Louisiana State University

Sulfate Ion Transport in C-S-H Nanopores: Effects of Temperature and Ca/Si Ratio

Course: CHE7530

Sabit Timilsina, Graduate Student

Advisor: Dr. Yaxin An







Why Sulfate attack matters??

- Sulfate attack is a major durability issue in concrete- marine, underground, and industrial exposure conditions.
- SO_4^{2-} reacts with Calcium hydroxide and tricalcium aluminate (C3A) - causes gypsum formation, and ettringite expansion.
- Cause cracking, spalling, loss of stiffness, and shorter service life.



Fig 1: Degradation of concrete due to sulfate attack

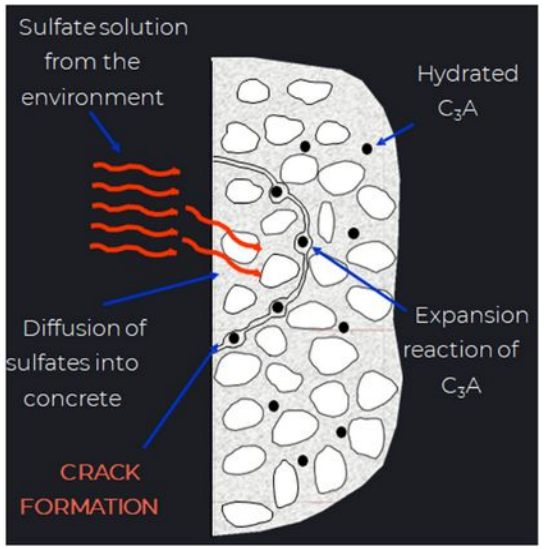


Fig 2: Mechanism of Sulphate attack

Source: [What is Sulfate Attack on Concrete? - Çimsa]

How calcium leaching can be precursor to Sulfate attack?

- Sulfate attack and calcium leaching are coupled processes — SO_4^{2-} ions infiltrate the pore network of cement-based materials and trigger calcium leaching and chemical degradation.
- When SO_4^{2-} penetrates C-S-H, it destabilizes Ca–O bonds in the interlayer, driving Ca^{2+} out of the structure, known as decalcification (Liu et al., 2022).
- Loss of Ca^{2+} lowers the local Ca/Si ratio, weakens the C-S-H framework, and opens up the nanopore network.



Fig 1: Calcium leaching in concrete (https://remedialengineers.com.au/blog/f/leeching-causes-effects-and-engineering-solutions)

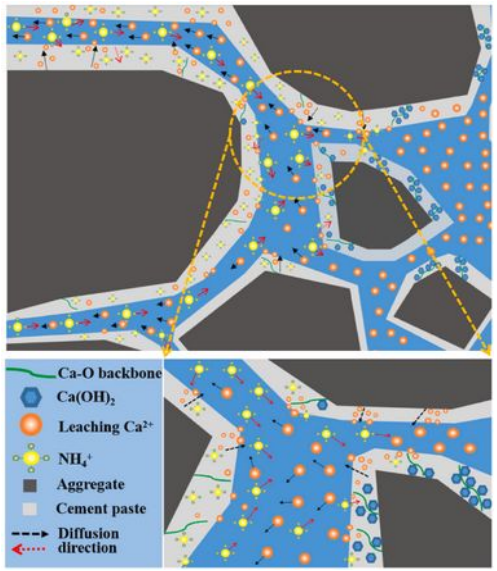
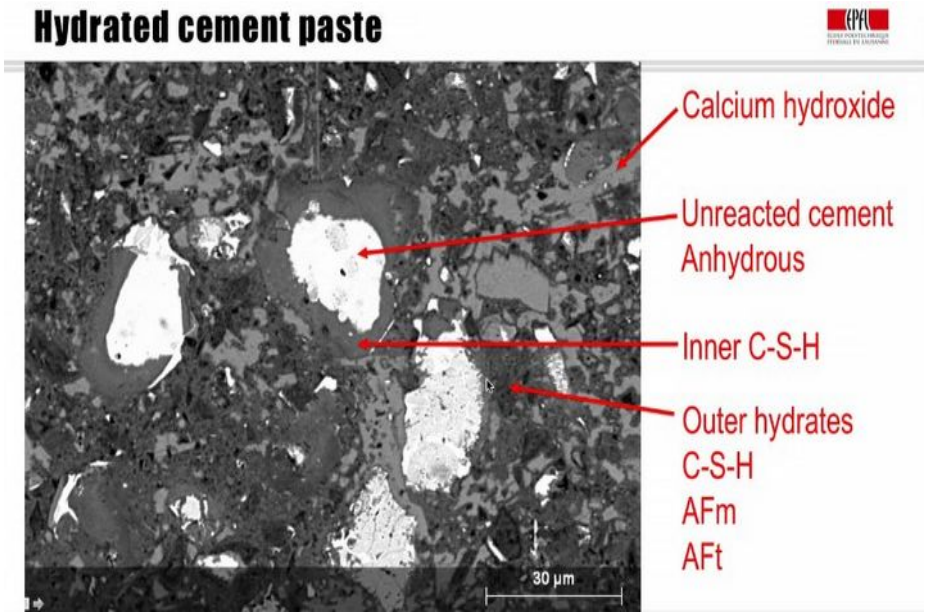


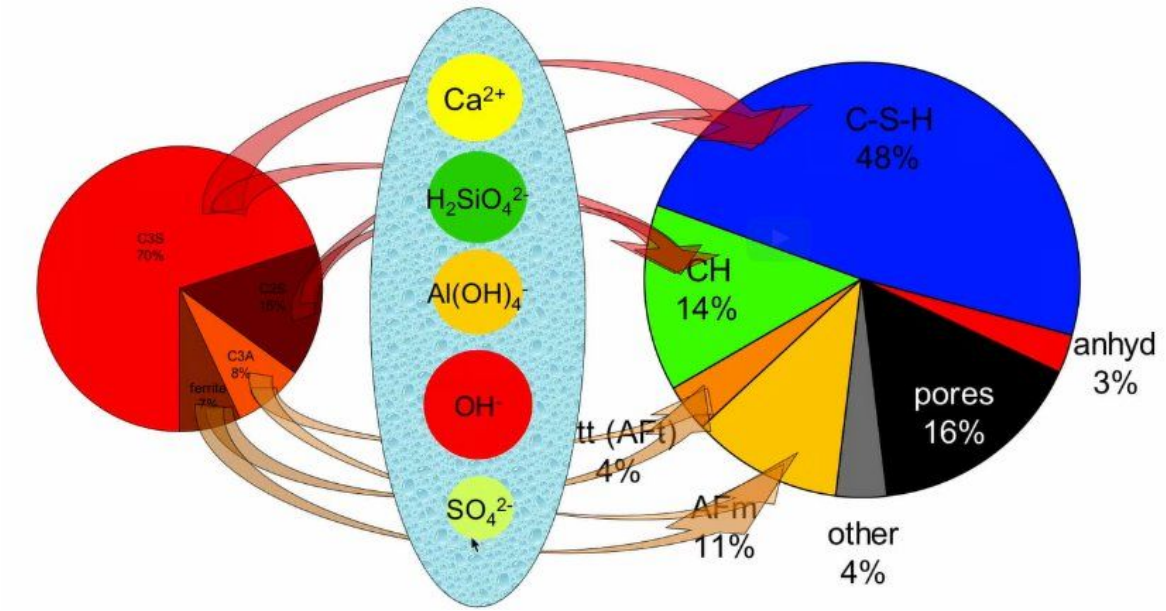
Fig 2: Calcium leaching phenomenon (https://www.sciencedirect.com/science/article/pii/S2214509525000142)

Why C-S-H can be used as main phase of cement?

- Hydrated cement paste contains C-S-H, CH, AFt, AFm, pores and anhydrous cement.
- C-S-H is the dominant hydrated product and the principal binding phase.
- The phase distribution shows C-S-H makes up about 48%.



Source: adapted from Karen Scrivener, LC3 hydration lecture slides.



Source: adapted from H. F. W. Taylor, Cement Chemistry.

Literature Review

- Wang et al. (2020) showed via MD that elevated temperature promotes water transport in C-S-H nanopores but reduces the transport rate of Na^+ and SO_4^{2-} ions, because the weakened hydration shell favors ion clustering and adsorption onto the channel surface.
- Zhang et al. (2024) used MD to show that the Ca/Si ratio governs Ca^{2+} stability in C-S-H under Na_2SO_4 attack, with SO_4^{2-} carrying interfacial Ca^{2+} into the pore solution via a diffusion–adsorption–desorption process.

Study Gap:

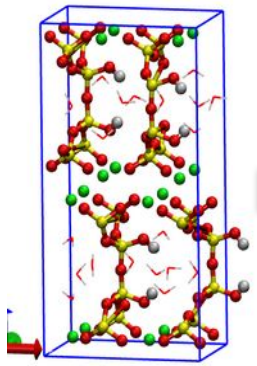
- Temperature and Ca/Si ratio have each been studied separately — their combined, coupled effect on Ca^{2+} leaching under Na_2SO_4 attack has not been systematically investigated.

Objective:

- Quantify how temperature (300, 330, 360 K) and Ca/Si ratio (1.0 and 1.3) *jointly* govern Ca^{2+} leaching from C-S-H nanopores exposed to Na_2SO_4 solution.

Methodology: C-S-H Model Construction

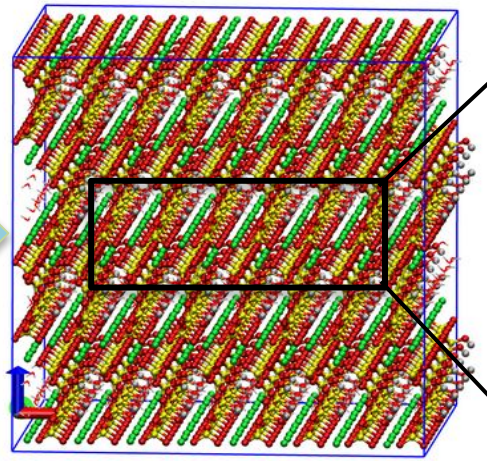
a)



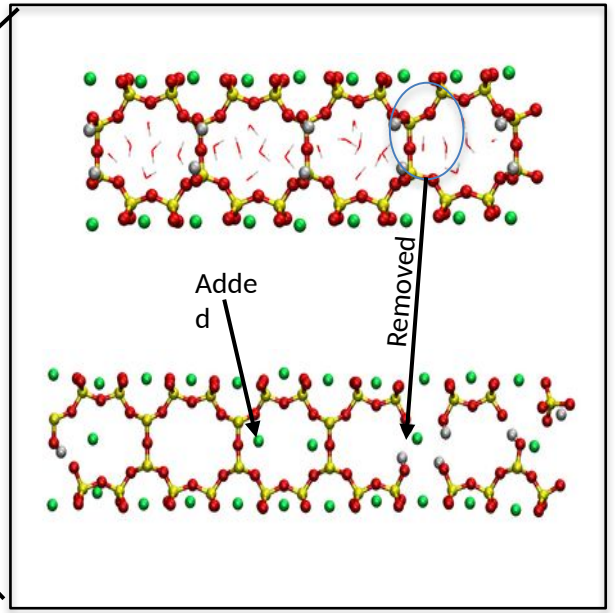
Tobermorite 11 Å
Ca/Si = 0.67

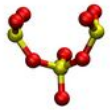
Enlarged

4*6*2 crystals



4*6*2 Tobermorite Crystal





Silicate Tetrahedra

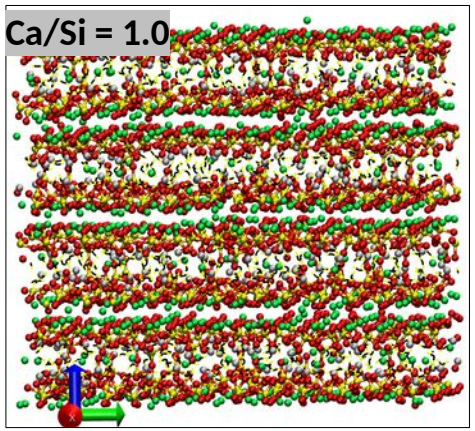


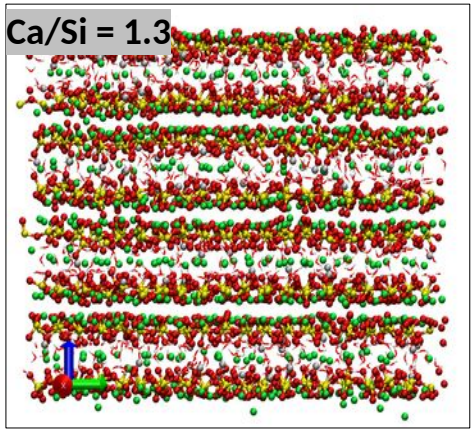
Water



Calcium Ion

b)





Methodology: Simulation Details

Solution Setup:

- 1 mol/L Na_2SO_4 placed above C-S-H slab.
- ~3 nm pore region with periodic boundary conditions.

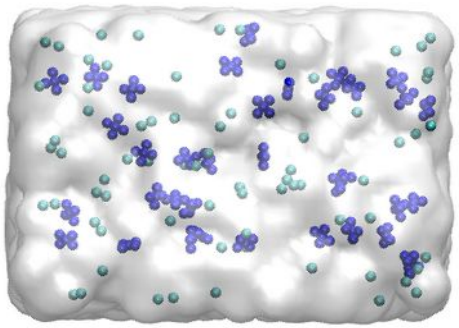
Force Field:

- INTERFACE force field for C-S-H.
- CHARMM parameters for Na^+ and SO_4^{2-}.
- TIP3P model for water

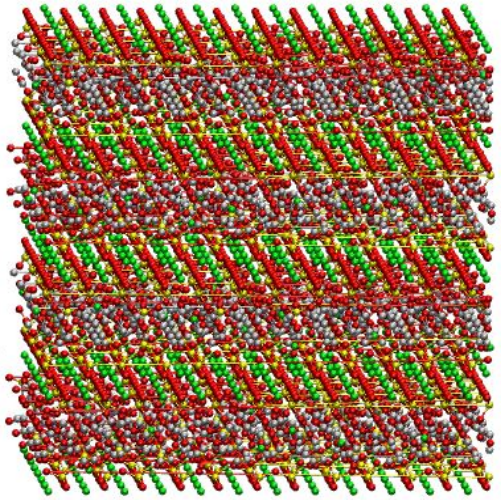
Simulation Protocol:

- Minimization: Conjugate gradient
- Equilibration: NPT ensemble (50 ps)
- Production: 15 ns NVT at each temperature

a) Water + Ions (Na2SO4)

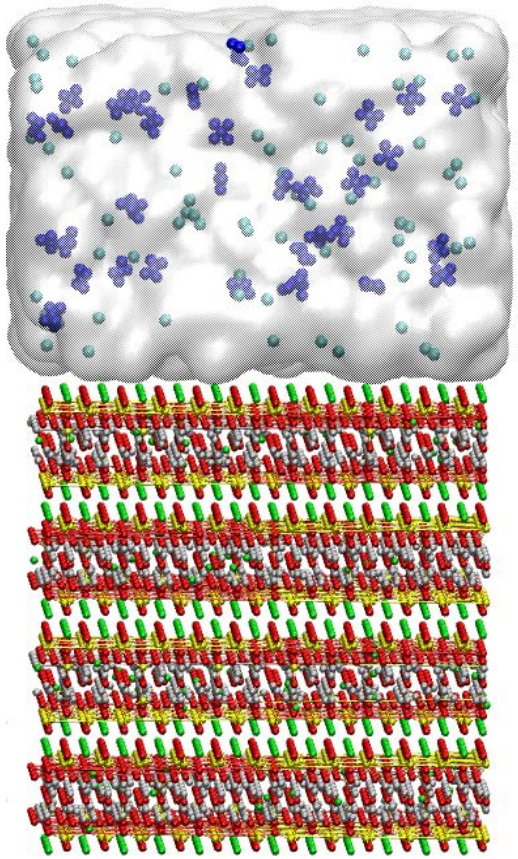


b) CSH (Ca/Si = 1.0)



Combined together

c) CSH + Water + Ions





Sulphate (SO4)

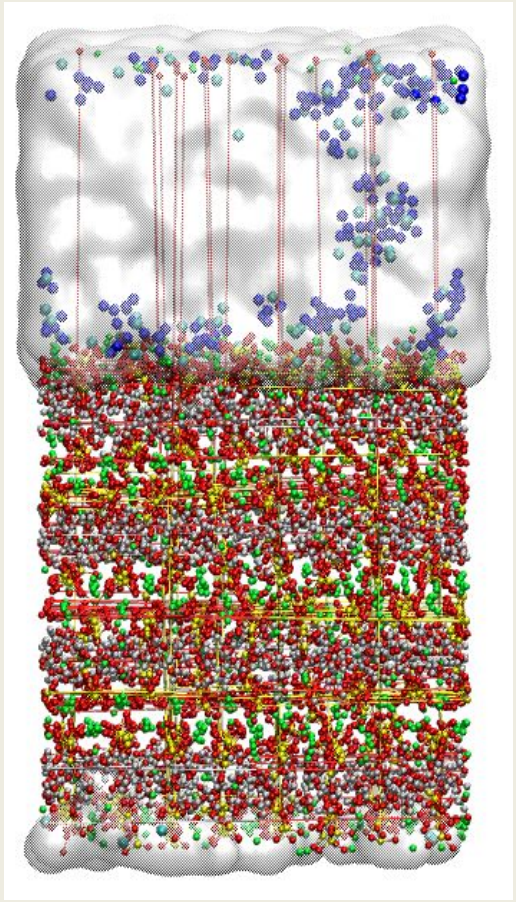


Sodium Ion

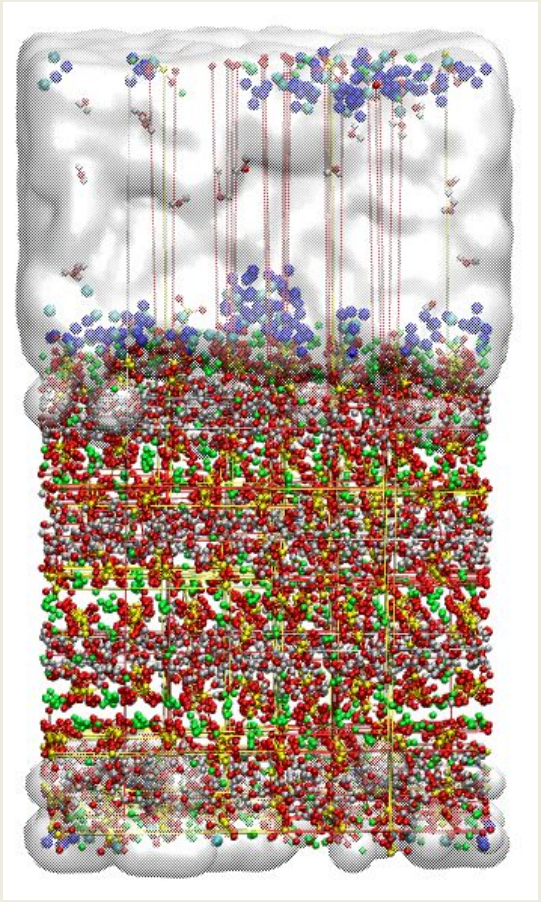
Results: Representative Simulation Snapshot

Ca/Si = 1.0, Temperature = 360K

a) 0.1 ns

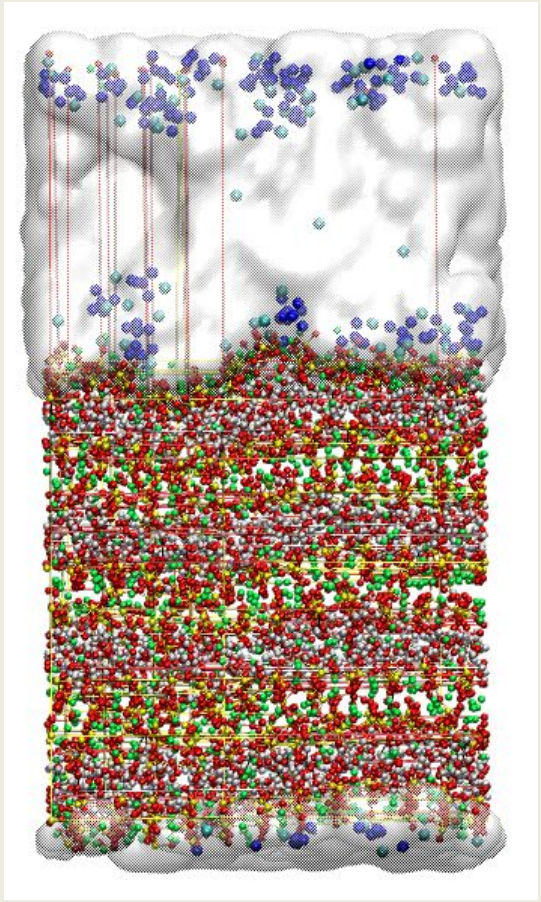


b) 15 ns

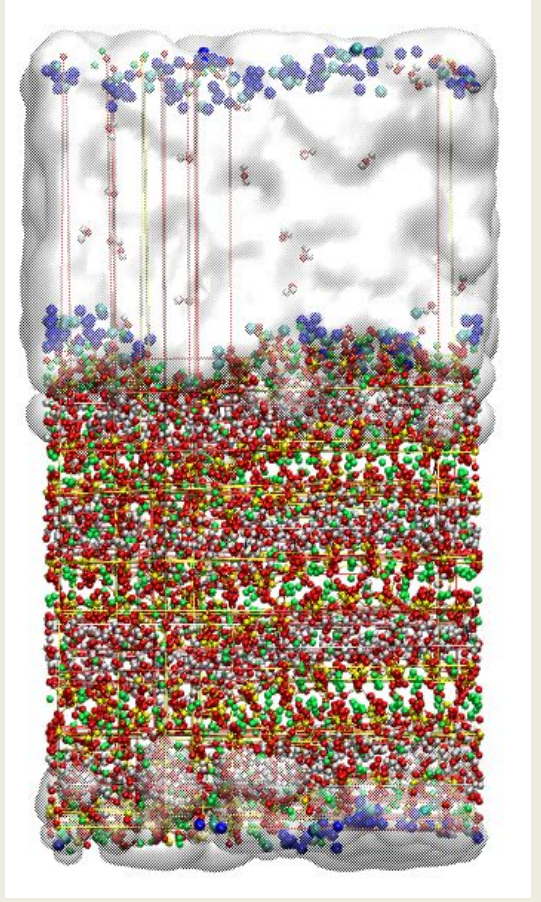


Ca/Si = 1.3, Temperature = 360K

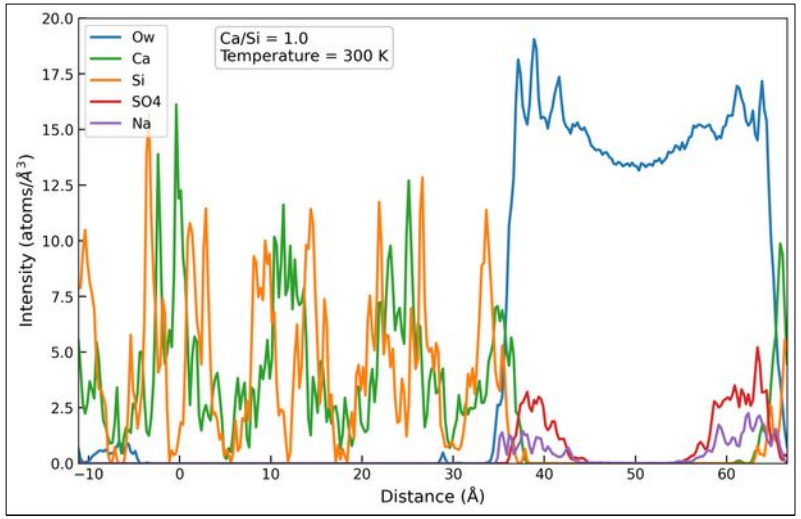
c) 0.1 ns

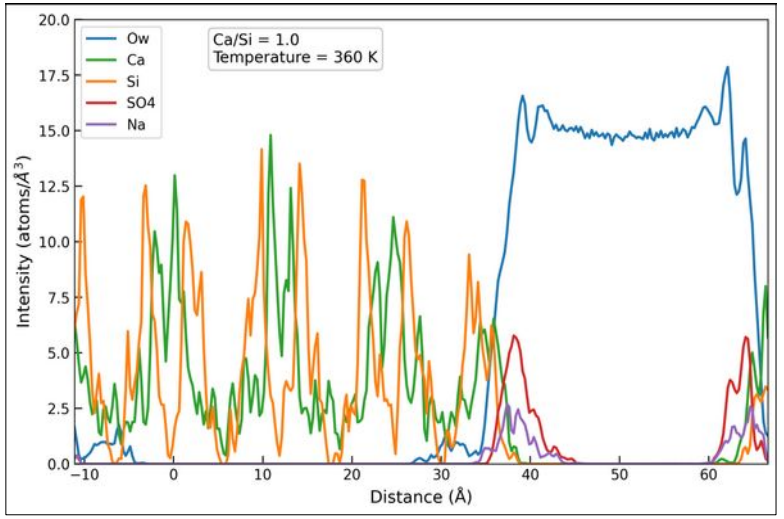


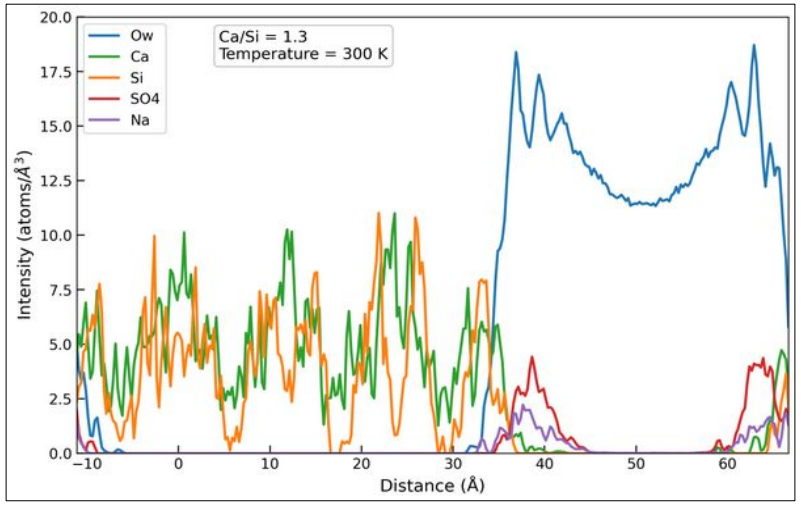
d) 15 ns

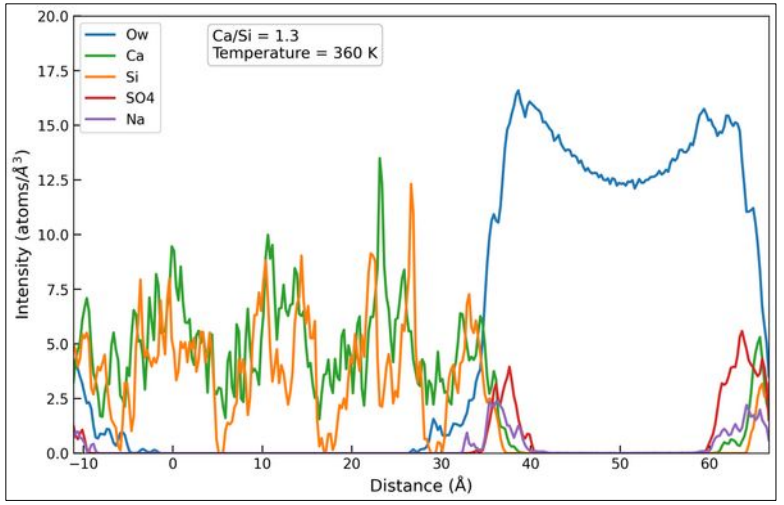


Results: Representative Z-density profile

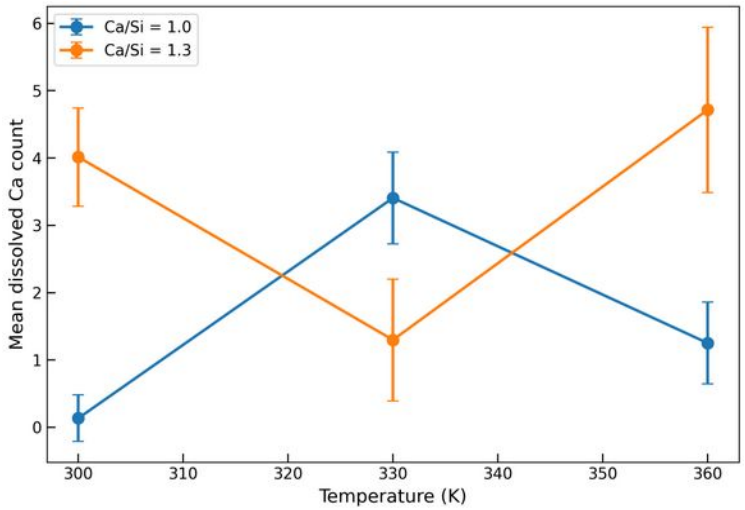


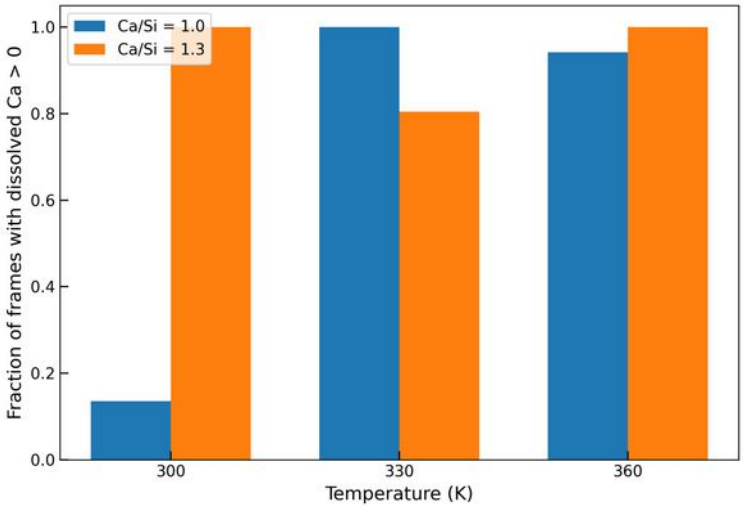


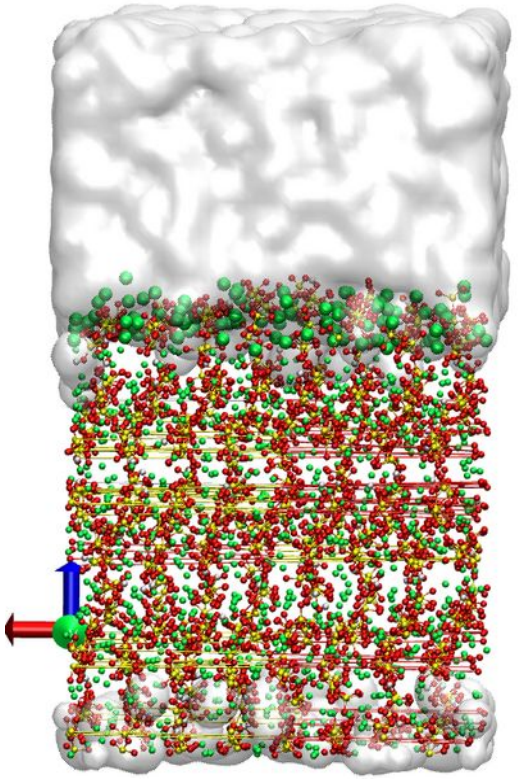




Results: Calcium leaching behavior







- No clear monotonic temperature dependence was observed, indicating dissolution did not systematically increase from 300 to 360 K.
- Ca/Si = 1.3 generally exhibited higher dissolved Ca counts than Ca/Si = 1.0 under comparable conditions.
- Dissolution remained intermittent and localized, suggesting transient Ca detachment rather than continuous large-scale leaching behavior.

RDF Analysis of Calcium Coordination Environment

Ca/Si	Temperature (K)	CN(Ca–O_{CSH})	CN(Ca–O_w)	CN(Ca–O_{SO_4})
1.0	300	5.958	0.525	0.092
1.0	330	6.454	0.472	0.132
1.0	360	7.049	0.474	0.137
1.3	300	5.787	0.463	0.099
1.3	330	6.227	0.487	0.100
1.3	360	5.784	0.451	0.147

Table 1: Co-ordination number of Ca with different atoms.

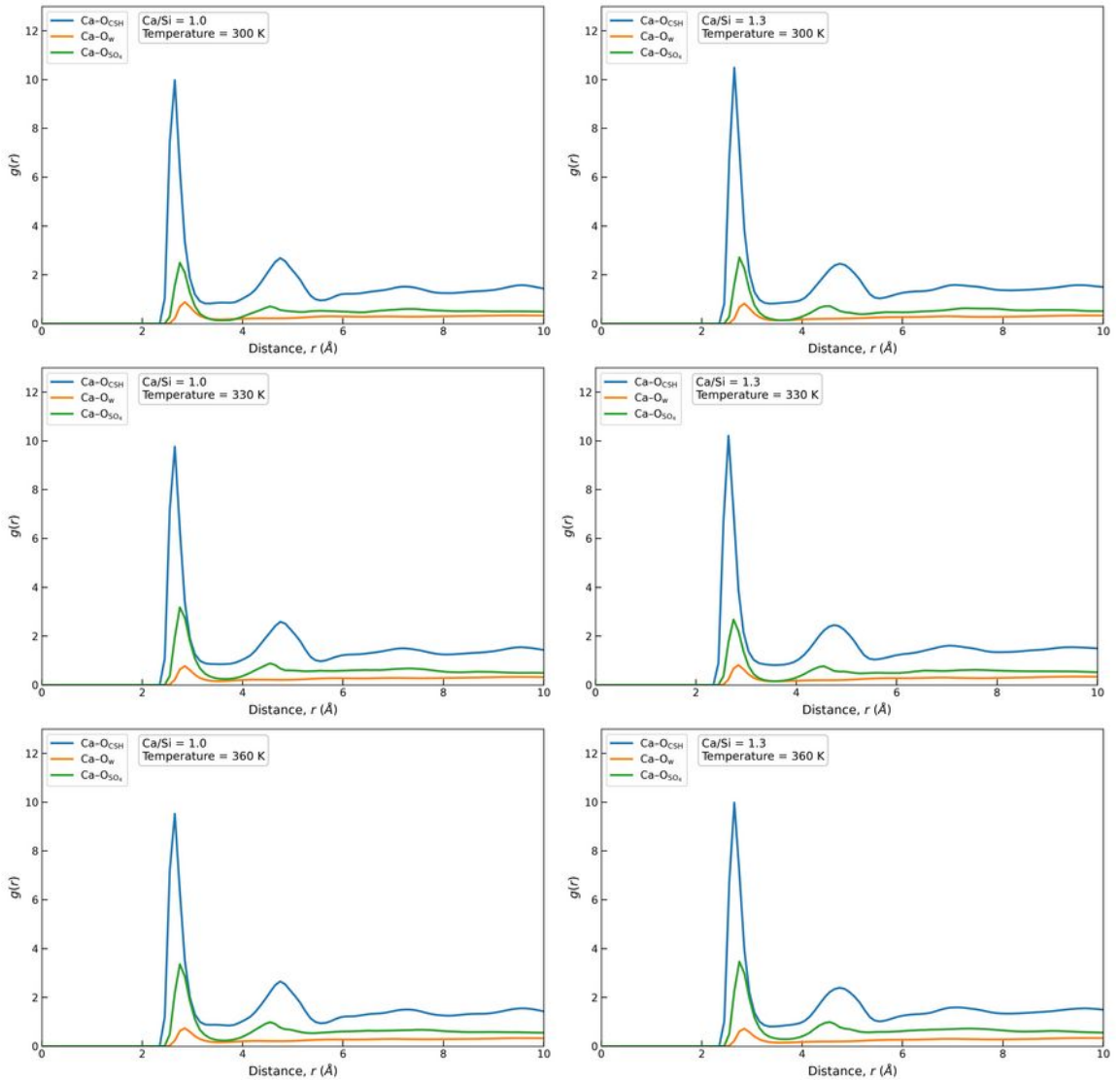


Figure 1: Radial distribution function (RDF) of Ca with different atoms.

Conclusion

- **A clear C-S-H/solution interface was observed** from the z-density profiles in all simulated systems.
- **Dissolved Ca remained low and intermittent**, with no clear monotonic temperature dependence from 300 to 360 K.
- **RDF results showed Ca–O_CSH as the dominant interaction**, indicating that most Ca remained framework-coordinated.
- **Ca–O_SO4 was consistently stronger than Ca–Ow**, suggesting sulfate associates more strongly with exposed Ca sites.

Limitation

- **The 15 ns simulation window is short**, so long-term calcium leaching behavior may not be fully captured.
- **Only selected Ca/Si ratios and temperatures were examined**, while the unstable Ca/Si = 1.7 case was not analyzed further.
- **Water penetration and sulfate participation were not yet quantified directly** and should be included in future analysis.

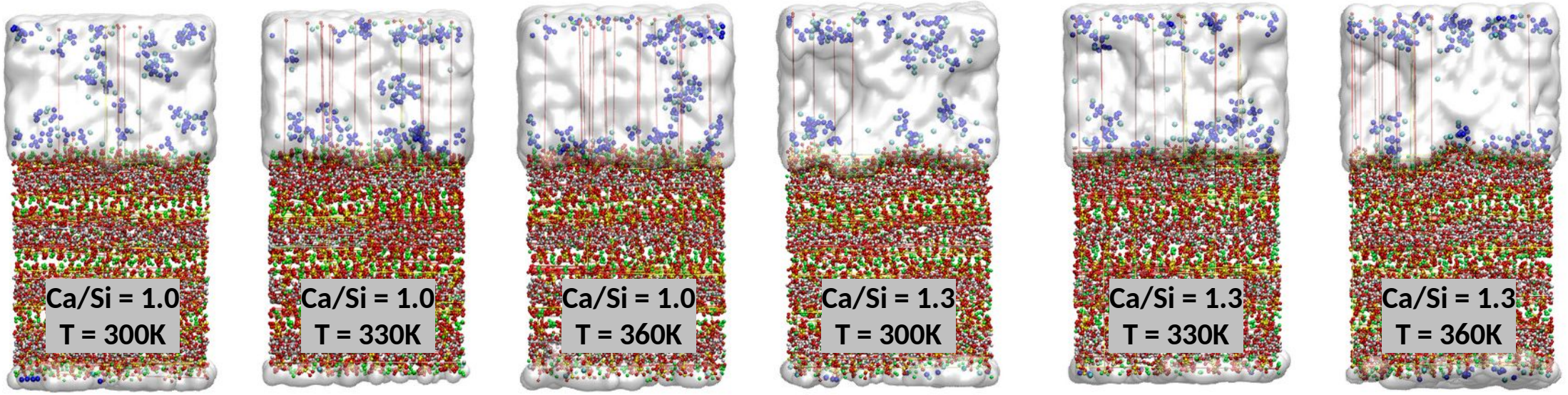
References:

1. Liu, X. et al. *Decalcification of calcium silicate hydrate (C-S-H) under aggressive solution attack*. Construction and Building Materials 342 (2022) 127988.
2. Wang, F., Zhang, Y., Jiang, J., Yin, B., Li, Z. (2020). *Effect of temperature on the capillary transport of sodium sulfate solution in calcium silicate hydrate nanopore: A molecular dynamics study*. Construction and Building Materials, 231, 117111.
3. Zhang, Y. et al. (2024). *Unveiling the dissolution mechanism of calcium ions from CSH substrates in Na_2SO_4 solution: Effects of Ca/Si ratio*. Applied Surface Science, 161585.

Appendix: Snapshot of all simulation in different frames

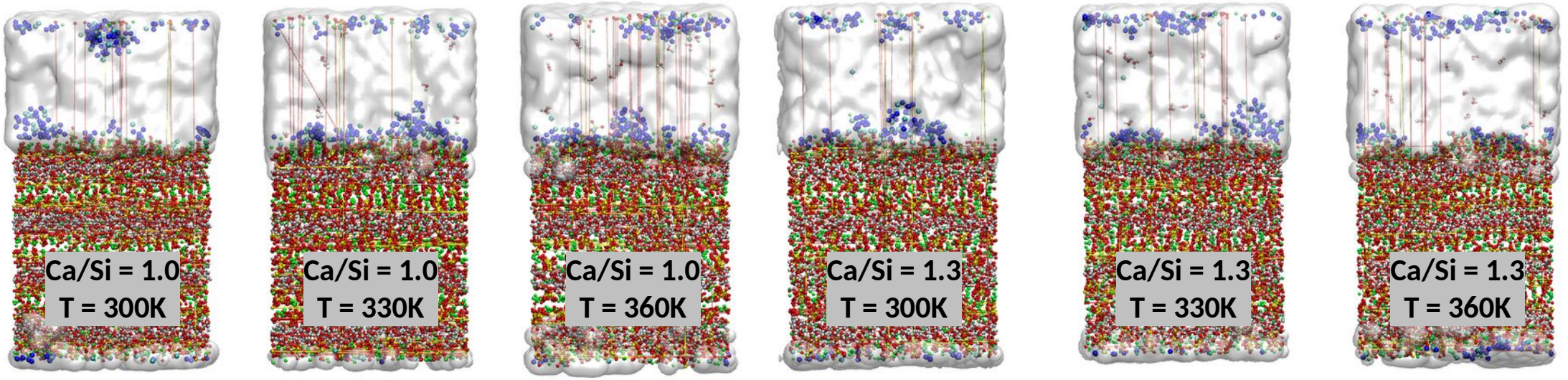
a)

0.1 ns



b)

15 ns



Appendix: Z-density profile

