillo-Botero,^{*,‡} William A. Goddard, III,^{*,‡} and Huai Sun[†]

⁵ [†]Computational Chemistry Group, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan
⁶ Road, Min Hang, Shanghai 200240, China

⁷ [‡]Materials and Process Simulation Center (MC 139-74), Chemistry and Chemical Engineering Division, California Institute of
⁸ Technology, 1200 East California Boulevard, Pasadena, California 91125, United States

⁹ Supporting Information

ABSTRACT: Ettringite is a hexacalcium aluminate trisulfate hydrate mineral that forms during Portland cement hydration. Its presence plays an important role in controlling the setting rate of the highly reactive aluminate phases in cement paste and has also been associated with severe cracking in cured hardened cement. To understand how it forms and how its properties influence those of hardened cement and concrete, we have developed a first-principles-based ReaxFF reactive force field for Ca/Al/H/O/S. Here, we report on the development of this ReaxFF force field and on its validation and application using reactive molecular dynamics (RMD) simulations to characterize and understand the elastic, plastic, and failure response of ettringite at the atomic scale. The ReaxFF force field was validated by comparing the lattice parameters, pairwise distribution functions, and elastic constants of an ettringite crystal model obtained from RMD simulations with those from experiments. The predicted results are in close agreement with published experimental data. To characterize the atomistic failure modes of ettringite, we performed stress-strain simulations to find that Ca–O bonds are responsible for failure of the calcium sulfate and tricalcium aluminate (C3A) column in ettringite during uniaxial compression and tension and that hydrogen bond re-formation during compression induces an increase in plastic strain beyond the material's stress-strain proportionality limit. These results provide essential insight into understanding the mechanistic role of this mineral in cement and concrete degradation, and the ReaxFF potential developed in this work serves as a fundamental tool to further study the kinetics of hydration in cement and concrete.



1. INTRODUCTION

The trisulfate mineral ettringite, with chemical formula $\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$, is a precipitate formed in hydrated Portland cement as a result of the reaction of calcium aluminate (A) with calcium sulfate (C), and its presence depends on the ratio C3A. Changes in this ratio as well as the permeability of ettringite to water and its reactions with other chemical species (e.g., sulfates) affect its structural evolution during cement hydration and, consequently, cement properties. The formation of ettringite during the early cement hydration stage plays an important role in controlling the setting rate of the highly reactive aluminate phases. Its formation results in a volume increase in the fresh, plastic concrete, which has also been associated spatially with severe cracking in cured hardened concrete¹ during what is referred to as delayed ettringite formation, or DEF, and during cement degradation via sulfate attacks.²

To help settle the mechanistic issues, it would be most useful to understand the atomistic processes involved with mechan-

ically loaded ettringite. However, the quantum mechanics (QM) methods usually applied to studies of chemical reaction processes are not capable of treating the spatial and time scales involved. Consequently, we have used QM to train the parameters of a ReaxFF³ reactive force field and then used it to simulate the physical properties and reaction processes that occur during ettringite loading.

This paper focuses on investigating the chemical processes relevant to the mechanical properties of ettringite, including its failure modes under pressure loading, using reactive molecular dynamics (RMD). We first develop the ReaxFF first-principles-based reactive force field to describe the structures, energetics, and forces from QM on prototypical systems. Then, we carried out RMD to study the decomposition and growth of various phases over a broad set of conditions. In section 2.1.1, we

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64 describe the ReaxFF reactive force field developed (see
 65 Supporting Information), and section 3.1 provides a description
 66 of several validation tests performed on ettringite. Then, in
 67 section 3.2, we describe how ReaxFF was used to characterize
 68 the mechanical response and failure modes of ettringite under
 69 strain loading. We consider that these modes of failure are
 70 critical to understand and control the long-term properties of
 71 Portland-based concrete structures.

2. COMPUTATIONAL DETAILS

72 Modern QM methods provide reaction surfaces and geometries
 73 of molecular systems sufficiently accurate to predict a reaction
 74 mechanism in advance of experiment. However, scaling of
 75 computational cost with system size (i.e., the number of atoms)
 76 limits these methods to within ~ 100 atoms. QM can be used to
 77 derive the forces for describing the dynamical equations of
 78 motion of all particles involved; however, again, computational
 79 costs restrict the time scale to a few picoseconds. This stems
 80 from the high cost of solving self-consistently the Schrödinger
 81 equation for all nuclear and electronic interactions. Con-
 82 sequently, the use of QM to study the reaction processes
 83 occurring in ettringite as the system is dynamically strain
 84 loaded/unloaded is well beyond the current practical limits of
 85 QM calculations.

86 **2.1. ReaxFF Force Field.** To provide a practical solution to
 87 such problems, we developed the ReaxFF reactive force field,³
 88 which provides nearly the accuracy of the best QM but at a
 89 computational cost of solving Newton's equation of motion on
 90 nuclei only. This allows us to accurately compute the atomic
 91 interactions found in ettringite. Essential elements of ReaxFF
 92 include:

- 93 1. an analytic relation between bond order and bond
 94 distance and between bond energy and bond order that
 95 establishes smooth transitions as bonds form and break
- 96 2. a rule for how charge depends on geometry and atomic
 97 character that allows charges to flow continuously as
 98 bonds form and break
- 99 3. functional forms that describe well the barrier heights of
 100 both allowed and forbidden reactions, including the
 101 effects of resonance.

102 ReaxFF partitions the total energy of interactions similarly to
 103 those found in nonreactive force fields like Dreiding, that is, in
 104 valence, nonbonded, and H-bond terms, but it introduces bond
 105 order dependencies on valence terms and additional potential
 106 energy corrections to properly describe bond formation and
 107 dissociation under different environmental conditions. The
 108 overall energy of the system in ReaxFF is given as

$$\begin{aligned} U_{\text{Total}} = & E_{\text{bonds}} + E_{\text{angles}} + E_{\text{torsions}} + E_{\text{H-bonds}} \\ & + E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{lp}} + E_{\text{over}} + E_{\text{under}} \\ & + E_{\text{pen}} + E_{\text{coa}} + E_{C_2} + E_{\text{triple}} + E_{\text{conj}} \end{aligned} \quad (1)$$

109 where E_{lp} corresponds to the lone pair energy penalty based on
 110 the number of lone pairs around an atom, E_{over} to the energy
 111 penalty for overcoordinated atoms, E_{under} to the energy
 112 contribution for the resonance of the π -electron between
 113 attached undercoordinated atomic centers, E_{pen} to an energy
 114 penalty needed to reproduce the stability of systems with
 115 double bonds sharing an atom in a valency angle (e.g., allene),
 116 E_{coa} to the three-body conjugation term to describe the stability
 117 of $-\text{NO}_2$ groups, E_{C_2} to an energy contribution that captures

118 the stability of C_2 , E_{triple} to a triple bond stabilization energy in
 119 CO bonded pairs, and E_{conj} to the contribution of conjugation
 120 effects to the molecular energy. 120

In ReaxFF, each element is described using a single atom
 121 type, even through bonding during a chemical reaction. This
 122 also facilitates the transferability of the parameters. For each
 123 element, several parameters to describe valence bond
 124 parameters, electronegativity, hardness, and other effects are
 125 optimized to reproduce the QM-derived energies and charges.
 126 ReaxFF can reproduce energies near the accuracy of the
 127 training set at a much lower computational cost. The reactive
 128 site or pathways need not be predefined in a ReaxFF MD
 129 simulation, and connectivities between the atoms are not
 130 predetermined. Instead, bond orders are calculated from the
 131 interatomic distances r_{ij} . By using a bond length/bond order
 132 relationship, smooth transitions from nonbonded to single,
 133 double, and triple bonded systems, and vice versa, are obtained.
 134 This requires bond orders to be updated every iteration, for
 135 single (σ), double (π), and triple ($\pi-\pi$) bonds as a function of
 136 interatomic distances (r_{ij}), using scaling parameters
 137 fitted from QM calculations on small representative systems
 138 and making all of the connectivity-dependent interactions
 139 bond-order-dependent to ensure that their energy contribu-
 140 tions disappear upon bond dissociation. Bond orders are
 141 computed initially as 142

$$\begin{aligned} \text{BO}'_{ij} = & \exp \left[p_{\text{BO},1} \left(\frac{r_{ij}}{r_0^\sigma} \right)^{p_{\text{BO},2}} \right] + \exp \left[p_{\text{BO},3} \left(\frac{r_{ij}}{r_0^\pi} \right)^{p_{\text{BO},4}} \right] \\ & + \exp \left[p_{\text{BO},5} \left(\frac{r_{ij}}{r_0^{\pi-\pi}} \right)^{p_{\text{BO},6}} \right] \end{aligned} \quad (2)$$

From these (uncorrected) bond orders, BO' , an uncorrected
 143 atomic overcoordination Δ' is calculated as the difference
 144 between the total bond order around the atom and the number
 145 of its bonding electrons, Val , that is 146

$$\Delta'_i = -\text{Val}_i + \sum_{j=1}^{\text{neighbors}(i)} \text{BO}'_{ij} \quad (3)$$

Equation 3 is then used to obtain corrected bond orders, BO_{ij} ,
 147 and subsequently a new corrected overcoordination. For more
 148 details on the exact functional forms, see the Supporting
 149 Information from ref 4. 150

The bond energies are then computed from the corrected
 151 bond orders by 152

$$\begin{aligned} E_{\text{bond}} = & -D_e^\sigma \text{BO}_{ij}^\sigma \exp[p_{\text{bel},1}(1 - (\text{BO}_{ij}^\sigma)^{p_{\text{be},2}})] - D_e^\pi \text{BO}_{ij}^\pi \\ & - D_e^{\pi-\pi} \text{BO}_{ij}^{\pi-\pi} \end{aligned} \quad (4)$$

where D_e is the corresponding dissociation energy for each
 153 bond type and $p_{\text{bel},2}$ correspond to atomic parameters that are
 154 fitted from QM calculations on small representative cases.
 155 According to eq 4, the bond energy term E_{bond} gradually
 156 disappears as the bond order BO approaches zero during the
 157 dissociation of a bond. The ij valence angle and torsion angle
 158 energy terms are also functions of bond orders and go to zero
 159 upon bond dissociation. This ensures continuity of the energy
 160 and forces during bond dissociation/formation. 161

Table 1. Atom Parameters

atom type	EEM parameters			bond order correction				
	χ (eV)	η (eV)	γ (Å)	$p_{ov/un}$	p_{val3}	p_{bo4}	p_{bo3}	p_{bo5}
H	3.7248	9.6093	0.8203	-19.4571	4.2733	3.0408	2.4197	0.0003
O	8.5000	8.3122	1.0898	-3.5500	2.9000	3.5027	0.7640	0.0021
Ca	-1.7130	6.5096	1.0000	-2.0000	3.8301	49.9248	0.3370	0.0000
Al	1.7429	6.8319	0.4265	-22.7101	1.7045	20.0000	0.2500	0.0000
S	5.8284	8.2545	1.0336	-11.0000	2.7466	5.7487	23.2859	12.7147

Table 2. Bond Energy and Bond Order Parameters (D_e in kcal/mol; r in Å)

atom pair	$D_{e,\sigma}$	$D_{e,\pi}$	p_{be1}	p_{be2}	r_σ	p_{bo1}	p_{bo2}	r_π	p_{bo3}	p_{bo4}
Al–O	227.9327	0.0	-0.8375	0.3686	1.5382	-0.1740	5.2057			
S–O	161.0562	220.0	0.6070	0.7150	1.4608	-0.1109	5.4501	1.3987	-0.2741	8.3216

162 Nonbonded interactions (van der Waals, Coulomb) are
 163 calculated between every atom pair, irrespective of connectivity
 164 and avoiding excessive close-range contributions by shielding.
 165 ReaxFF parameters have been developed for a variety of
 166 materials, including hydrocarbons,³ silicon/silicon oxide,⁵
 167 metals,⁶ metal oxides,⁴ and metal hydrides,⁷ among others. It
 168 has also been used to study a variety of complex chemical
 169 systems.^{4,8–10}

170 **2.1.1. ReaxFF Force Field for Ettringite.** We developed the
 171 ettringite ReaxFF force field to accurately reproduce the first-
 172 principles QM interactions in hydrous calcium aluminum
 173 sulfate systems (H/Ca/Al/S/O) and to provide a way to
 174 extend the first-principles accuracy to the much larger length
 175 and time scales needed to examine the processes of interest
 176 here.

177 We started with recently derived ReaxFF parameters for Al/
 178 O from ref 11 and Ca/O from ref 12. These parameters had
 179 been optimized to describe the crystals of various phases of Al
 180 and Ca and of various aluminum oxides and calcium oxides. As
 181 discussed below, we prepared additional training data to
 182 complete the Al, Ca, O, S, and H interactions present in
 183 ettringite and validated ReaxFF charges for its constituent
 184 molecular motifs against QM Mulliken populations.

185 This involved performing QM density functional theory
 186 (DFT) calculations on representative finite clusters using the
 187 B3LYP hybrid functional with the LACVP** basis set using the
 188 Jaguar 4.2 package.¹³ The **calculator** on periodic systems used
 189 the PBE functional with double- ζ plus polarization basis of
 190 contracted Gaussian functions with SeqQuest.¹⁴ The complete
 191 QM-derived force field training set includes EOS, atomic bond
 192 energy curves, dissociation energies, angle bend energy curves,
 193 and other relevant material properties, such as heats of
 194 formation, overcoordination, and others, for all possible
 195 interactions between Ca, Al, O, S, H, and H₂O. Angle bend
 196 energies in ettringite were also trained to achieve an accurate
 197 geometrical representation of the crystal structure. These
 198 included Ca–Ca–Ca in a triangle [Ca(OH)₂]₃ bend to
 199 represent the potential surface of Ca–O–Ca and O–Ca–O
 200 angles, the distance of Al–Al in Ca[AlO₄]₂ scanned to
 201 represent the potential surface of the Ca–O–Al angle, which
 202 is typical in ettringite along the c direction, the Al–O–S angle
 203 in Al(OH)₂–O–SO₃H, and the Ca–O–S angle in CaSO₄ gas.

3. RESULTS AND DISCUSSION

204 The geometries and energies of the species and complexes in
 205 ettringite were calculated using DFT, and the ReaxFF force
 206 field parameters were optimized to minimize the differences

207 between the DFT and ReaxFF energies. Tables 1–5 provide a
 208 summary of the ReaxFF force field parameters for ettringite. 209

Table 3. van der Waals Parameters

atom pair	R_{vdW} (Å)	ϵ (kcal/mol)	α	γ_{vdW}
Al–O	1.8928	0.1745	11.2476	7.3490
S–O	1.7931	0.2047	10.2391	8.2411

210 The corresponding ReaxFF potential functional forms may be
 211 consulted in ref 4. These optimized parameters are available in
 212 a ffield file (see the Supporting Information section of ref 4)
 213 that can be directly used in the freely available “Large-scale
 214 Atomic/Molecular Massively Parallel Simulator” (LAMMPS¹⁵)
 215 molecular dynamics program from Sandia National Laborato-
 216 ries. 217

218 **3.1. Ettringite ReaxFF Force Field Validation.** We began
 219 by constructing a 2 × 2 × 1 molecular triclinic unit supercell
 220 model from the crystal structure determined by Moore,¹⁶ as
 221 shown in Figure 1. This molecular model served as the basic
 222 structure for the calculations reported here. 223

224 Charges play an important role in computing charge
 225 distributions and overall electrostatics during bond breaking
 226 and formation in ReaxFF. To confirm the accuracy of the net
 227 molecular charges calculated with ReaxFF (using the charge
 228 equilibration method QEg from Rappe et al¹⁷) on subspecies
 229 found in ettringite, including H₂SO₄, CaSO₄, Al(OH)₃,
 230 Al(OH)₂–O–SO₃H, and the C₃A₂ cluster, we compared
 231 these to Mulliken charge populations. Figure 2 shows that
 232 ReaxFF charges for the different species of interest are in close
 233 agreement with the QM results. 234

235 In addition to validating bond energies, EOS, and other
 236 properties, we compared DFT-calculated angle bend energies
 237 against equivalent scans using the ettringite ReaxFF force field.
 238 Angle bend energies for Ca–O–Ca, O–Ca–O, Ca–O–Al,
 239 Al–O–S, and Ca–O–S angles are important to the structural
 240 conformity of the model (see Figure 3). 241

242 To determine the structural stability and conformity of our
 243 model during room-temperature dynamics, the 2 × 2 × 1
 244 ettringite supercell model shown in Figure 1 was equilibrated
 245 for 20 ps in an NPT ensemble with RMD calculations at 300 K
 246 and a 0.25 fs time step. The last 10 ps were used for statistical
 247 calculation of the cell parameters and for computing radial
 248 distribution functions (RDFs). The calculated unit cell
 249 parameters accurately reproduce the experimental values within
 250 ~4%, as shown in Table 6. The total averaged RDFs and all of
 251 the RDF pairs were also calculated (Figure 4), revealing
 252

Table 4. Angle Parameters

angle type	$\Theta_{0,0}$ (deg)	p_{val1} (kcal/mol)	p_{val2}	p_{coal}	p_{val7}	p_{pen1}	p_{val4}
O—Al—O	54.0864	9.7594	1.9476	0.0	3.0000	0.0	1.4400
O—O—Al	34.4326	25.9544	5.1239	0.0	2.7500	0.0	1.7141
H—O—Al	90.0000	19.7491	1.8227	0.0	1.0000	0.0	2.5337
Al—O—Al	23.7270	19.5973	4.0000	0.0	0.6619	0.0	1.9380
Ca—O—Al	79.6174	23.7025	5.7958	0.0	0.9119	0.0	1.6244
Al—O—S	102.1915	7.3381	0.4786	0.0	0.5846	0.0	1.4022
Ca—O—S	114.2370	19.7117	0.5240	0.0	3.0000	0.0	0.8335
O—S—O	81.7931	31.2043	6.5492	-4.4116	2.6067	0.0	3.0000
O—O—S	83.9753	31.0715	3.5590	0.0	0.8161	0.0	1.1776

Table 5. Torsion Angle Parameters (V in kcal/mol)

torsion angle	V_1	V_2	V_3	p_{tor1}	p_{cot1}
H—O—S—O	2.5000	2.5000	0.2237	-10.0000	-1.0000
X—O—S—X	0.1000	50.0000	0.0100	-10.0000	0.0000

predicted structures from our MD simulations that are in close agreements with experiments.

3.2. Elastic Constants of Ettringite. To characterize the stiffness of ettringite, we calculated its elastic constants from the linear relation between the stress and strain tensors in the limit of infinitesimal deformation. We computed the adiabatic constants (at 0 K) considering that the thermal expansion of the unit cell at ambient temperature, relative to that at 0 K, was within the error bars of our method (as estimated from our NPT-RMD structure equilibration simulations at 300 K). This involved deforming the unit cell by less than 1% in the different directions of interest and calculating the change in the corresponding stress tensor components. This way, we avoided the higher uncertainty and computational costs of calculating the elastic constants at ambient temperature, which requires time averages of differential properties (e.g., stress tensor components using a canonical or isothermal–isobaric ensemble approach) and balancing the systematic and statistical errors to fully equilibrate the deformed cell before sampling the stress tensor. Table 7 shows that the results from our simulations are

quantitatively consistent with the isothermal elastic constants reported from experiments.¹⁸

3.3. Atomistic Failure Modes of Ettringite under Mechanical Loading. To understand the failure modes of ettringite, we carried out RMD deformation simulations, with the ReaxFF force field reported here, along the y and z directions on the model system depicted in Figure 1. We started from a relaxed volume $2 \times 2 \times 1$ supercell using NPT-RMD at 300 K temperature and 1 atm of pressure. The system was equilibrated at every 1% strain for 20 ps up to 15% strain in the y direction and 20% strain in the z direction, and the last 10 ps was used for data collection at each deformation strain.

The uniaxial stress–strain characteristics along the z direction, under compression and tension, are presented in the Figure 5. These results indicate that the true elastic limit along the z direction is at ~3% under strain in compression and ~7% in tension, while failure occurs between 11 and 12% deformation. These results also indicate that in this particular direction, ettringite is more resistant under tensile strain than under compression. We observed hydrogen bonds breaking and re-forming during compression, which accounts for the increase in plastic strain in this mode. The longitudinal elastic anisotropy due to the crystallographic structure is $C_{11}/C_{33} = 0.63$, while the shear anisotropy is $C_{66}/C_{44} = 0.6$. The stiff octahedra chains of $[\text{Al}(\text{OH})_6]_3^-$ alternating with triplets of Ca_2^+ in eight-fold coordination along the z -axis lead to higher stiffness in this direction.

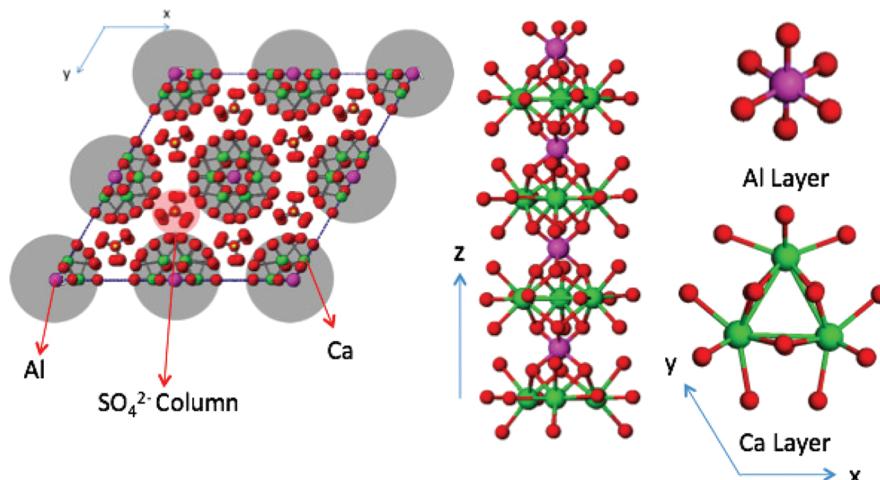


Figure 1. The triclinic $2 \times 2 \times 1$ molecular supercell crystal model of ettringite contains a total of 496 atoms, ignoring hydrogens, arranged in 4 stacked layers (center image) of intercalated Ca and Al sublayers (right image). The left image shows the projection of crystal structure on to the (0001) plane. C3A columns lay parallel to the z -axis (c) with sulfate and water molecules in the intercolumn channels. The SO_4^{2-} groups are located at the interstitials between columns, along with water molecules, and 132 hydrogen atoms (not shown) on the surface of the columns and around the SO_4^{2-} groups neutralize the system.

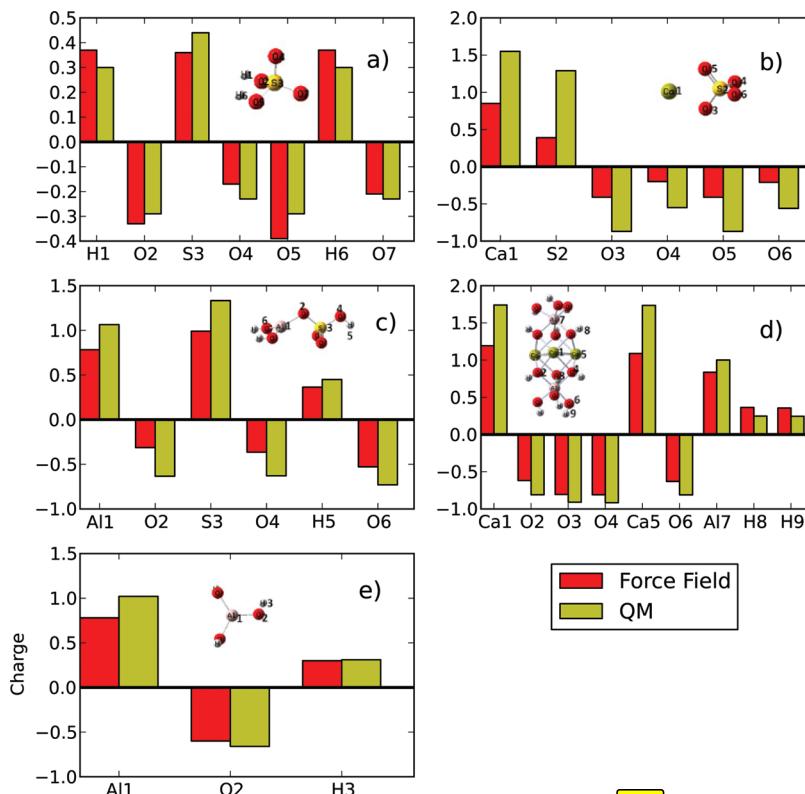


Figure 2. Comparison of the charges for Ettringite from the ReaxFF force field and from QM calculations for (a) H_2SO_4 , (b) CaSO_4 , (c) the C_3A_2 cluster, (d) $\text{Al}(\text{OH})_2-\text{O}-\text{SO}_4\text{H}$, and (e) $\text{Al}(\text{OH})_3$.

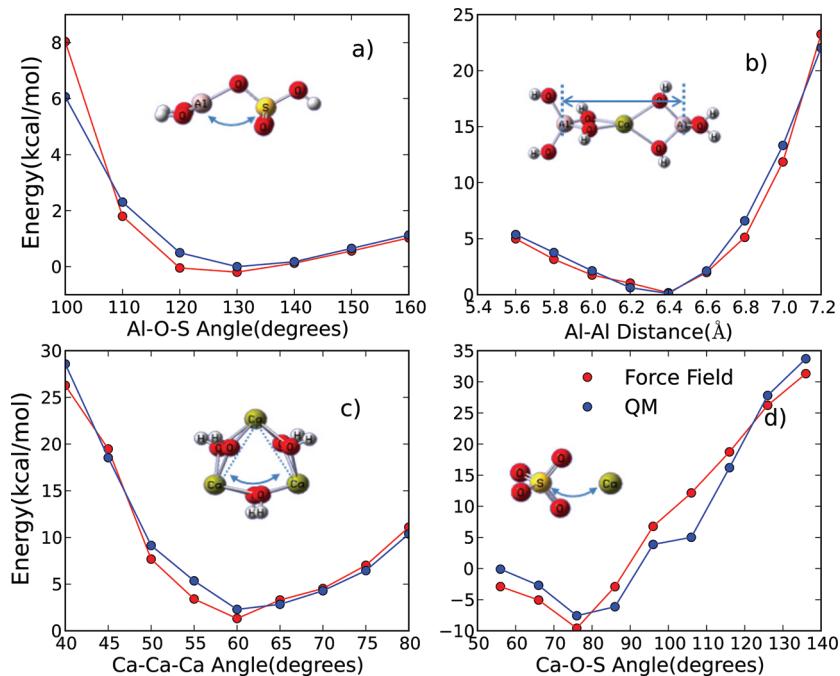


Figure 3. Comparison of the ettringite angle bend energies from ReaxFF and from QM angle scans for (a) $\text{Ca}-\text{O}-\text{Ca}$ and $\text{O}-\text{Ca}-\text{O}$, (b) $\text{Ca}-\text{O}-\text{Al}$, (c) $\text{Al}-\text{O}-\text{S}$, and (d) $\text{Ca}-\text{O}-\text{S}$ angles.

The stress-strain characteristics of the system along the y direction are shown in Figure 6. Material failure during compression in the y direction occurs at $\sim 13\%$ strain and at $\sim 8\%$ strain during tension. The intermolecular hydrogen bonding network that provides mechanical stability to the

C3A columnar conformation are responsible for the decreased loading capacity in the a/b directions of the material.

The number of bond changes during the dynamics of mechanical strain was used to provide further insight into the failure mechanisms of ettringite.

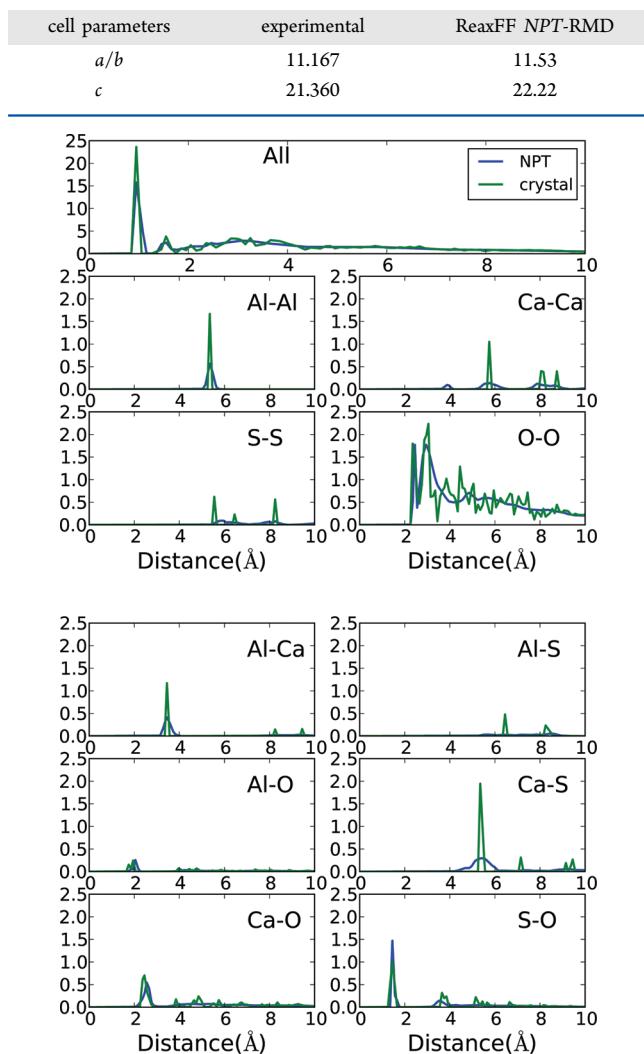
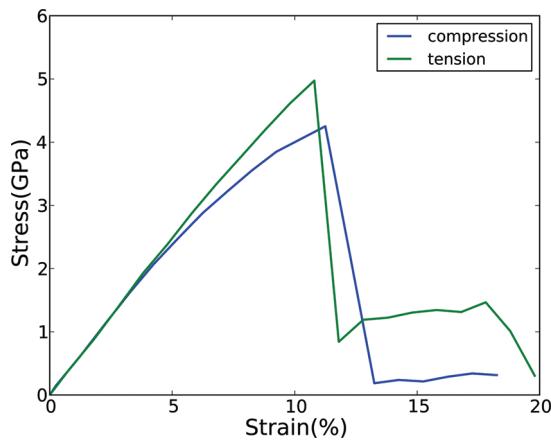
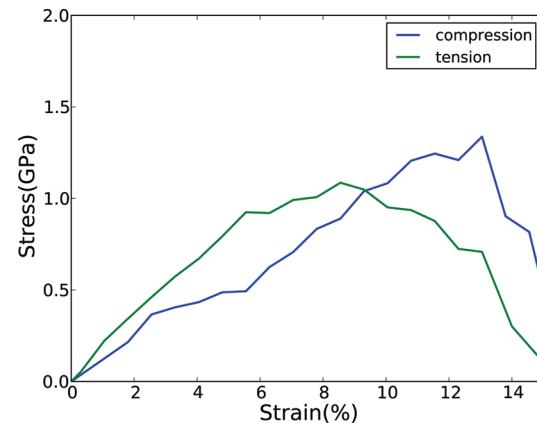
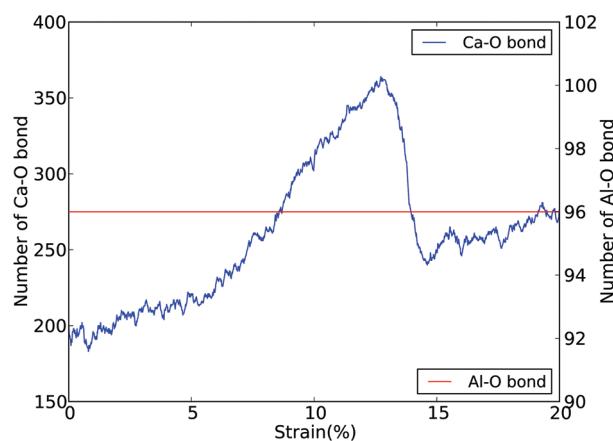
Table 6. Comparison between Calculated Ettringite Cell Parameters and Experiment**Figure 4.** Radial distribution functions (RDFs) for Ettringite; experimental and ReaxFF NPT-RMD simulation results agree.

Figure 7 shows that during the initial stages of compression along the z direction, the number of Ca–O bonds increases slowly until $\sim 7\%$ compression, and they increase at a faster pace thereafter, until the failure point ($\sim 11\%$ strain). On the

Table 7. Computed (Adiabatic) versus Experimental (Isothermal) Elastic Constants in Ettringite Crystal^a

elastic constants	expt ¹⁸	ReaxFF
C_{11}	35.1 ± 0.1	45.4
C_{12}	21.9 ± 0.1	25.0
C_{13}	20.0 ± 0.5	23.0
C_{14}	0.6 ± 0.2	1.9
C_{33}	55 ± 1	53.9
C_{44}	11.0 ± 0.2	11.1
C_{66}	$6.6^* \pm 0.1$	8.1
bulk modulus (K)	27.3 ± 0.9	26.76
shear modulus (G)	9.5 ± 0.8	12.44
Poisson ratio(ν)	0.34 ± 0.02	0.30

^aNote: C_{66}^* is calculated as $(C_{11} - C_{12})/2$.**Figure 5.** Stress–strain curve along the z direction under compression and tension deformation.**Figure 6.** Stress–strain curve along the y triclinic (a/b) direction under compression (blue) and tension (black).**Figure 7.** The number of Ca–O bonds increases piecewise linearly between 0 and 7% and 7 and 11%, until failure at $\sim 11\%$ elongation in the z direction, while the number of Al–O bonds remains constant during the full range of compression deformation in the same direction.

other hand, the numbers of Al–O bonds do not change during compression; therefore, the failure in this mode is attributed to Ca–O bond breaking in the C3A column. We observe that during tension, the number of Ca–O bonds decreases at a constant rate before reaching the failure point of the material, at $\sim 11\%$ tension, and sharply increases thereafter (Figure 8). The

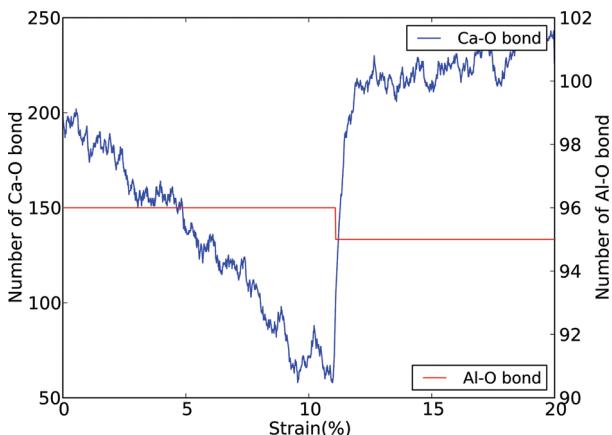


Figure 8. The number of Ca–O bonds decreases linearly during elongation in the z direction until failure at $\sim 11\%$, while the number of Al–O bonds decreases by one at the failure point.

314 C3A column loses its structural character after one Al–O bond
315 is lost, which occurs after the system's failure point at $\sim 11\%$
316 elongation.

317 From Figures 7 and 8, it is evident that the change in the
318 number of Ca–O bonds is much less than that observed for the
319 z (c) direction. Moreover, these changes are mainly due to the
320 Ca–water interactions because the conformation of the C3A
321 column is not changed during the deformation. The failure
322 mechanism in this case is associated with hydrogen bond
323 breaking between neighboring C3A columns.

324 The monocline structure in ettringite, which causes some
325 shear stress, and hydrogen bond breaking are responsible for
326 the oscillatory nature of Figures 9 and 10.

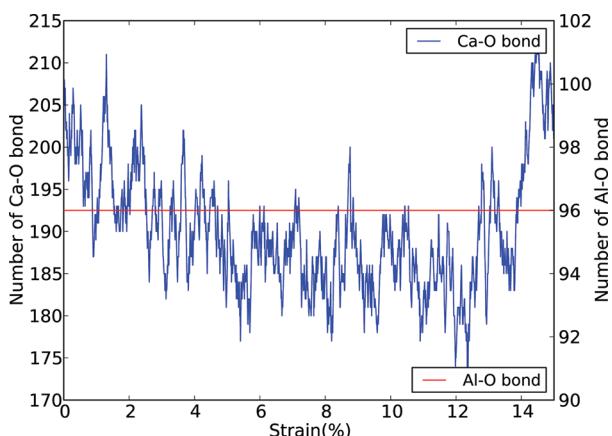


Figure 9. The number of Ca–O bonds decreases linearly during compression in the y triclinic direction, and a small increase is observed after failure at $\sim 12\%$, while the number of Al–O bonds remains constant even after the failure point.

4. SUMMARY AND CONCLUSIONS

327 We have developed and validated a first-principles-derived
328 ReaxFF reactive force field for ettringite and applied it to study
329 the general mechanical properties and atomistic failure
330 mechanisms of the ettringite mineral. In particular, we
331 determined the structural stability and geometry of ettringite
332 at ambient temperature to be in close agreement with

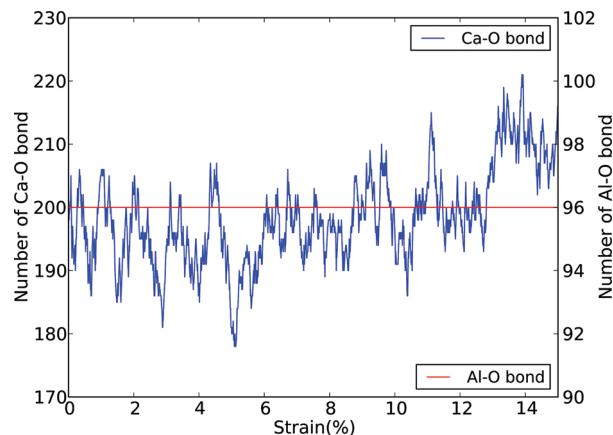


Figure 10. The number of Ca–O bonds changes little during tensile deformation in the y triclinic direction, with a slight increase after failure at $\sim 12\%$.

333 experimental RDFs, its adiabatic elastic constants to be in 333
334 quantitative agreement with experimentally obtained constants, 334
and from isothermal–isobaric RMD simulations, the sequence 335
336 of molecular events that lead to its failure under mechanical 336
337 compression and tension. We found that Ca–O bond breaking 337
338 in the C3A column leads to failure during compression and 338
339 tension, while hydrogen bond network formation leads to an 339
340 increase in plastic strain during compression. 340

341 The results presented here are essential for understanding 341
the role of ettringite in cement and concrete properties. We are 342
now using this ReaxFF force field to study the hydration 343
kinetics of ettringite and the effect of water on ettringite (and 344
delayed ettringite formation, DEF) as it pertains to the long- 345
term degradation of cement paste and concrete properties. This 346
will be the subject of a subsequent publication. 347

■ ASSOCIATED CONTENT

● Supporting Information

Description of the ReaxFF reactive force field developed. This 350
material is available free of charge via the Internet at <http://pubs.acs.org>. 351
352

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ajaramil@caltech.edu (A.J.-B.); wag@wag.caltech.edu 355
(W.A.G.). 356

Notes

The authors declare no competing financial interest. 358

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