Comparison of TiO_2 and SnO_2 (100) and (110) hydrated surfaces via molecular modeling

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Periodic density functional theory (DFT) calculations using the programs CASTEP and VASP were carried out to model the H_2O-TiO_2 and the H_2O-SnO_2 (100) and (110) interfaces. These two minerals have the same crystal structures but different unit cell dimensions and dielectric constants. Comparisons of the behavior of H_2O at each surface can be used to test the effects of these two parameters on H_2O dissociation and interfacial structure. Energy minimization and molecular dynamics (MD) simulations were conducted with periodic DFT methods to examine the relative energetic stability of a variety of configurations. In order to more completely sample configuration space, interatomic force fields were developed for the H_2O-TiO_2 and H_2O-SnO_2 interfaces using the program GULP. Thus, classical MD simulations could be carried out over longer time periods than practical with the DFT method. The force field reproduces structures calculated with DFT reasonably well and the relative energies of configurations are similar between the two methods. In addition, the effects of deprotonating the surfaces to mimic the negative surface charge on real surfaces are examined. Differences in H_2O adsorption mechanisms are attributable to unit cell parameters and basicities of surface oxygen atoms. Starting with the associated H_2O molecules we have obtained the mixed associative-dissociated structure in the case of SnO_2. The most interesting observation is that dissociation of H_2O occurred indirectly. In the first stage, the H^+ bonds to a bridging oxygen from one of nearest H_2O, forming the intermediate OH^- state. In the second stage, the terminal H_2O H^+ transfers to the OH^- ion forming the new H_2O molecule and terminal OH^-. No such process was observed for TiO_2 surface. A stable mixed adsorption structure was obtained by optimization after manual H^+ transfer on the same path as was spontaneously passed in the case of SnO_2. Analogously, starting with the broken H_2O molecules in the first layer, we have obtained the stable dissociated structures both for TiO_2 and SnO_2 where hydroxyls were attached to 5-fold Me and H^+ were bonded to the bridging oxygens.

References

Molecular Simulations User's Guide (1999) CASTEP – Cambridge Serial Total Energy Package Version 4.2, San Diego, CA

Kresse, G.; Furthmüller (1996), *J. Phys. Rev. B* **54**, 11169-86.

Gale, J. D. (1997), *J. Chem. Soc. Faraday Trans* **93** 629–37.

Reactive transport simulation of mineral trapping of CO_2 in operated geothermal aquifers

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Innovative technology

Costs for carbon dioxide (CO_2) sequestration into deep saline aquifers can be transformed into a benefit in combination with ecologically desirable geothermal heat or power production. The current "CO_2Trap" project aims to develop a scientifically and technically feasible new technology to achieve a safe and economically attractive long-term storage of CO_2 trapped in minerals. Numerical models are applied to study injection of aqueous CO_2 into the subsurface and to quantify subsequent precipitation of calcite ($CaCO_3$) in potential geothermal reservoirs.

Geothermics and CO_2 storage

Exploitation of geothermal energy in Germany is mainly provided from deep sandstone aquifers. The common arrangement of boreholes is the well doublet, consisting of one well for hot water production and one well for cooled water re-injection. The cooled water is loaded with dissolved CO_2 generating carbonic acid. After re-injection into the reservoir this cold water becomes enriched in calcium e.g. due to dissolution of anhydrite ($CaSO_4$). Because the solubility of anhydrite increases with decreasing temperature, injecting cold water dissolves anhydrite in a growing region around the well. The favored reaction path, the transfer of anhydrite into calcite, leads to a surplus of acid. Alkalinity to buffer the reaction can be provided from rock forming minerals (e.g. oligoclase). Subsequently CO_2 will react with the calcium ions to form and precipitate calcium carbonate.

Conclusion

We demonstrate the feasibility of transforming anhydrite into calcite by reactive transport modeling. Buffering capacity (alkalinity) from the reservoir rock is necessary for the transformation of anhydrite into calcite. Although it turns out that anhydrite is not the major player from the chemical point of view, its dissolution with concurrent pore space increase is important to balance the pore space reduction by precipitation of calcite and secondary silicates in the geothermal reservoir.