

2.1.P05**Surface and structure analysis of amorphous aluminum hydroxide by acid/base titration**

K. FUKUSHI AND K. TSUKIMURA

Research Center for Deep Geological Environments, AIST,
Tsukuba, Ibaraki 305-8567, Japan
(FUKUSHI.Keisuke@aist.go.jp)

Introduction

Amorphous aluminum hydroxide controls the concentrations of dissolved aluminum and heavy metals in subsurface water via dissolution, precipitation, crystallization and sorption 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 structure of amorphous aluminum hydroxide.

Material and Methods

The specimen was synthesized by neutralization of acidic aluminum nitrate solution with sodium hydroxide solution. The resultant suspension was dialyzed and freeze-dried.

The specimen was added to the support electrolyte solutions ($I = 0, 0.01, 0.05$ and 0.1M NaNO_3) to make the solid/solution ratio of initial suspension 1gL^{-1} . Under the condition of N_2 atmosphere and 25°C , the alkalimetric titration with 1M or 0.1M NaOH solution was performed in order to measure the amount of hydroxide ion consumed by the solid phase. In $I=0\text{M}$ system, an aliquot of suspension was removed from the system after the equilibration. The filtered solution was analyzed by ion-chromatograph and ICP-MS in order to examine the solubility of amorphous aluminum hydroxide. The speciation analyses and geochemical modeling were performed by geochemical program REACT with MINTEQ thermo database.

Results and Discussions

The solution analysis at $I = 0$ system showed that the log form of solubility of amorphous aluminum hydroxide was 10.3. 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 calculated by using the estimated solubility. The re-calculated titration curves showed that the point of zero charge of amorphous aluminum hydroxide is 9.1. The surface acidity constants and surface hydroxyl density were calculated by the FITEQL analysis of titration curve. The estimated parameters with assumption of gibbsite fragment model showed that the structure of the amorphous aluminum hydroxide is aggregates of monolayer gibbsite sheet of which diameter is c.a. 15 nm.

2.1.P06**Aluminum dissolution from alumina induced by heavy metal adsorption**A. MIYAZAKI¹, Y. NAKANO¹, T. YOKOYAMA² AND I. BALINT³

¹Tokyo Institute of Technology, Japan
(akanem@chemenv.titech.ac.jp)

²Kyusyu University, Japan
(yokotscc@mbox.nc.kyushu-u.ac.jp)

³Romanian Academy (ibalint@chimfiz.icf.ro)

Aluminum oxide, contained in soils and sediments, is one of the most important adsorbent for heavy metal ions. The adsorption of heavy metal ions onto alumina has been thought to simply occur through formation of surface complexes between the metal ions and surface aluminol groups. On the other hands, recent findings suggest that the adsorbed heavy metal ions form $\text{M}^{2+}\text{-Al}^{3+}$ hydroxide co-precipitates with hydroxalite-type local structures. Thus, it is likely that Al^{3+} is mobilized from the oxide structure to liquid phase even at the neutral pH.

In order to reveal the chemical state of heavy metal ions on the surface of alumina we have performed Zn^{2+} adsorption experiments onto alumina at pH 6.50. The results indicate that the reaction of Zn^{2+} with alumina can be divided into three processes: surface complex formation with aluminol groups, desorption of Zn^{2+} , and co-precipitation of $\text{Zn}^{2+}\text{-Al}^{3+}$ hydroxide. In the early stage of the interaction, Zn^{2+} was adsorbed onto alumina forming a surface complex with two aluminol groups. After the reaction advance to some extent, the surface-complexed Zn^{2+} started to desorb. Then, the desorbed Zn^{2+} began to be adsorbed again. The last process was accompanied by the formation of Al^{3+} . In the case of zinc-free experiments, the formation of Al^{3+} was not evidenced. Therefore, it is rational to consider that the dissolution of alumina was induced by the surface complexation between Zn^{2+} and aluminol groups. In the case of $\text{Cu}^{2+}\text{-Al}_2\text{O}_3$ system, the adsorption of Cu^{2+} onto alumina at pH 7.0 and 9.0 was associated with the formation of Al^{3+} , too. We found 0.221 % of aluminum dissolved at pH 9 after 240 hours of interaction. In order to investigate the alumina interaction with anionic heavy metal ions, same type of experiments were performed with PdCl_4^{2-} . It was found that the adsorption of PdCl_4^{2-} can also induce the alumina dissolution. The experimental results proof that generally the heavy metal ions, both in cationic and anionic form, can trigger the dissolution of alumina even in the neutral pH range, where alumina is normally stable. The dissolution mechanism requires the heavy metal ions adsorbed onto alumina via surface complexation. The amount of resulted Al^{3+} was related to the amount of adsorbed heavy metal ions as well as to the interaction time. In the light of the experimental results, the formation of metal hydroxide on the alumina surface plays a key role in the generation of Al^{3+} .