Surface and nanomorphology analysis of amorphous Al hydroxide by means of acid/base titration

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Amorphous aluminum hydroxide controls the concentrations of dissolved aluminum and heavy metals in subsurface water via dissolution, precipitation, crystallization and soption processes. The mineralogy and geochemistry of amorphous aluminum hydroxide, however, is not fully understood. Thus we have studied experimentally the interaction between amorphous aluminum hydroxide and water as a function of pH. These studies quantitatively showed the solubility, surface acidity constants, surface site density and nanomorphology of amorphous aluminum hydroxide.

The specimen was synthesized by neutralization of acidic aluminum nitrate solution with sodium hydroxide solution. The resultant suspension was dialyzed during one week. After the dialysis, the suspension was freeze-dried. The obtained powder specimen was characterized by X-ray diffraction analysis, thermal analysis, measurement of specific surface area and chemical compositional analysis.

The specimen was added to the support electrolyte solutions (I = 0, 0.01, 0.05 and 0.1M NaNO3) to make the solid/solution ratio of initial suspension 1g/L. Under the condition of N2 atmosphere and 25 C, the alkalimetric titration with 1M or 0.1 M NaOH solution was performed in order to measure the amount of hydroxide ion consumed by the solid phase. In I=0M system, each 20mL of suspension was removed from the system after the addition of NaOH solution and the equilibration. The aliquot suspension was filtered with 0.2 um membrane. The filtered solution was analyzed by ion-chromatography and ICP-AES in order to examine the solubility of amorphous aluminum hydroxide. The solid mounted on the filter paper was washed and characterized by XRD to examine the degree of transformation of amorphous aluminum hydroxide. The speciation analyses and geochemical modeling were performed by geochemical program REACT. The Visual Minteq database was used for the thermo data in the calculation.

The specimen was characterized to the amorphous material showing the four broad peaks from XRD analysis. The specimen contain significant amount of impurity nitrate anion despite the thoroughly sample washing.

The XRD analyses of reacted solid in titration experiment at I = 0 system showed that crystalline bayerite occurred at the condition of pH over 10. The solution analysis showed that the log form of solubility of amorphous aluminum hydroxide was 10.3. The geochemical modeling by using the estimated solubility well reproduced the dependency of dissolved aluminum concentration on pH found in the experimental and natural system.

The amount of consumption of hydroxide ion during the titration experiment was explained by the combinative contribution of protonation / deprotonation of dissolved aluminum species and surface hydroxyl group. The discrete contribution from the surface hydroxyl group was measured by using the estimated solubility of amorphous aluminum hydroxide. The re-calculated titration curves revealed that the point of zero charge of amorphous aluminum hydroxide is 9.1. Moreover, the surface acidity constants and surface hydroxyl density were calculated by the FITEQL analysis of titration curve obtained in I = 0.05 system. The geochemical modeling by using the obtained parameters well described the titration curve obtained from I = 0.1 and I = 0.01 system. Moreover, the estimated parameters showed that the nanomorphology of amorphous aluminum hydroxide would be aggregates of monolayer gibbsite sheet of which diameter is c.a. 15nm.