XRD and ^{113}Cd MAS NMR study on hydrolysis products of Cd^{2+}

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Behavior of cadmium ion (Cd^{2+}) in environment is greatly concerned because of its strong toxicity. In soil sphere, Cd^{2+} has been thought to adsorb onto surface of soil particles by forming inner sphere complexes. With increasing the surface coverage of Cd^{2+}, they may convert to hydroxide (β-$Cd(OH)_2$). However, no report has been published on another behaviour of Cd^{2+} in spite of the possibility. Therefore, in this study, hydrolysis of Cd^{2+} was investigated in cadmium nitrate ($Cd(NO_3)_2$) aqueous solution because of abundance of nitrate ion (NO_3^-) in soil sphere and relatively strong coordination of NO_3^- to Cd^{2+}.

Hydrolysis experiments were performed by adding 2.0 M NaOH to 0.33 M $Cd(NO_3)_2$. The initial pH of $Cd(NO_3)_2$ solution was around 4. Immediately after the addition of NaOH solution, pH increased to neutral range and then it was approximately constant for a while. The addition of NaOH solution was continued until pH increased to more than 12. Majority of the hydrolysis took place around pH 7. Solid samples were collected in the course of hydrolysis, i.e., at several points with different amount of NaOH additions. XRD patterns of the samples collected around pH 7 revealed they were not β-$Cd(OH)_2$ but Cd double salts containing NO_3^- in their structure. According to the XRD results, β-$Cd(OH)_2$ was not formed until the pH increased up to 12. From chemical analysis of the solid samples, the existence of NO_3^- was confirmed and NO_3^-/Cd ratios agreed well with those predicted from XRD results. The ^{113}Cd MAS NMR spectrum of the solid sample collected at pH 12 showed a peak at 142 ppm relative to 1 M $Cd(ClO_4)_2$ solution, which corresponds to β-$Cd(OH)_2$. However, the solid samples obtained at neutral pH range showed various peaks from 142 to 159 ppm. These peaks probably correspond to Cd species in double salts.

In conclusion, we could reasonably demonstrate that hydrolysis products of Cd^{2+} in hydrosphere was not β-$Cd(OH)_2$ but double salts containing co-existing anions in their structure, such as $Cd_5(OH)_8(NO_3)_2{\cdot}2H_2O$ and $Cd(OH)NO_3{\cdot}H_2O$.