

## Mineral Precipitation Between Solutions Flowing in Parallel

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Engineering mineral precipitation in the subsurface requires generating supersaturated conditions in order for desired minerals to nucleate or grow. For multi-component precipitation reactions, reactants must become mixed at the molecular scale. Different strategies can be used to mix reactants, either prior to introduction into the subsurface or *in situ*. Due to the strong coupling between reactant transport, mixing, and nucleation/growth processes, different mixing strategies will produce different spatial and temporal distributions of precipitates in the subsurface, with distinctly different outcomes with respect to the location of precipitates, changes in media properties and volume averaged rates of reactions. We have been studying the formation of precipitation reaction fronts that are generated by transverse mixing across the interface between solutions flowing in parallel.

Using a flow cell with a homogeneous sand packing, separate solutions containing calcium and carbonate were injected upward in a parallel flow configuration (Figure 1). The solutions, if mixed directly, would create strongly supersaturated conditions for calcite.

The objectives were to quantify: 1) the dimensions of the precipitation zone, 2) changes in transverse permeability with distance along the zone, and 3) transient changes in the chemical properties (e.g., pH) on either side of the zone. In addition, we investigated the influence of differences in density of the two solutions on the position of the precipitation zone. The precipitation zone was found

to be on the order of 1-2mm across. (This is in contrast to related experiments that involved mixing by double diffusion without advection, where the width of the precipitation zone was >1cm.) A low pH wedge formed on the side containing unbuffered calcium. Formation of asymmetric chemical conditions was consistent with expectations based on the  $\text{CaCO}_3$  precipitation reaction stoichiometry and the properties of the solutions; however an anticipated disappearance of the pH wedge due to reduced permeability in the precipitation zone was not observed. A two-dimensional numerical model has been developed to simulate the nonlinearly coupled processes of flow, transport, and reaction in the system. Different scenarios with varying flow rate and solution concentrations (engineering controls) have been tested.

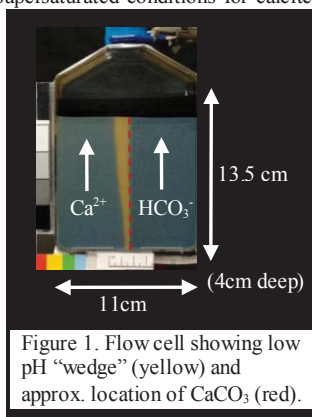


Figure 1. Flow cell showing low pH "wedge" (yellow) and approx. location of  $\text{CaCO}_3$  (red).

## Bioaccessibility of arsenic in soil: method evaluation, comparison to *in vivo* primate data, and influence of soil chemistry

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Several studies have shown relatively limited human and animal absorption of arsenic from contaminated soils. Extensive efforts are presently underway to develop less expensive laboratory (*in vitro*) tests that simulate *in vivo* results, and validate them against live animal data. In this study, *in vitro* tests using three common methods were performed on soils for which *in vivo* primate data were available. *In vitro* and *in vivo* test results were then compared. The same soils were treated with iron amendments, to determine if iron treatment reduced arsenic bioaccessibility. Prior to testing, soils were extensively characterized to enable better interpretation of the results of the *in vitro* tests. *In vitro* data by all three methods correlates poorly with primate data. Specifically, with the exception of one iron-rich soil, *in vitro* tests over-estimate bioavailability by factors ranging from 1.3 to 16.7. The presence of calcium carbonate or iron in soil affects the results of the *in vitro* tests. The largest *in vitro* over-estimate occurred for calcium carbonate soils, and iron binds arsenic such that it is less extractable in the *in vitro* tests. As expected, iron treatment significantly reduced arsenic bioaccessibility in the soils studied. A large data base of physical and chemical information was generated for these soils, and with more detailed analysis, could be used to help determine other geochemical influences on arsenic bioavailability and bioaccessibility.