Local structure of Al and Cd in Al-Cd hydroxide coprecipitates

AKANE MIYAZAKI[1*], YUI YAMANISHI[2], HIRONORI OHASHI[3] AND TAKUSHI YOKOYAMA[2]

[1]Faculty of Science, Japan Women's University, 112-8681 Tokyo, Japan, (*correspondence: miyazakia@fc.jwu.ac.jp)
[2]Faculty of Science, Kyusyu Univerity, 812-8581 Fukuoka, Japan (yokoyamatakushi@chem.kyushu-univ.jp)
[3]Faculty of Symbiotic Systems Science, Fukushima University, 960-1296 Fukushima, Japan

Structural transformation from AlO_6 to AlO_4 in $Al(OH)_3$ was found to be induced by Zn^{2+} adsorption onto $Al(OH)_3$ [1]. The mechanism was explained by inner-sphere complexation followed by dissolution of $Al(OH)_3$ and coprecipitation of Zn^{2+} and Al^{3+}[2]. In this study, local structure of Cd in Al-Cd hydroxide coprecipitates was studied as a model substance of Cd^{2+} adsorbed onto $Al(OH)_3$. Chemical structures of Al-Cd and Al-Zn hydroxide precipitates were compared.

Chemical State of Al

Al-Cd hydroxide coprecipitates having Cd/Al ratios of 100, 10, 3, and 1 were prepared. ^{27}Al MAS NMR spectra showed the existance of AlO_4 structure in coprecipitates with low Cd/Al ratio, Cd/Al = 1. This was the same tendency to Al-Zn hydroxide coprecipitates and seemed to suggest the formation of $CdAl_2O_4$-like structure by Cd^{2+} adsorption onto $Al(OH)_3$.

Chemical State of Cd

In order to see the chemical states of Cd in Al-Cd hydroxide coprecipitates, ^{113}Cd MAS NMR, XRD, and EXAFS were applied. EXAFS result suggested that Cd is 6 coordinated in all the coprecipitates. However, XRD pattern of the coprecipitates did not agreed with $CdAl_2O_4$ or $Cd(OH)_2$ but $Cd(OH)NO_3{\cdot}H_2O$. Moreover, ^{113}Cd MAS NMR peaks of these samples had different values of chemical shift from each other and also from $Cd(OH)_2$.

The above results suggested that adsorption product of Cd^{2+} on the surface of $Al(OH)_3$ was not $CdAl_2O_4$, which was expected by analogy to Zn^{2+}. On the other hand, they showed that $Cd(OH)NO_3{\cdot}H_2O$ and $Cd_5(OH)_8(NO_3)_2{\cdot}2H_2O$ are the possible hydrolysis products of Cd^{2+} in natural water systems.

[1] Miyazaki *et al*. (2013) *Colloid and Surface A* **420**, 115-121.
[2] Miyazaki *et al*, (2003) *Geochem. Cosmochim. Acta* **67**, 3833-3844.