

## Molecular dynamics simulations of CO<sub>2</sub>-brine interfacial tension and mutual solubility

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Predicting and controlling the behavior of supercritical CO<sub>2</sub> in geologic repositories hinge on understanding the interactions between CO<sub>2</sub>, aqueous brines, and host rock phases. Long-term stability depends strongly on the interfacial tension (IFT) between CO<sub>2</sub> and brine [1], because IFT controls wetting of and reaction with host rocks and determines capillary breakthrough overpressure, the pressure above which CO<sub>2</sub> may escape through caprock fissures [2, 3]. Overall, the timescales of CO<sub>2</sub> capillary trapping depend on the relationship between CO<sub>2</sub>-brine interfacial characteristics and the state variables, pressure (P), temperature (T), and composition (X).

Experimental and simulation studies of the supercritical CO<sub>2</sub>-water interface at P, T relevant to geologic storage (~5-45 MPa, 300-383 K) show that IFT decreases with increasing P until around 15 MPa<sup>2,4</sup>. Experimental studies have also shown that increasing brine salinity causes an increase in IFT at a given T, P, but experimental data are limited.

Using well known water and CO<sub>2</sub> interatomic potential models, we applied molecular dynamics methods to simulate the supercritical CO<sub>2</sub>-brine interface over a range of brine X to assess the relationship between IFT and brine salinity. We determined the IFT between CO<sub>2</sub> and brine at 373 K and 15 MPa between 0.086 and 2.45 M NaCl salinity. Our results to date agree with experimental data<sup>2</sup>. Significant CO<sub>2</sub> dissolution into the brine phase occurred over nanosecond timescales. We shall present a series of simulations encompassing a broad range of P-T-X which will provide not only IFT predictions, but also improved understanding of the relationship among interfacial structure, CO<sub>2</sub> solubility kinetics, and state variables.

[1] Kuznetsova & Kvamme (2002) *Phys. Chem. Chem. Phys.* **4**, 937–941. [2] Chiquet, Daridon, Broseta & Thibeau (2007) *Energy Conversion & Management* **48**, 736–744. [3] Chalbaud, Robin, Lombard, Martin, Egermann & Bertin (2009) *Advances in Water Resources* **32**, 98–109. [4] Kvamme, Kuznetsova, Hebach, Oberhof & Lunde (2007) *Computational Materials Science* **38**, 506–513.

## Are hydrothermal vents natural microbial fuel cells?

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Microbial fuel cell (MFC) research has exploded over the past decade since the discovery that microbes can reduce solid-phase oxidants via extracellular electron transfer (EET). Most MFC investigations focus on the application of MFCs as alternative power sources or on the biological mechanism of EET. Comparatively little attention is devoted to MFCs as basic research tools. We report on the use of MFC technology to investigate rates of EET in hydrothermal systems. We hypothesize that hydrothermal vents are natural MFCs because they have spatially separated redox zones connected by conductive minerals (e.g. pyrite). To test this hypothesis, we designed a MFC that mimics a hydrothermal vent with respect to chemistry and has a pyrite electrode. The open circuit voltage of the MFC was about 0.4 V. We inoculated the MFC with a sulfide sample collected from a vent at Axial Volcano. The circuit generated an average of approximately 100 nA for 21 days. Assuming current was driven by sulfide oxidation to elemental sulfur, the oxidation rate was 48 nmol d<sup>-1</sup> (consistent with low biomass in the reactor). Using scanning electron microscopy, we observed ubiquitous but patchy coverage of the pyrite by microbes. The phylogeny of the anode-attached community will be investigated via whole genome amplification and 454 pyrosequencing to elucidate the community responsible for EET in this system. These experiments demonstrate that 1) there are microbes in hydrothermal samples capable of EET and 2) pyrite can serve as an electron acceptor if it is in electrical continuity with a terminal electron acceptor (e.g. oxygen).