

Spectroscopic and Quantum Chemical Investigation of Selective Incorporation of Arsenate and Selenite into Calcite

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Calcite (CaCO_3) is known as a mineral which can play a role as an effective scavenger of toxic elements in the surface environment. This study focused on the interactions of arsenic (As) and selenium (Se) oxyanions with calcite. The contamination of natural water with them is occurring in various areas in the world. Especially, migration of ^{79}Se from nuclear wastes to biosphere will pose a serious problem for the safe geological disposal of nuclear wastes.

Our coprecipitation experiments and XANES measurements revealed that calcite selectively incorporated arsenate rather than arsenite [1], and selenite was selectively incorporated rather than selenate. Although molecular geometries of dissolved selenite and selenate are similar to those of arsenite and arsenate, respectively, there is no relationship between their molecular geometries and incorporation behavior into calcite. EXAFS analyses using FEFF shows that these oxyanions are incorporated into calcite through substitution with carbonate ion, which indicated that these impurities are combined with Ca^{2+} ion when they deposit on the calcite surface. In order to determine the factor controlling the preferences of arsenate and selenite for the incorporation of As and Se, respectively, into calcite, their affinities to Ca^{2+} ion, which reflect their reactivities with calcite at the calcite-water interface, were evaluated based on the quantum chemical calculation (QCC).

Estimation of intermolecular binding energies between each oxyanion and Ca^{2+} ion by QCC shows that the affinity orders for Ca^{2+} ion are arsenite > arsenate and selenite > selenate. The preference of selenite for incorporation into calcite is related to its higher affinity to Ca^{2+} ion than selenate. On the other hand, though QCC shows that arsenite has higher affinity for Ca^{2+} ion than arsenate, arsenite is hardly incorporated into calcite as shown experimentally [1]. This preference can be attributed to the difficulty of arsenite deprotonation as shown in its large dissociation constant ($\text{p}K_a = 9.3$). Other oxyanions (arsenate, selenite, and selenate) dissociate into their anionic forms and can interact with Ca^{2+} ion under pH conditions where calcite can precipitate, whereas neutrally charged arsenite cannot display its high affinity for Ca^{2+} ion except for under high alkaline condition. Hence, the factors controlling their preferences for the incorporation into calcite are different between As and Se; for As, the charge of the aqueous species is important, whereas affinity to Ca^{2+} ion is important for Se. Additional QCC of the interactions between the oxyanions and calcite surface with the cluster models mimicking calcite-water mineral interface is expected to contribute to further investigation at the molecular-scale. The present findings should provide some insights into natural behavior of As and Se, because their oxidation states are variable in subsurface environment.

[1] Yokoyama *et al.* (2009) *Chem. Lett.* **38**, 910-911.

Pore-scale evaluation of calcium carbonate precipitation and dissolution kinetics in a microfluidic pore network

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Introduction and background

Dissolved CO_2 during geological CO_2 storage may react with minerals in fractured rocks or confined aquifers resulting in mineral precipitation and dissolution. The overall rate of reaction can be affected by coupled processes among hydrodynamics, transport, and reactions at the (sub) pore-scale. Pore-scale models of coupled fluid flow, reactive transport, and heterogeneous reaction at mineral surfaces developed in our previous work [1] are applied to account for transient experimental results of calcium carbonate precipitation and dissolution in a microfluidic pore network [2]. In the micromodel, precipitation is induced by transverse mixing along the centerline in pore bodies. Pore-scale modeling is used as a basis for understanding the significance of pore-scale processes that may account for large-scale phenomena involving geochemical reactions.

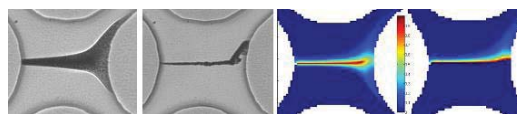


Figure 1: Experimental images (left) and simulated results (right) of CaCO_3 precipitates at 13 min and 118 min in the micromodel

The model is used to test the influence of different reaction rate laws on spatial and temporal reaction patterns. These include elementary reaction-based, affinity-based, and nano-scale in-situ measurement-based rate laws in the literature. The sensitivity of diffusion coefficient, reactive surface area, and rate constant on precipitate morphology, reaction rate, and amount of precipitates are evaluated in order to evaluate the governing physics of sub-micron scale reactions. Implications for evaluating mineral precipitation patterns observed in natural analogues for CO_2 storage and leakage are discussed to link pore-scale models to domains of relevance for geological CO_2 storage.

Hongkyu Yoon and Thomas Dewers were supported as part of the Center for Frontiers of Subsurface Energy Security, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001114. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

[1] Yoon *et al.* (2012) *Water Resour. Res.* (In press). [2] Zhang *et al.* (2010) *ES&T* **44**(20), 7833–7838.