Reactive transport modeling of carbon sequestration in volcanogenic sandstone formations

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Geological storage of carbon dioxide in deep saline formations can decrease the accumulation of CO_2 in the atmosphere, and thus slow down global warming. Most injected CO_2 remains for a long time as either a separate supercritical phase or in solution in brine; both forms constitute increased risk of leakage back to the surface or other environmental impacts. Mineralogical trapping of injected CO_2 is more secure but usually very slow. For standard sandstones (quartzite and arkose) investigated so far, it takes up to 10000 years to achieve 5 percent CO_2 mineralization [1]. Volcanogenic sandstones have relatively high reaction rates and larger amounts of reactive minerals, which means that if they were used for storage, there could be a larger fraction of CO_2 mineralized in a shorter time. However, porosity and permeability tend to decrease with increase of volcanic rock fragments (VRF) in sandstones, which limits the rate of CO_2 injection. We have attempted to quantitatively evaluate these tradeoffs to assess the feasibility of using volcanogenic sandstone to achieve highly secure CO_2 storage. We determined relationships between VRF percent, porosity, permeability and CO_2 injection rate from available geological data, and used TOUGHREACT to evaluate the trade-off between higher reactivity and lower porosity and permeability. Preliminary results show that roughly 5% VRF is optimal, and can result in almost complete CO_2 mineralization, but this depends on the magnitude of reactive surface area (RSA) specified. Varying RSA between 2 cm^2/g and 50 cm^2/g changes the fraction mineralized from 13% to almost 100% at 1000 years. Baseline simulations were done with a 1-D model. A corresponding 2-D radial model shows a slight increase of mineralized CO_2 due to a larger interface between the CO_2 plume and saline water.

[1] Audigane, P., *et al.* (2007) *American Journal of Science* **307**(7): p. 974-1008.

Biomethylation potential of mercury depends on the kinetics of HgS precipitation

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Monomethylmercury (MeHg) is an extreme neurotoxin that accumulates in food webs and poses a significant risk to human health. In natural aquatic systems, the predominant mechanism of MeHg production is microbial methylation of inorganic mercury (Hg) by sulfate-reducing bacteria (SRB). MeHg production rates are largely controlled by the availability of Hg species for uptake into SRB and the productivity of those microbes. In sediments, sulfide controls Hg speciation due to its high abundance and strong affinity to bind Hg^{2+}. Previous studies have demonstrated that natural organic matter (NOM) interferes with the precipitation of $HgS_{(s)}$ by preventing aggregation of HgS nanoparticles that are formed during the initial stages of precipitation. We hypothesize that bioavailable Hg concentration is related to the kinetics of HgS precipitation, and not necessarily to equilibrium speciation of Hg in sulfidic porewater.

We conducted methylation bioassays using pure cultures of two methylating SRB, *Desulfobulbus propionicus* (1pr3) and *Desulfovibrio desulfuricans* (ND132). The bacterial cultures were exposed to three different forms of Hg-sulfides, including dissolved $Hg(NO_3)_2$ and Na_2S, humic-coated HgS nanoparticles (<30 nm), and metacinnabar particles (>1000 nm), which were formulated to represent three different 'aging' states of mercury in sulfidic sediments. Our results showed that methylation rates were greatest with the dissolved Hg-sulfide treatment. In the treatments with HgS nanoparticles, MeHg production was observed at a rate that was significantly faster than the metacinnabar treatment. These results may be due to: 1) the relatively poor crystallnity of HgS nanoparticles compared to bulk minerals that are inherently less soluble; 2) the larger extent of nanoparticle-bacteria surface contact that allows nanoparticulate Hg to be spatially more accessible for the methylating bacteria than micro-scale metacinnabar. Moreover, methylation potential appeared to decrease as HgS nanoparticles 'aged' (16 hrs~1 week), which may be attributed to the enhanced crystallinity of nanoparticles during aging. Overall, our study points to a new paradigm for modeling aqueous mercury speciation in anaerobic environments and the bioavailability of inorganic mercury to methylating bacteria.