

The effect of pH, HClO₄, HNO₃ and ΔG_r on the dissolution rate of natural gibbsite using column experiments

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The composition of soil solutions depends not only on the solubility of minerals and the complexation of aqueous species, but also on mineral dissolution/precipitation kinetics and the rate of transport of fluids. Recently, it has been shown that the dissolution rate of minerals such as gibbsite (Nagy and Lasaga, 1992) are a non-linear function of the solution saturation state, expressed as the Gibbs Free Energy of reaction Δ_rG_r. A general form of the rate law for dissolution and crystal growth of minerals, can be written as:

$$\text{Rate} = k_0 A e^{-E_a/RT} a_{H^+}^{n_H} a_i^{n_i} f(\Delta G_r) \quad (1)$$

where k_0 is a constant, A is the surface area, and E_a is the activation energy of the overall reaction. Terms involving activities of species in solution, a_i , incorporate possible catalytic or inhibitory effects on the overall rate. The final term, $f(\Delta G_r)$, accounts for the important variation of the rate with the deviation from equilibrium ($\Delta G_r = 0$). Far from equilibrium ($\Delta G_r < -0.7$ kcal/mol at 80°C and pH = 3.0) the dissolution rate is constant (Nagy and Lasaga, 1992). This region in Rate vs ΔG_r space is termed the dissolution plateau. In this paper we focus on the influence of flow rate and pH on gibbsite dissolution rate. In order to adjust the initial pH of the solutions, both HNO₃ (commonly found in nature) and HClO₄ (to compare with previous studies) were used. In addition, the possible influence of the different anions on the rate was tested.

Methods and calculations

The experimental setting consists of a column reactor, filled with an unconsolidated material (from Pijiguaos, Venezuela) rich in gibbsite. Experiments were conducted at a constant temperature of 25 ± 0.1°C and at input pH ranging from 3.2 to 4.5. Input solutions were prepared using concentrated analytical grade

HClO₄ and HNO₃. Flow rate, surface area, Al concentration and pH were determined using the same methods as Nagy and Lasaga (1992). Mogollón *et al.*, (1994) demonstrated that under far from equilibrium conditions, R_{gib} can be calculated using the following equation:

$$R_{\text{gib}} = \frac{\Delta c \cdot q_v}{A_{\text{gib}}} \quad (2)$$

where Δc is the molarity change in Al concentration during flow in the column (mol/l), q_v is the volume flow rate of the fluid (l/sec) and the area, A_{gib} , is calculated from the product of mass (g) and BET specific surface area (m²g⁻¹). Typical errors in R_{gib} should be around 15–20 percent. The ΔG_r of the output solutions was calculated as in Nagy and Lasaga (1992).

Results and discussion

Three kinetic regions were identified in the experiments.

For inputs in the pH range from 4.0 to 4.5 the output Al concentrations and the output pH are independent of flow velocity. This observation suggests that the dissolution rate is fast enough to enable the solution to reach equilibrium with the solid before the solution reaches the exit point in the column (Mogollón *et al.*, 1994). The solubility calculated from these experiments agrees quite well with previous solubility studies. For input pH in the range 3.2 to 3.5 the output Al concentration, in some cases, varies as an inverse function of the flow rate. This inverse relation reflects a constant far-from-equilibrium dissolution rate throughout most of the column. Finally, complex variation of the output solution composition as a function of flow rate indicates close to equilibrium dissolution (Mogollón *et al.*, 1994).

The output concentrations found in experiments of varying pH carried out at constant flow

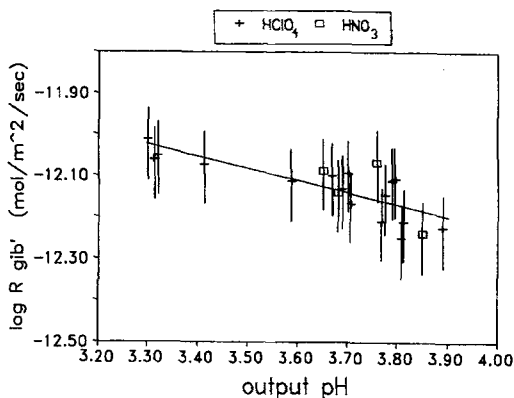


FIG. 1. The straight line slope predicts a reaction order (n) of 0.28 ± 0.06 as suggested by Mogollón *et al.*, (1994) based on fewer data than this study. Therefore, there is a slight dependence of R_{gib} on pH.

velocity demonstrate a pH effect on the rate. The dissolution rate was assumed to be a power function of H^+ activity, i.e.

$$\log R'_{\text{gib}} = \log k_0 - npH \quad (3)$$

here R'_{gib} is the area-normalized gibbsite dissolution rate. Equation (3) requires that the $f(\Delta G_r)$ term in equation (1) be constant. This condition is satisfied only if experiments are conducted far from equilibrium. Therefore, only data from experiments conducted far-from-equilibrium (i.e. output concentration varied as an inverse function of flow rate) are used in figure 1, which plots $\log R'_{\text{gib}}$ versus output pH.

Another important feature that can be appreciated in figure 1 is the lack of influence of the anions (ClO_4^- and NO_3^-) on the gibbsite dissolution rates. Current experiments are addressing the effects of different anions under far from equilibrium conditions at higher concentrations than those used in this work.

In order to corroborate the ΔG_r values at which the dissolution plateau starts for the different acids used, the dissolution rates, were corrected for the pH effect. That is, all the rates were normalized to the equivalent rate at $\text{pH} = 3.6$. It must be stressed that, in the region near equilibrium, use of eq. (3) will only yield a rough and averaged value of the dissolution rate. However, those values were included because they give useful insight about the ΔG_r at which the rates deviate from far-from-equilibrium behaviour. The details of the near-equilibrium dissolution rate law are discussed further below.

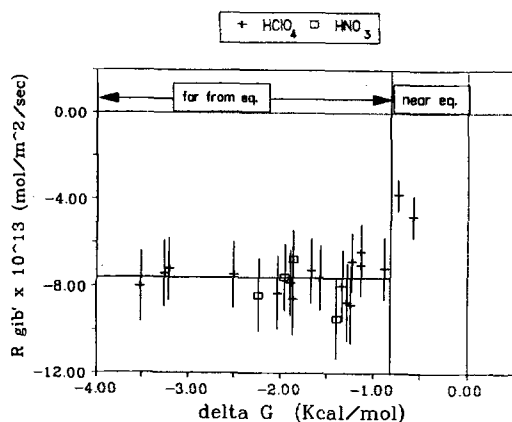


FIG. 2. Corrected dissolution rate of a natural gibbsite versus the Free Energy of reaction. $T = 298 \text{ K}$, input $\text{pH} = 3.2$ and 3.5 .

None of the far from equilibrium experiments (Fig. 2) showed ΔG_r values less than -0.7 kcal/mol . This suggests that the ΔG_r at which the dissolution plateau starts does NOT depend on other solution characteristics.

One dimensional reaction-transport numerical simulations were used by Mogollón *et al.*, (1994) to reproduce the experimental output Al and pH, over the whole range of solution saturation states, within an error of 20 %. To reproduce the entire column experiment data set, calculations assumed the ΔG_r functionality for gibbsite dissolution at 80°C and $\text{pH} = 3.0$ reported by Nagy and Lasaga (1992) and then used the far-from-equilibrium dissolution rate, the dependence of the rate on H^+ activity and the solubility product for natural gibbsite obtained in this study at 25°C . The excellent agreement near equilibrium between the calculations and the experiments show that, while pH and temperature affect the dissolution plateau rate, the $f(\Delta G_r)$ function changes only slightly with both temperature and pH.

References

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