Reaction rate of ferric hydroxide formation at pH 2-4

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Iron hydroxides widely exist in the Earth’s environment, and their formation processes, adsorption properties, and transport behavior have been attracting great attention. Dissolved Fe$^{3+}$ reacts with water and transforms to ferric hydroxide (Fe(OH)$_3$) as time passes. We focused on the early process of ferric hydroxides formation and evaluated the reaction rate constants and activation energies under a wide range of solution conditions (pH 2-4, initial Fe concentration 5-300 ppm, temperature 5-55 °C, and dissolved anion species Cl$^-$, NO$_3^-$, SO$_4^{2-}$). Aqueous solutions containing ferric ions were prepared by dissolving one of the following FeCl$_3$, Fe(NO$_3$)$_3$·9H$_2$O, and Fe$_2$(SO$_4$)$_3$·nH$_2$O in pure water.

As dissolved ferric ions change to ferric hydroxide, the pH of the solution gradually decreases. The time variation of pH was monitored under the constant temperature, and the rate constant $k$ was determined by converting the pH change to the change in the concentration of dissolved ferric species (assumed to be a 1st order reaction as with Grundl and Delwiche, 1993) using a geochemical code PHREEQC (Parkhurst and Appelo, 1999). Comparison of the $k$ values of ferric hydroxide formation at pH 2-3 under the presence of the different anion species revealed that the $k$ values for Cl$^-$ and NO$_3^-$ were almost the same and that for SO$_4^{2-}$ was approximately one half to one fourth of the values for Cl$^-$ and NO$_3^-$. Despite the dependence of the rate constants on the anion species, activation energies were almost the same between Cl$^-$, NO$_3^-$, and SO$_4^{2-}$ (~120 kJ/mol). In the experiment using FeCl$_3$ solution, the $k$ value increased as the initial pH increased from 2 to 4. On the basis of the pH dependence of $k$ at 25 °C, an equation to predict $k$ for various pH was obtained.

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