

Ab initio molecular dynamics study of Ca²⁺ in water: Speciation as a function of P,T, and pH

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Ab initio molecular dynamics (AIMD) simulations of Ca²⁺ in water have been performed at {T=300 K, P=0.3 GPa}, {T=500 K, P=0.5 GPa}, and {T=900 K, P=0.9 GPa}. The water coordination of the Ca²⁺ ion is found to increase from 6 at {T=300 K, P=0.3 GPa} to an average of 7 at {T=900 K, P=0.9 GPa}. On the time scale of 20 ps no chemical changes such as the formation of Ca(OH)⁺ or Ca(OH)₂ were observed for the periodic Ca²⁺ + 63 H₂O system. Coordination constrained AIMD simulations [1-3] have been carried out to determine the free energy barrier for dissociation of a H₂O molecule in the first solvation shell.

When CaO is introduced into a unit cell containing 62 H₂O molecules, Ca²⁺ and 2 OH⁻ are formed within femtoseconds. Subsequently, the two species are found to form transient Ca(OH)⁺ and Ca(OH)₂ complexes. At {T=500 K, P=0.5 GPa} we predict the relative average concentrations 3%, 26%, and 71% for the species Ca²⁺, Ca(OH)⁺, and Ca(OH)₂, respectively, while at {T=900 K, P=0.9 GPa} we obtain 4%, 35%, and 62%.

References

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Combining CSIA with ground water dating: A first step toward the determination of *in-situ* PCE degradation rates

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Method and field site description

In order to predict the fate of organic pollutants in groundwater systems it is essential to know degradation rates. The combination of compound-specific stable isotope analysis (CSIA) with transient groundwater tracer techniques allows determining degradation rates *in situ*.

To demonstrate the feasibility of this concept, a former industrial site was investigated. Due to leakage of perchloroethene (PCE) solvent tanks, PCE as well as its transformation products trichloroethene, *cis*-dichloroethene and vinyl chloride were detected in ground water in concentrations up to 50 mg/L. We measured carbon stable isotopic signatures of these compounds and performed tracer-based ground water dating to determine the efficiency and typical biodegradation rates of these pollutants under natural conditions.

Principle findings and discussion

Along selected flow pathways, the isotopic signature $\delta^{13}\text{C}$ of PCE changed from -24 ‰ up to -1 ‰ (vs. VPDB), which was a clear evidence for on-going degradation. Using a simple Rayleigh evaluation scheme and a set of isotopic enrichment factors deriving from literature, a range of degree PCE-biodegradation was calculated. However, since the published enrichment factors differ for more than an order of magnitude, the degree to which amount PCE was degraded could not reliably be determined. If the relevant enrichment factor of the site would be known, the biodegradation could be exactly quantified from isotopic data. Together with the determined local ³H-³He ground water age differences of more than 20 years, PCE degradation rates can be obtained.

As ¹³C enrichment along with increasing water residence time was also observed in all the transformation products, the total dechlorination of PCE to non-toxic products was evident. However it remains open whether the degradation of the intermediates is complete.

Conclusions and outlook

In order to track and to quantify the degradation of chlorinated ethenes, the site-specific enrichment factor has to be determined. Such work is in progress and will allow us to obtain the effective degradation rates under the natural conditions being characteristic for our contaminated field site.