

## Atomistic simulations of CO<sub>2</sub>—H<sub>2</sub>O fluid transport and reactivity within cement nanopores

SYLVIA M. MUTISYA\* AND ANDREY G. KALINICHEV

SUBATECH (IMT-Atlantique, Université de Nantes, CNRS-IN2P3) Nantes, France. (\*correspondence: mutisya@subatech.in2p3.fr, kalinich@subatech.in2p3.fr)

Geological carbon capture and sequestration (CCS) is a promising technology for curbing the global warming crisis by reduction of the overall carbon footprint of human activity. One of the conventional problems in sequestration operations is the degradation of cement wellbore casings due to its exposure to supercritical CO<sub>2</sub>. This can pose several environmental risks, and lead to the failure of the CCS operation. To minimize these risks and to optimize stable and reliable CCS operations, a detailed molecular level understanding of the interactions between cement and CO<sub>2</sub> rich fluids is necessary, as well as clear understanding of the fluid transport pathways in wellbore cement materials.

We employ atomistic computer simulation techniques to study, at the fundamental molecular scale, CO<sub>2</sub>/H<sub>2</sub>O fluid interactions with cement's main hydration phase: calcium silicate hydrate (C-S-H). The molecular level investigations contribute to an improved understanding and quantification of fluid—cement interactions and migration through wellbore leakage pathways. Tobermorite is taken as a basic mineral structure to develop atomistic models of C-S-H phase with varying C/S ratio from 0.83 to 1.75 and pore sizes from 1 to 5 nm. Firstly, the intercalation potential of CO<sub>2</sub>/H<sub>2</sub>O fluid mixtures is investigated using grand canonical Monte Carlo (GCMC) simulations for the C-S-H porous systems in equilibrium with binary CO<sub>2</sub>/H<sub>2</sub>O bulk mixtures at 323 K / 90 bar and 348 K / 130 bar, mimicking typical *T/P* conditions of geological CO<sub>2</sub> sequestration. Increasing the C/S ratio of the confining cement pores decreases the CO<sub>2</sub> adsorption as water competitively adsorbs on the calcium cations, blocking access of CO<sub>2</sub>. The equilibrium fluid compositions and structures obtained from the GCMC simulations are then used as an input for molecular dynamics simulations with both classical ClayFF [1] and reactive ReaxFF [2] interatomic potentials. The structure, transport and reactivity of the nano-confined CO<sub>2</sub>/H<sub>2</sub>O fluids are then quantitatively evaluated and compared for the two approaches.

[1] Cygan R.T.; Liang J.-J.; Kalinichev A.G. (2004) *J. Phys. Chem. B*, **108**, 1255-1266. [2] Senftle, T. P.; Hong, S.; Islam, M. M. et al. (2016) *Npj Computational Materials*, **2**, 15011.