Molecular Dynamics Calculation of the Calcite Zeta Potential in Brine

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Introduction

The surface charge on minerals in an aqueous enironment can affect rock strength, oil-particle adhesion, and other properties. The surface charge originates from defects in the minerals, but the charge that often counts is the electrostatic potential (zeta potential) at the distance from the mineral surface at the which the aqueous fluid becomes mobile. Here we use molecular dynamic (MD) methods to calculate the zeta potental adjacent to a calcite surface emersed in water of diffirent salinities.

Our forcefield for calcite is from a 2010 publication where MD methods successfully simulated the growth of calcium carbonate [1]. The brine solution is placed between a pair of planar numerical (1 0 4) calcite surfaces. We set the surface charge by removing Ca^{2+} or CO_3^{2-} ions from the top layer of the calcite crystal, and then calculate the electrostatic potential from the outer edge (symmetry boundary) of the calcite. The slipping plane is determined by inducing fluid flow with a gravity force and noting where the fluid movement starts. The electrostatic potential is shown as a function of distance from the calcite surface in Figure 1.

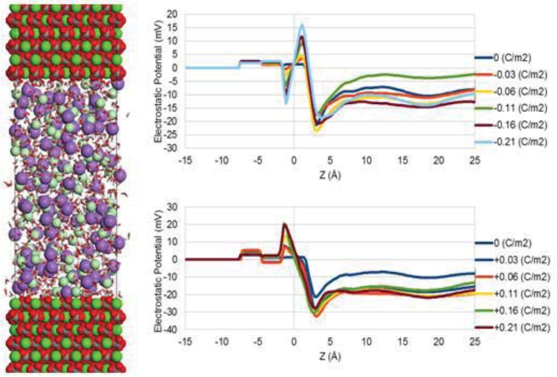

Figure 1: (a) The molecular calcite-brine sandwich (Ca: green, O: red, C: gray, Na: violet, Cl: aqua, and H_2O: red sticks). (b) The electrostatic potential of negatively charged surfaces and (c) postively charged surfaces. Z=0 marks the average VDW surface of the lower calcite layer.

Results and Conclusion

The vacancies where Ca^{2+} ions were removed are mostly ocuppied by sodium ions, while those where carbonate CO_3^{2-} ions were removed are occupied by Cl^- and Na^+ ions. The slipping plane lies about 5Å from the calcite surface (z=0 on plot). The plot shows that the sign of the zeta potential is negative whether the surface charge is positive or negative and ranges from -10 to -25 mV. If this holds true for other minerals it could help explain why the zeta potential of minerals tends to be negative.

[1] Raiteri, *et al.* (2010) *J.A.C.S* **132**, 17623-17634.

Characterization of various biochars used for mercury treatment and assessment of their potential to release soluble components

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21b. Soil and sediment remediation

Biochars (BCs), waste organic matter pyrolyzed under low temperature and oxygen conditions, have attracted great interest in environmental remediation processes [1]. However, few studies have focused on the characterization of BC prepared from a range of sources and their potential to release soluble components. In this study, eight groups of BCs produced from different materials at 300 °C and 600 °C, one group of charcoals (CL), and one group of activated carbon (AC) as a control were characterized for physical and chemical properties. Batch tests were conducted by adding BCs at a 1:75 mass ratio to river water (10 μg L^{-1} Hg). The experiments were sampled after two days to evaluate both the reduction of Hg and increase of soluble constituents in the river water. In the batch systems containing AC, CL and BCs pyrolyzed at 600 °C, concentrations of Hg were observed to decrease by >90%. In the systems containing the other BCs, concentrations of Hg decreased by 40-90%. The BCs with the highest Hg removals had relatively high specific surface areas, C and S contents, which likely contributed to Hg removal. Results obtained from FT-IR showed all BCs had hydroxyl, carboxylic and quinone functional groups, which also likely contributed to the Hg removal; the spectra of BCs prepared at 600 °C had fewer peaks compared to BCs pyrolyzed at 300 °C. Batch test results indicated that river water equilibrated with BCs prepared at 600 °C had higher pH and alkalinity and released more PO_4-P and NH_4-P than those prepared at 300 °C; however, BCs prepared at 300 °C released higher concentrations of dissolved organic carbon (DOC), short chain organic acids, NO_3^-, NO_2^-, and SO_4^{2-}, which were consistent with the FT-IR results. Biochars are promising reactive media to treat Hg contaminated waters and sediments; however, some BCs released DOC, sulfate, and organic acids, which could be utilized by methylating microbes to stimulate Hg methylation. Therefore further research needs to be performed to evaluate long term effect of the leached constituents from BCs amendments.

Results and Conclusion

Mercury concentration decreased by 40-99% in river water after two days of biochar amendment. Biochars pyrolyzed at different temperatures showed different chemical and physical properties.

Biochars are promising reactive media to treat Hg contaminated waters and sediments; however, further research still needs to be performed to evaluate long term effect of the leached constituents from BCs amendments.

[1] Lehmann (2009). *Biochar for Environmental Management: Science and Technology*. Earthscan, London & Sterling, VA.