

Mechanism and kinetics of smectite dissolution under alkaline conditions

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The mechanism and kinetics of montmorillonite dissolution were investigated by dissolution experiments of bulk samples in mixed-flow system and in situ observations on individual particles by Atomic Force Microscopy (AFM).

In the mixed-flow system, the dissolution rate was derived from the measured Si concentration in the output solutions, and surface area determined from N₂-BET, average of the total surface area (TSA) and edge surface area (ESA) from AFM. Three dissolution experiments were carried out by AFM: (1) short-term in situ experiments of batch system under room temperature (Run I); (2) long-term in situ experiments of flow-through system under room temperature (Run II); and (3) long-term batch experiments at 50C. The dissolution experiments used 0.3M NaOH solution (pH:13.3 at 25C).

Dissolution rates obtained from the mixed-flow experiments by considering the N₂-BET surface area, TSA and ESA are: 2.57X10⁻¹², 1.52X10⁻¹⁴, and 3.30X10⁻¹² mol/m²/sec (at 30C); 1.35X10⁻¹¹, 7.99X10⁻¹⁴, and 1.73X10⁻¹¹ mol/m²/sec (50C); and 4.37X10⁻¹¹, 2.59X10⁻¹³, and 5.60X10⁻¹¹ mol/m²/sec (70C), respectively.

Significant reduction in montmorillonite particle volume was observed in Run I. Since etch pits on the basal surface were not detected, the particle volume decrease can be attributed to edge surface dissolution. The dissolution rate based on the ESA is 1.30X10⁻⁹ mol/m²/sec. Change in particle volume was not detected in Run II since the observation time period (2 to 7 days) already correspond to the steady-state condition. Several hundred particles were observed in Run III after dissolution reactions were allowed to progress for an extended period of time (2, 6, 12, 19, 34 days). The dissolution rate was estimated based on variations in the median values of basal surface areas. Reduction in particle volume also observed at extended periods of dissolution reactions. Although etch pits formed on the basal surface of a few particles, they do not appear to be dominant. This suggests that the reduction in particle volume is mainly attributed to the dissolution of edge surfaces. The dissolution rates based on the TSA and ESA are 2.51 X10⁻¹³ and 3.86 X10⁻¹¹ mol/m²/sec, respectively, which is similar to values obtained from the mixed-flow experiment.

The mechanisms of montmorillonite dissolution elucidated by in situ AFM observations leads to the following conclusions:

1) Edge surfaces dominantly serve as the reactive sites during the dissolution (based on runs I and III). Etch pits are formed on the basal surface of montmorillonite. However, their contribution to the dissolution is minor and can be interpreted as an increase in edge surface area.

2) The relatively faster dissolution rate during the initial stages of the dissolution experiments (in Run I) is related to the dissolution of jagged and broken-off sections on the edge surfaces. The dissolution rate assumes constancy and similar to values indicated by the mixed-flow system once the euhedral faces are exposed as the reacting edge surfaces.