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Supplement of

Feedback mechanisms between precipitation and dissolution reactions across randomly heterogeneous conductivity fields

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1. The chemical system

In our simulated system, as described by equation (2) of the manuscript, the pH in the resident fluid is assumed to equal to 8. We simulate a laboratory scale scenario where a 60×24 cm^2 two-dimensional flow cell is filled with a porous system formed by a $CaCO_{3\,(s)}$ solid matrix that changes its porosity according to a dissolution- precipitation reaction. In our system, the $CaCO_{3\,(s)}$, or c, is represented by the volume to mole ratio. The h particle represents the molar value of H^+; this is calculated from the total domain fluid volume assuming a constant pH =3.5 and divided by the number of h particles used to discretize a full pore volume. As such, each h particle has a given molar value of H^+ protons. Furthermore, the total number of h particles for a pore volume is divided by the number of cells in our simulation, thus providing the local molar value for pH=3.5, which allows calculation of the local pH using the local h particles concentration.

The fractional amount of dissolved H_2CO_3 evolving in the system as a function of pH is evaluated as shown in Figure S1. The curve showing the fraction of H_2CO_3 is given by

$$\alpha_1(pH) = \frac{10^{-2pH}}{10^{-2pH}+10^{-pk_{a1}-pk_{a2}}+10^{-pH-pk_{a1}}} \qquad (S1)$$

with $pk_{a1} = 6.35$ and $pk_{a2} = 10.33$ (Manahan, 1991). Therefore, the local pH value along the advancing front of the injected fluid plays an important role in precipitation and dissolution patterns. The local pH decrease, due to the injection of h, must be locally compensated by co particles which are formed by the rock formation dissolution. The dissolution process is repeated until a new equilibrium between the h and co, or rather, H^+ and H_2CO_3, is reached, according to figure S1. The reverse precipitating reaction is initialized by the amount of co per location and the same equilibrium relation in figure S1. During precipitation, co particles are extracted from the simulation and replaced by h particles, while updating the conductivity of that specific cell. Both the dissolution and precipitation are initiated by first translating the local number of h and co particles to molar concentrations for that specific cell. The reactive method is deterministic and has no randomization in establishing the reaction type and amount.
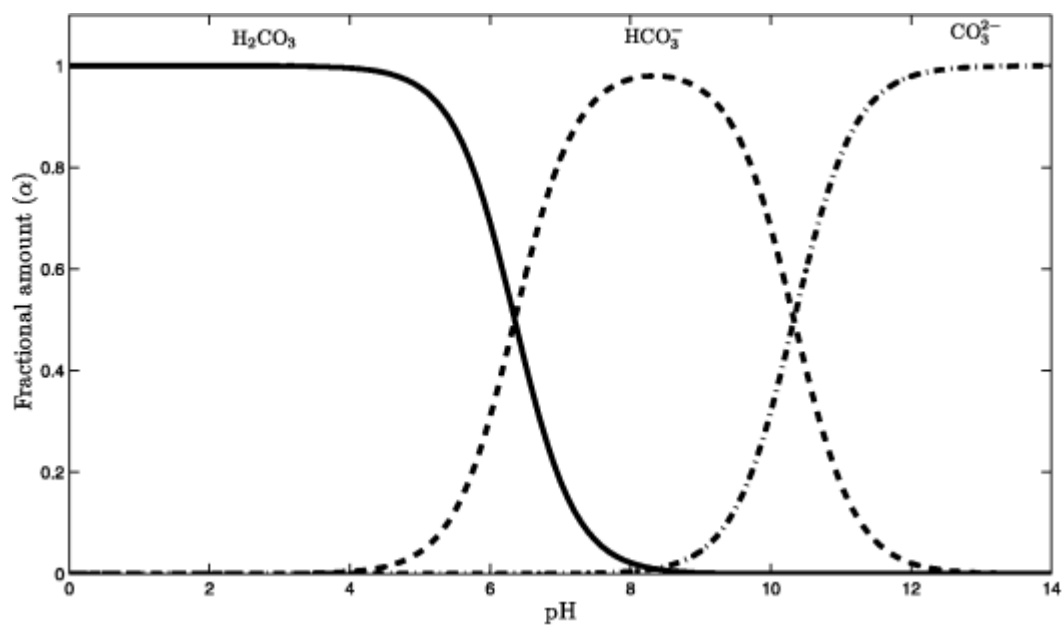
Figure S1. Fractional amunt of reactnts according to pH at equilibrium..

References

Manahan, S. E. (1991). *Environmental chemistry* (5th ed). Chelsea, Mich: Lewis Publishers.