

Atomistic computer simulations of the cement degradation mechanisms in the context of geological carbon sequestration

SYLVIA M. MUTISYA¹ AND ANDREY G. KALINICHEV²

¹Institute Mines-Telecom Atlantique

²IMT Atlantique

Presenting Author: mutisya@subatech.in2p3.fr

One of the major concerns of many subsurface operations, such as geological CO₂ sequestration, is the degradation of wellbore cement and the potential fluid migration to the surface through leakage pathways. While leakage can occur in wells due to faulty construction and other mechanical defects, geochemical reactions induced by the injected fluids could also cause cement degradation, damaging the wells and leading to the leaks. Cement is highly alkaline (pH > 12.5), and acidic CO₂-rich fluids (pH < 6) are thermodynamically incompatible with it. Thus, exposure of cement to CO₂-saturated fluids lowers the pH of the cement pore fluid, which may lead to failure of operations due to concrete degradation. To better understand these processes, we focus here on identifying and quantitatively characterizing on the fundamental molecular scale possible cement degradation mechanisms and reaction pathways, fluid transport rate and the geochemical variables that affect fluid-cement interactions.

We use biased ab-initio molecular dynamics (AIMD) simulations to explore the reactivity of CO₂ with the basal and edge surfaces of the portlandite cement phase in scCO₂ and water-rich conditions. The metadynamics approach is applied to accelerate the dynamics of the rare reaction events and to investigate their mechanisms. Our simulations show that supercritical CO₂ undergoes a rapid barrierless carbonation reaction with the edge surfaces of portlandite crystals. However, the carbonation reaction soon ceases due to the deposition of (bi)carbonate surface complexes which form a carbonate layer. On the other hand, the presence of water alters the interaction of CO₂ with the portlandite surfaces, as H₂O molecules form well-structured aqueous surface layers. Thus, the water content within the portlandite pores is the rate limiting step in the carbonation reaction of portlandite with H₂O/CO₂ fluid. As such, CO₂ reactivity for pores with highly structured water surface layers (with no bulk-like water) is expected to be limited due to the attenuated inward diffusion of the CO₂ molecules. Dissolution of calcium atoms can be expected to enhance the carbonation reaction by interacting with the dissolved (bi)carbonate/carbonic acid to form calcite in the presence of water. However, no such dissolution events were observed in our simulations.