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DISSOLUTION OF ALLOPHANE WITH ALKALINE SOLUTION

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Introduction
Detailed knowledge of clay dissolution and precipitation rates, as a function of solution composition and saturation state is essential for understanding various geochemical processes. Alkaline pH solution-mineral reactions occur in a variety of geological environments as well as in environments where conditions have been modified by human activity in various engineering projects. Emplaced concrete and alkaline flooding of sandstone reservoirs were suggested to raise strongly environmental pH (Savage et al., 1987; Bauer and Berger., 1998). For long time, concrete and cement are used as backfill materials. Solidification and desegregation of concrete in natural environments will produce high pH solution. The pore fluids in hydraulic cement range in pH from 12.5 to 13.5, and it will affect characteristics of clays in soils.

The effect of alkaline solutions on allophane has been studied by a few scientists. However, the dissolution mechanism of allophane during the reaction with alkaline solution have not been clarified yet. The main objective of this research was to understand the clear reaction step of alkaline solution with allophane in relation to detailed structure and physicochemical properties of nano-ball allophane.

Materials and Methods
The allophane samples used for experiments were taken from Kumamoto, near Mt. Aso (KnP, high Si/Al ratio) and Tottori, near Mt. daisen (KyP, low Si/Al ratio). The Si/Al atomic ratio of KyP and KnP were 0.696 and 0.983, respectively. In this experiment, 50 mg of sample was mixed with 100 mL sodium hydroxide with variety of concentrations from 0.001 M to 0.015 M. The reaction time was from 0 hour to 72 hours. The temperature was kept at 30°C (±0.1°C) by using an incubator. After the treatment, the sample was centrifuged at 7000 rpm for 30 minutes. Silicon and aluminum in the supernatant was determined by atomic absorption spectrophotometer. Reaction order between alkaline solution and allophane was determined by an integration method. The procedure is to measure the concentration of products at various time interval of the reaction and to substitute the data into a equation. The dissolution process for allophane was compared with those of layer silicates such as montmorillonite and kaolinite.

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Results and Discussion

The dissolution of allophane was observed by following Si and Al released as a function of time. Two kind of allophane was progressively dissolved by alkaline solutions with variety of concentrations, releasing Si and Al in solution. There were two steps in dissolution of the allophane. 1) During an initial step, both elements were released rapidly into solution. 2) The sudden change in the rate of Si and Al dissolution and it reached constant rate. After 24 hours, the rate of dissolution of two allophane samples reached constant.

The amount of Si and Al released from two allophane samples were much greater than those from kaolinite and montmorillonite. It indicates that allophane is more susceptible to OH" than crystalline layer silicates. The amount of Si released from kaolinite was more higher than that from mortmorillonite.

For KyP sample, at NaOH concentrations less than 0.005 M, the amount of Al released was higher than that of Si released. However, at NaOH concentrations more than 0.005 M, at higher pH, Si was released more than Al. For KnP sample, Si released more easier than Al at all NaOH concentrations. The amount of Si released from KyP sample was higher than that from KnP sample under a same reaction condition. This result contradict with the fact that KnP has higher Si/Al atomic ratio than KyP. In the structure of KnP, a lot of polymerized Si tetrahedra are bonded to the fundamental structure. The polymer in the KnP might protect the fundamental structure during the dissolution process.

Calculation results for the order of reaction by using integration method showed that for NaOH concentrations more than 0.005 M, both of the two samples showed second order kinetics during dissolution process. However, in NaOH concentrations less than 0.005 M, both of the samples showed first order reaction during dissolution process. There were differences in k values between KyP sample and KnP sample. The amount of Si released from KyP sample reached constant faster than KnP sample. In all cases, Si/Al atomic ratio of dissolved materials was different from Si/Al atomic ratio of the allophane samples, it indicating incongruent dissolution. The reaction mechanism between OH" and allophane was investigated by calculating change in bond strength of Si–O and Al–O of allophane before and after OH" adsorption, by using molecular orbital method.

References