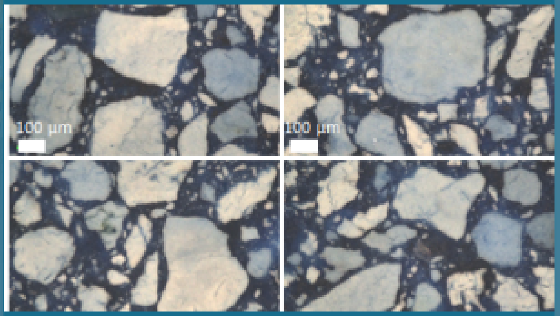
SAND2022-2937C

Chemically Assisted Weakening of CaO



Jessica M. Rimsza and Anastasia G. Ilgen

Sandia National Laboratories, Albuquerque, NM USA

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Introduction – Chemical Weakening and CaO

- CaO (quick lime) is a common material with varying applications that is reactive with the environment through the formation of hydrated and carbonate based phases
    - Stabilize clay-containing soil

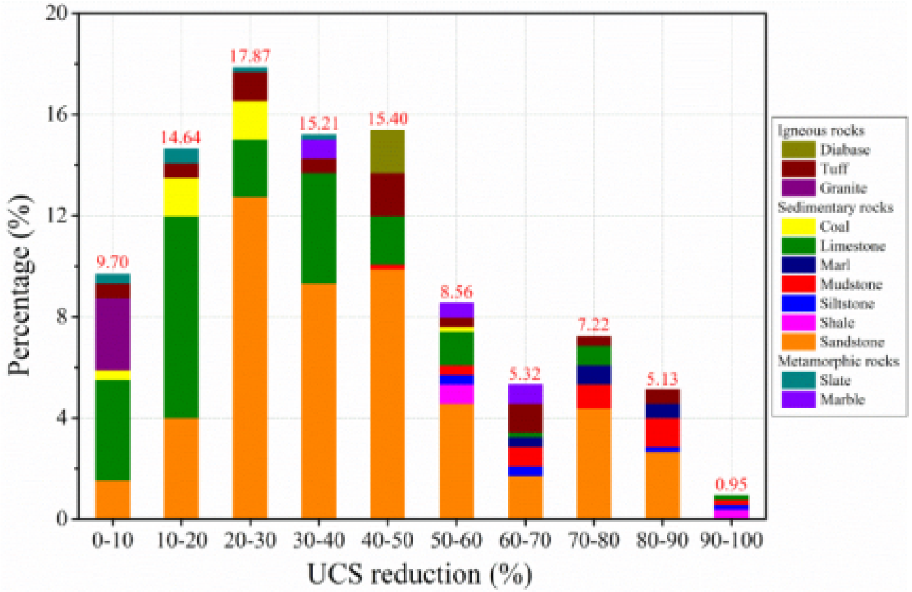
      Rafalko et al. Transportation Research Record 1 (2007) 39-46
    - Carbon adsorbent

      Liu et al. Energy & Fuels 26.5 (2012) 2751-2767
    - Component in cement compositions

      Temuujin et al. Journal of Hazardous Materials 167. 1-3 (2009) 82-88

- Chemical weakening is a well documented phenomena in multiple oxide-based systems
- Most oxide systems exhibit *some* amount of weakening in the presence of water
- Assumed to be caused by:
    - Reactions of water with the strained bonds at the crack tip
    - Change in surface energies during hydration

Molecular scale modeling can be used to identify *mechanisms* of chemical weakening in specific oxide systems



Percentage distribution of uniaxial compressive strength (UCS) reduction induced by water saturation for different rock types

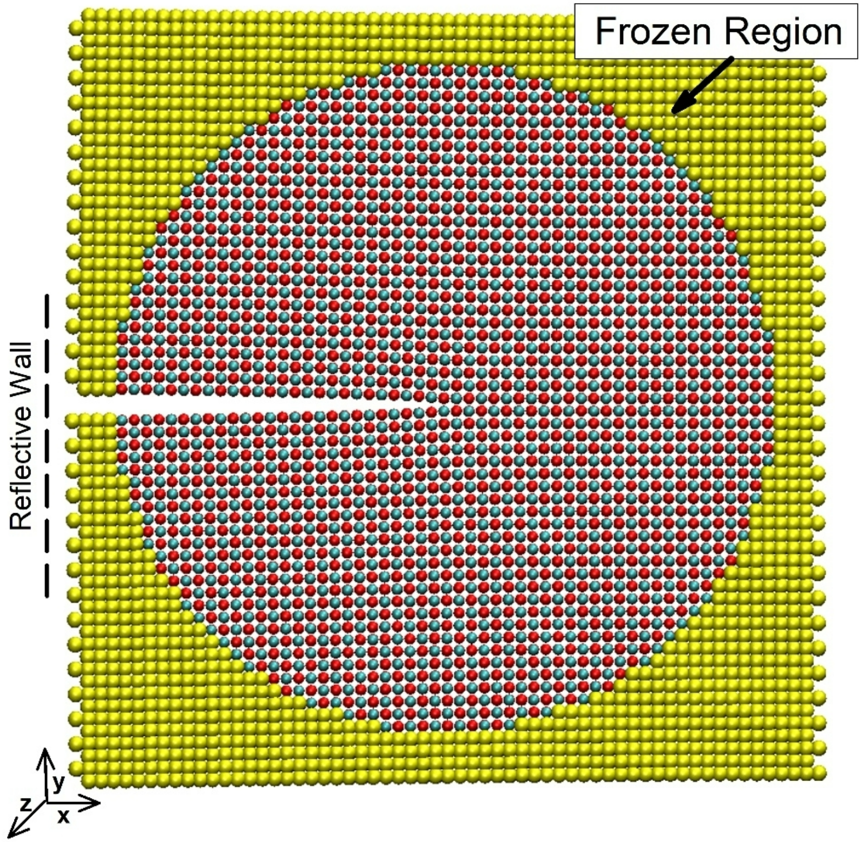
Cai et al. Applied Surface Science 9.20 (2019) 4450

Computational Methods

- Classical molecular dynamics for large scale simulation of CaO fracture
- ReaxFF: bond order based forcefield including Ca-O and O-H bond breakage and formation

$$E_{Total} = E_{Bond} + E_{Over} + E_{Under} + E_{LP} + E_{Val} + E_{Pen} + E_{Tors} + E_{Conj} + E_{VDW} + E_{Coul}$$

- Slit crack is formed by removing neighboring, creating a singular high stress condition
- Boundary atoms are fixed and atomic positions are adjusted to introduce far-field loading as a mode I fracture
- Interior atoms (radius = 6.5 nm) are allowed to freely move by integration with a canonical (NVT) ensemble

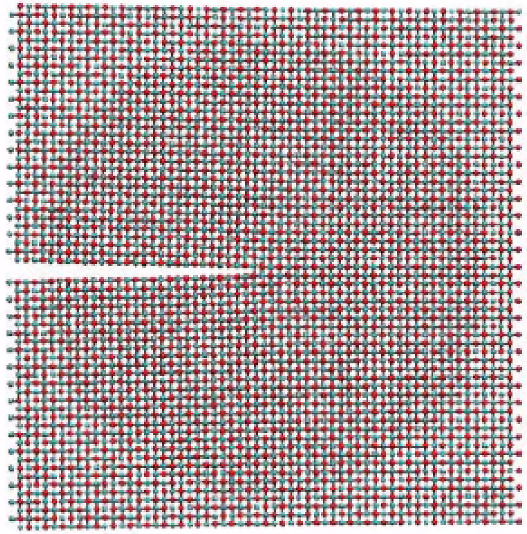


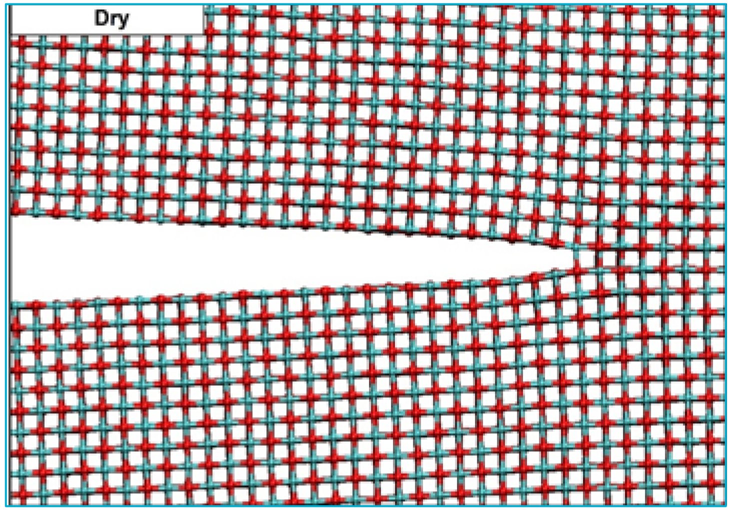
- Initial loading was varied between 0.065-0.188 MPa√m, with limited effect on the results
- Quasi-static loading occurs with loading increases of 0.01 MPa√m followed by 5ps of NVT up to a final loading of 1.2 MPa
- Similar methods have been used for fracture simulations of silica in vacuum, water, and aqueous electrolyte solutions

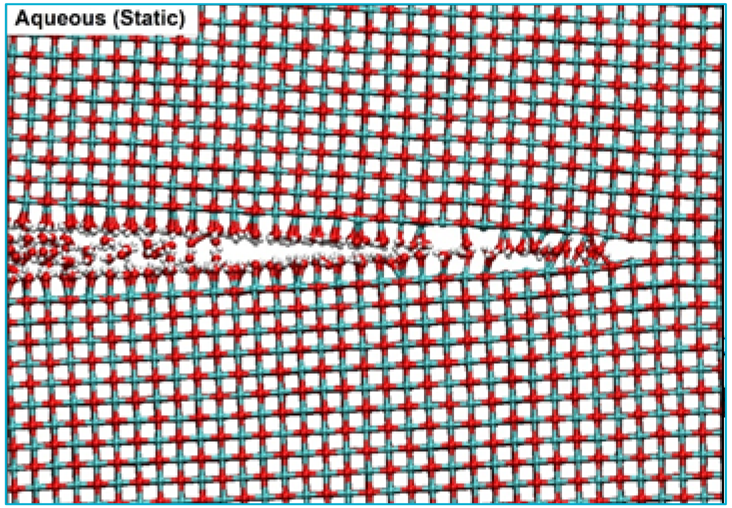
Rimsza et al. (2018). *J. Amer. Ceram. Soc. 101*(4), 1488-1499., Rimsza, J. M. et al. (2018). *J. Geophys. Res.: Solid Earth*, *123*(11), 9341-9354., Rimsza et al. (2019). *Front. Mater. 6*, 79

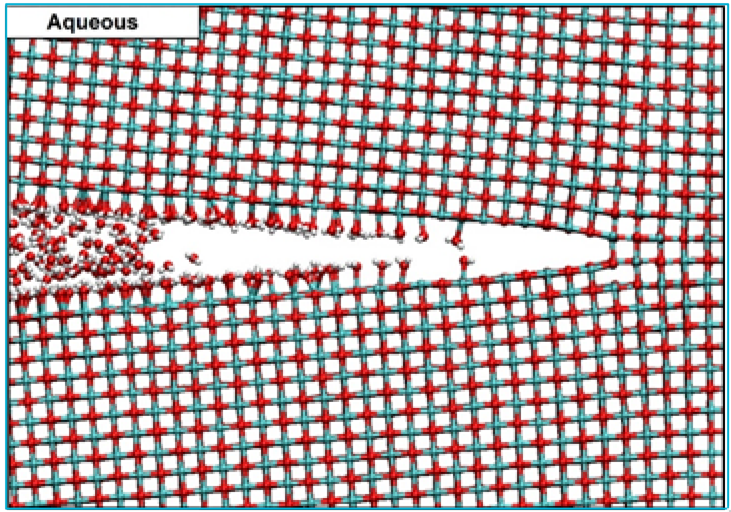
Water Introduction During Loading

- Three different environmental conditions are introduced:
  - Dry (vacuum) conditions = no water molecules
  - Aqueous (static) conditions = water is introduced at the beginning of the simulation and is added during the static loading (500 ps)
  - Aqueous (quasi-static) conditions = water is added to the crack volume and at the beginning of each loading step (μ = 250 kcal/mol)



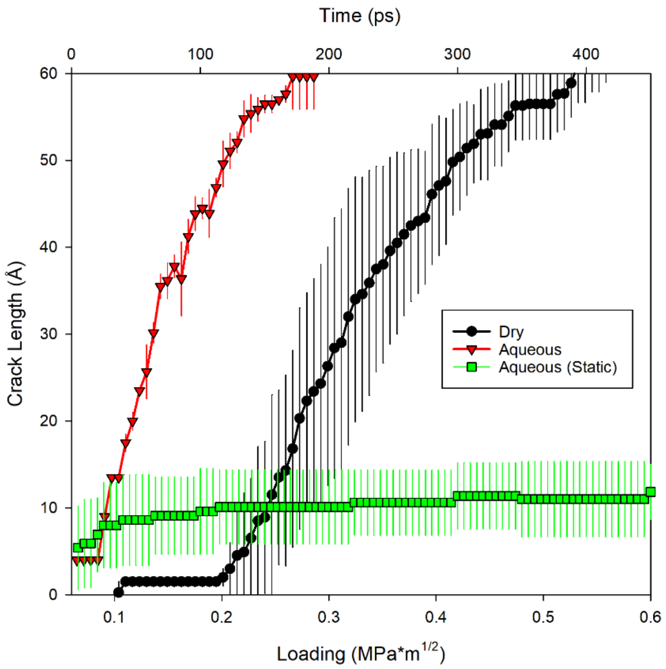






Water Significantly Weakens Fracture Properties in CaO

- During static loading with water, small amounts of fracture occur during the simulation (0.91 ± 0.57 nm)
- Under quasi-static loading in *vacuum* conditions, fracture is delayed to ~0.2 MPa√m
- Under quasi-static loading in *aqueous* conditions, fracture starts much earlier and more often
    - 3x the amount of fracture events
    - 20% longer average fracture length
    - 50% longer "longest" fracture



Comparison of fracture growth in dry or aqueous condition

	Final Fracture Length (nm)	Fracture Events (#)	Average Fracture Length (nm)	Longest Fracture (nm)	K_{IC} (MPa√m)
Dry	1.45±1.07	3.60±2.33	0.35±0.09	0.56±0.25	~0.2
Static Aqueous	0.91±0.57	1.80±0.98	0.41±0.27	0.59±0.43	-
Aqueous	3.51±1.18	9.00±4.20	0.41±0.05	0.85±0.22	~0.08

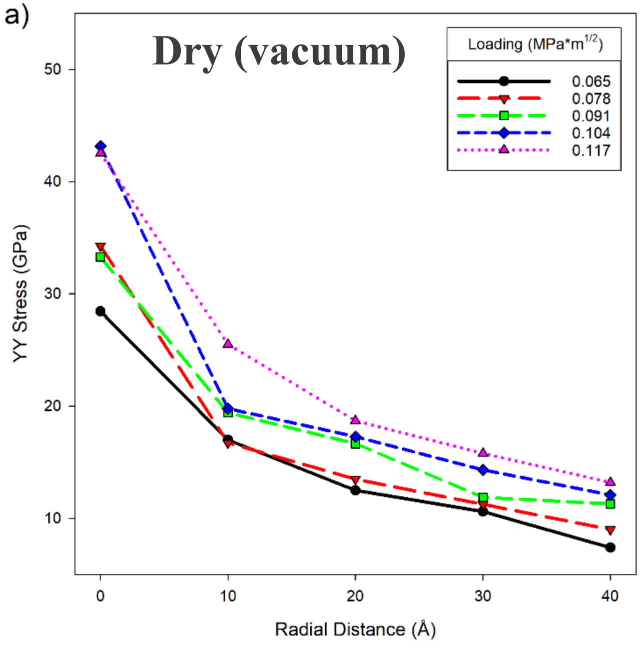
Final fracture length = total distance the fracture has propagated; average fracture length = average crack propagation during each fracture event

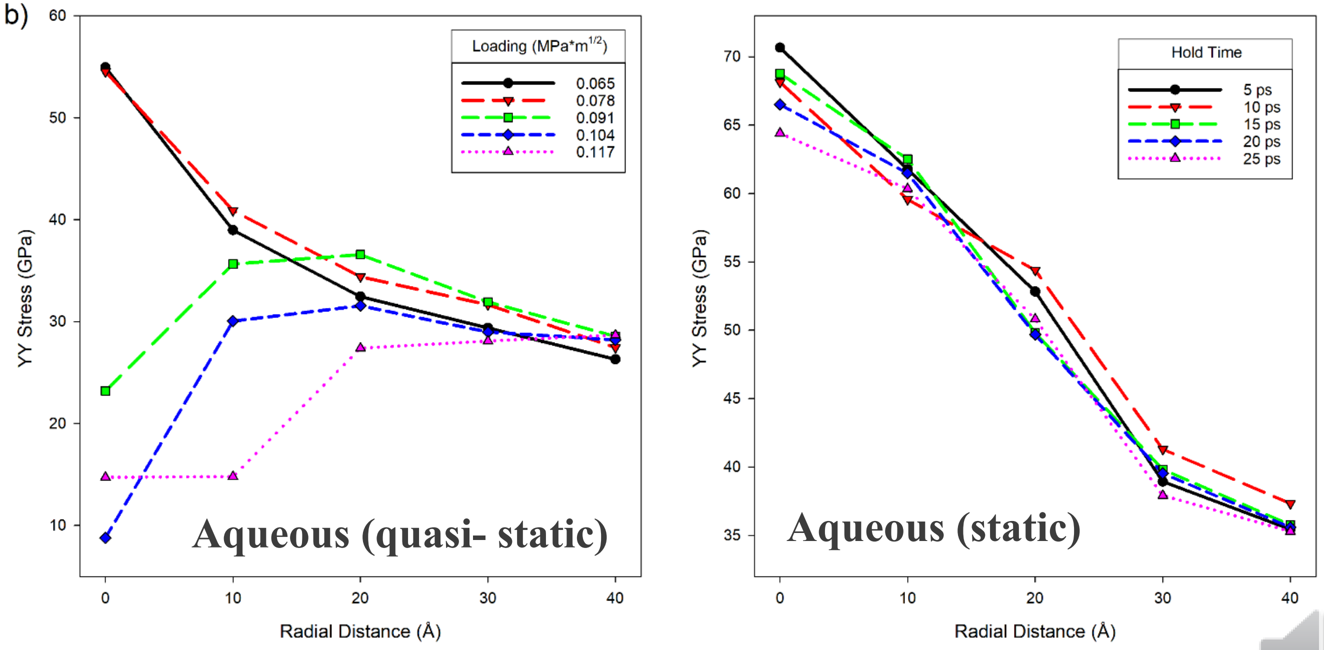
Stress dissipation is highest with quasi-static loading and water infiltration

- Systems initially develop a high stress condition at the crack tip, which decreases radially
- In dry conditions with quasi-static loading, increases in loading also increase the stress at the crack tip
- In aqueous conditions at static loading, more time decreases the stress at the crack tip

- In aqueous conditions with quasi-static loading, significant decreases in the stress occurs at the crack tip, including higher stress *ahead* of the crack tip location

The introduction of water is changing the stress surrounding the crack tip, and not just causing reactions on the surface or at the crack tip

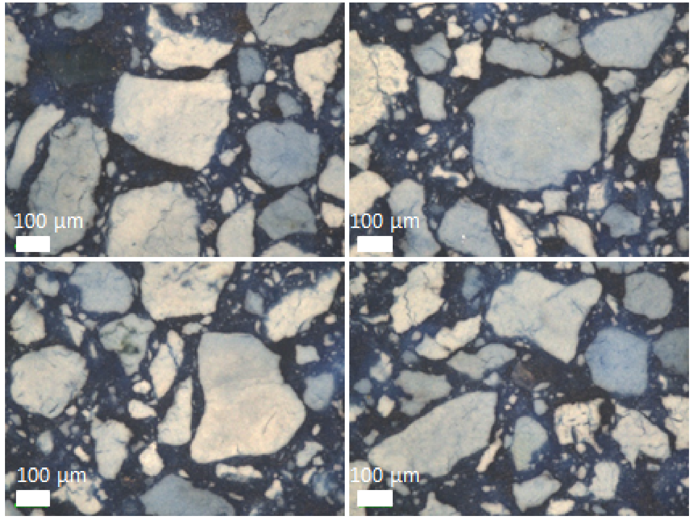




YY stress (GPa) as a function of radial distance from the crack tip with increasing loading from 0.065-0.117 MPa√m

Experimental In-Situ Liquid Nanoindentation

- In-situ liquid nanoindentation was used to asses chemical weakening of CaO grains
- CaO systems with 97.0%+ purity were used and 500 µm grains were separated by dry sieving were used for petrographic thin sections
- Large grains were selected from a polished thin section surface for nanoindentation



Optical images of representative CaO grains indented under dry and water-submerged conditions

- CaO surfaces were indented first under ambient conditions (22°C and ~33% RH) and then in de-ionized water (~ 3mm)
- 28 individual indents (2x3 and 3x3 grids) were performed and spaced 50 µm apart
- Reduced modulus (E_r) and contact hardness (H) were calculated with the following equations:

initial slope of the load-displacement trace

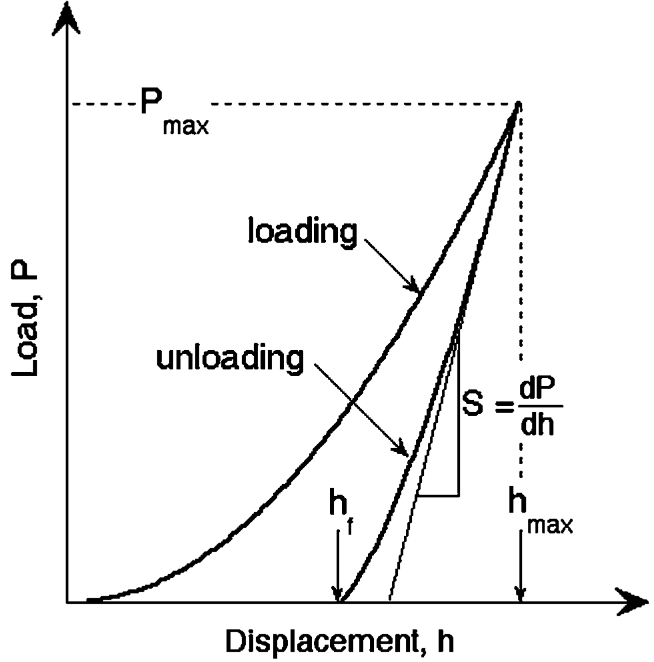
$$E_r = \frac{1}{2\alpha}\sqrt{\frac{\pi}{A_c}}\frac{dP}{dh}$$

geometric parameter of the indenter tip

peak load

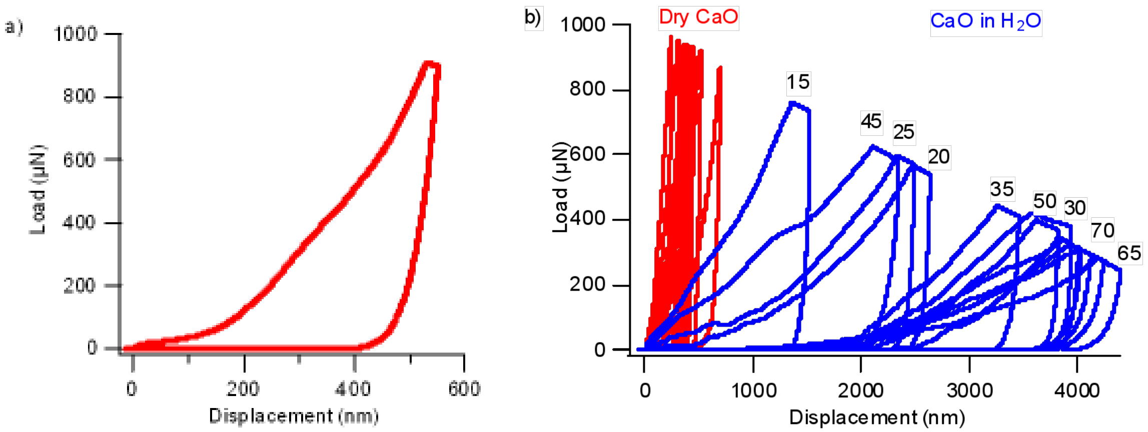
$$H = \frac{P_{max}}{A_c}$$

projected contact area

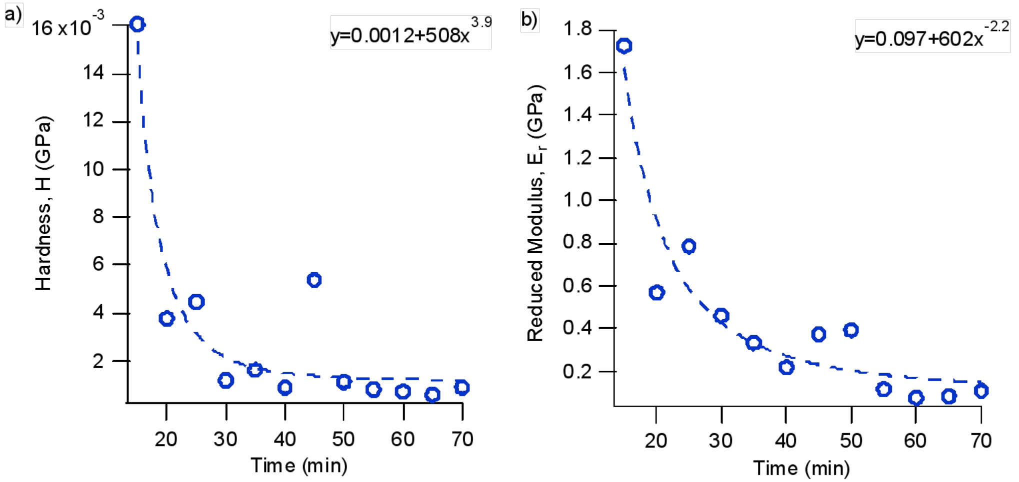


Time-Dependent Chemical Weakening Observed in CaO

- Evaluation of in-situ nanoindentation data can identify the *longer term* processes that impact chemical weakening
- Indentation depth increased 6x-7x in aqueous conditions for the same 1000 µN load (dry CaO = 190-690 nm, wet CaO = 1500-4350 nm)
- The contact hardness and reduced modulus decreased upon exposure to water, with time-dependent weakening
- Contact hardness decreased by more than two orders of magnitude during the 70 minute exposure
- Time dependent behavior can be attributed to water diffusion within the polycrystalline CaO grains



(left) Typical load displacement trace for dry CaO surface, (right) all load-displacement traces analyzed in this study



Time-dependent degradation of (left) contact hardness and (right) reduced modulus of CaO following exposure to water.

Reduction in properties is consistent with what occurs in molecular dynamics studies over longer time frames

Conclusions

- Water-weakening effects on the mechanical and fracture properties of CaO were evaluated via computational modeling and experimental characterization.
- Molecular dynamic (MD) simulations identified a decrease in K_{IC} by one order of magnitude in the presence of water and additional crack growth by more and longer fracture events.
- Incorporation of water into the crack volume resulted in nearly instantaneous physisorption of water molecules.
- Water adsorption altered the stress distribution, with increases in stress at the crack tip with increased loading in vacuum conditions, but decreases in stress when water is present.
- Changes in stress may create a driving force for crack growth ahead of the crack tip.
- Experimental results also identified that time-dependent water-weakening occurred.
- CaO contact hardness decreased by 1-2x orders of magnitude during exposure to aqueous conditions and the reduced modulus decreased by 2-3x orders of magnitude.
- Clear chemo-mechanical effects are identified in CaO, a common component of cements and natural geomaterials that can be evaluated mechanistically through the combination of molecule scale modeling and experimental characterization.

Acknowledgements

- Scott Grutzik, Charles Choens, and Michael Buche (SNL) for insightful discussions
- William Mook, Frank Del Rio, and Brad Boyce (SNL) for support with developing the liquid nanoindentation experimental procedures
- Funding: Sandia National Laboratories LDRD Program (Project #222398)

Questions?

Contact Information:
Simulations: Jessica Rimsza (jrimsza@sandia.gov)
Experiments: Anastasia Ilgen (agilgen@sandia.gov)