

NOTES

HYSTERESIS OF THE COLLOIDAL STABILITY OF IMOGOLITE

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INTRODUCTION

Imogolite is a unique clay mineral that flocculates under alkaline conditions and disperses under acidic conditions. Although it is a variable charge clay possessing a point of zero net charge (PZNC) at about pH 6 (Karube et al. 1998), it flocculates above the PZNC due to the fact that the negative charge arises on the

inside surface of its tubular structure (Horikawa 1975) and also due to its thin fibrous shape (Karube et al. 1992). Furthermore, during the preparation of pure imogolite from a weathered pumice, we found that this clay mineral often does not disperse well even under acidic conditions. We therefore examined the effect of pH on the colloidal stability of imogolite in terms of relative turbidity and electron microscopic morphology.

MATERIALS AND METHODS

Imogolite Sample

A gel-like substance was collected from a weathered pumice fall deposit, "Y_K-M", in Kitakami-city, Japan, by washing with water. The gel was treated successively with H₂O₂, Na₂S₂O₄-NaHCO₃-Na-citrate (Mehra and Jackson 1960) and 2% Na₂CO₃ (Jackson 1956; modified by Wada and Greenland 1970) to remove impurities from the sample. The colloidal particles less than 100 nm in Stokes' diameter were collected from the suspension using the centrifugal sedimentation method, controlling the pH at 4–5 with HCl and agitating the sample repeatedly with a screw-vane stirrer and sonication. After 100 cm³ of saturated NaCl solution was added per 1 dm³ of the separated imogolite

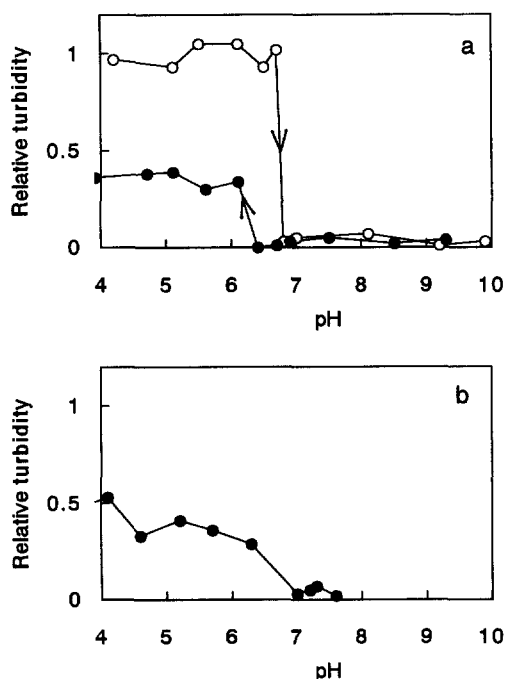


Figure 1. a) Hysteresis of the colloidal stability of imogolite observed as a relative turbidity. The relative turbidity approaches 1 when the system is dispersed and 0 when coagulated. Measurements were done without sonication or strong agitation after changing the initial pH. Open symbols: increasing pH; closed symbols: decreasing pH. b) Imogolite indicated with closed symbols did not disperse even 37 d after pHs were lowered from 9.6.

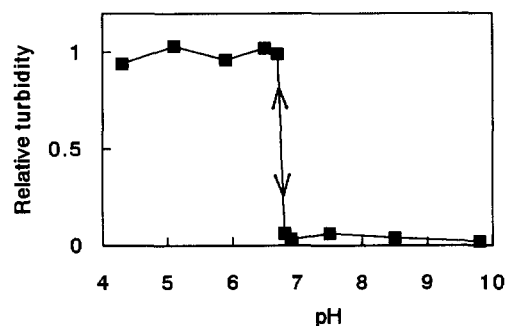
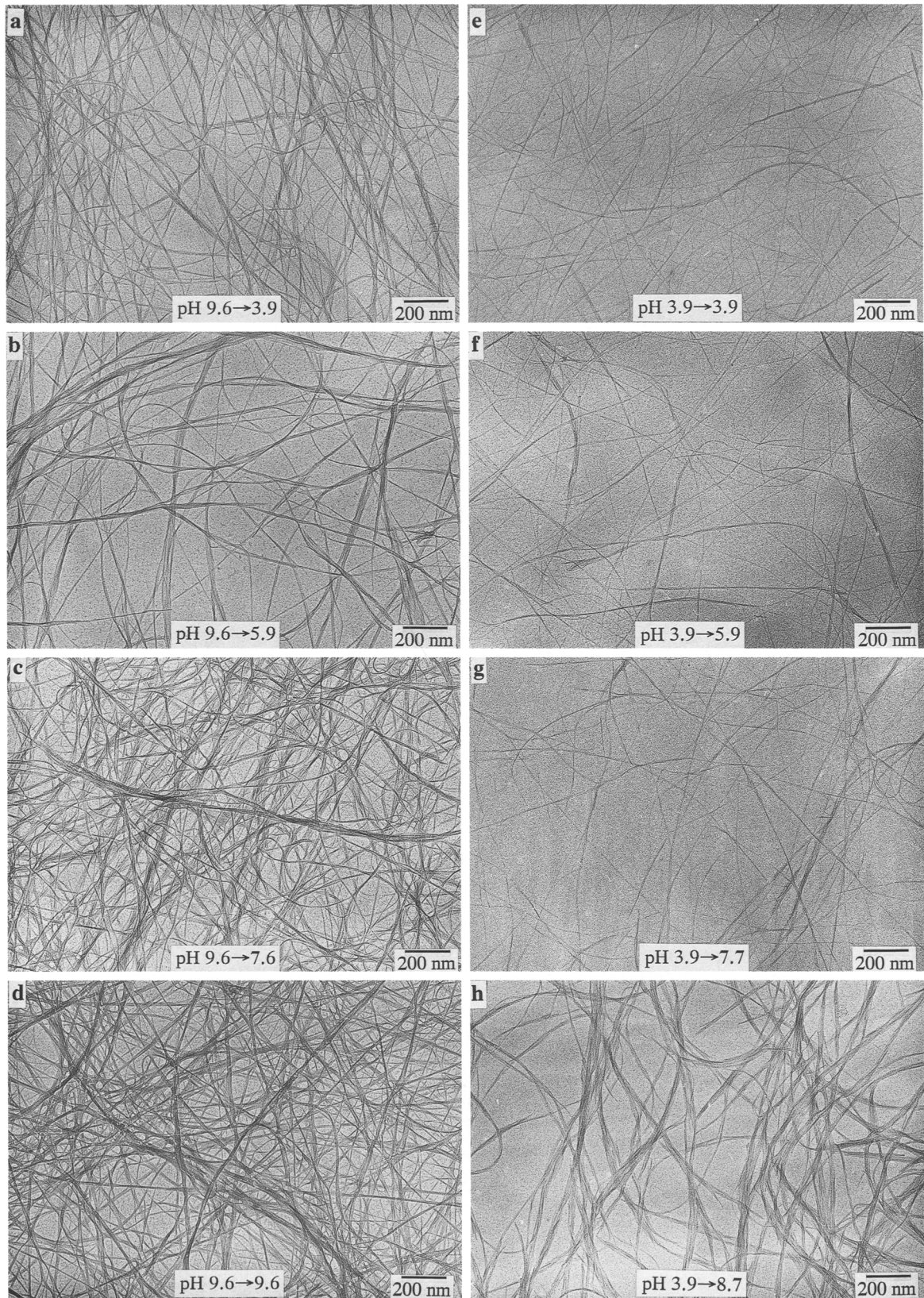


Figure 2. Relative turbidity of imogolite sonicated after pH alteration.



suspension, the sample was dialyzed to reduce the electrical conductivity of the equilibrated outer solution to be less than 1 mS m^{-1} . This sample prepared from $Y_K\text{-M}$ was free of allophane or impurities.

Observation of the Hysteresis of Colloidal Stability Due to pH Change

Imogolite suspensions with 25 g m^{-3} clay concentration and pHs adjusted at about 4.0 and 9.5 with HCl or NaOH were prepared in 50 cm^3 screw vials. They were agitated well with sonication for 15 min and a magnetic stirrer for 5 min repeatedly for 4 times. These initial pHs (about 4.0 and 9.5) were changed variously using HCl or NaOH with shaking lightly, without sonication, and the samples stood for 24 h before the observation of the relative turbidity.

Dilute samples with 7.5 g m^{-3} of clay concentration were prepared by the same procedure for observation with a transmission electron microscope (TEM). With shaking lightly after 24 h, they were pipetted and put on TEM meshes with carbon-coated collodion films.

Measurement of Colloidal Stability in Terms of Relative Turbidity

The solutions at the surface and the bottom of each sample were pipetted out and their turbidities measured in terms of light scattering intensities. Their pHs were also measured. The relative turbidity, the ratio of the turbidity at the surface and bottom, was taken as an index of the colloidal stability. This relative turbidity approaches 1 when the system is dispersed and 0 when coagulated, and showed good agreement with qualitative observations.

RESULTS AND DISCUSSION

Figure 1a shows the hysteresis of the colloidal stability of imogolite due to pH change. With increasing pH, well-dispersed imogolite under acidic conditions coagulated sharply at pH 6.8. On the other hand, as pH was lowered, imogolite that had flocculated under alkaline conditions did not disperse well even at pH 4, despite having partially dispersed below pH 6.4. These states did not change even after 37 d, as shown in Figure 1b. These samples with pH lower than 6.8 dispersed well with sonication.

When sonicated well after pH alteration, the critical flocculation pH of imogolite, the pH at which imogolite changes its colloidal stability, was constant regardless of former pH, as shown in Figure 2. The critical flocculation pH following sonication agreed with that measured in the direction from dispersion to flocculation (Figure 1a). This means that the hysteresis of the colloidal stability of imogolite occurs when the system changes from flocculation to dispersion.

The colloidal stability of imogolite must be closely related to its fibrous structure. Figures 3a–h shows that the thickness of the fibrous particles principally reflects the colloidal stability of imogolite. In well-dispersed systems (Figures 3e and 3f), the fibers appear to consist mostly of single strands, and in flocculated systems (Figures 3a–3d and 3h), mostly multi-stranded. Here, Figure 3g looks dispersed at pH 7.7, in contrast to Figure 1a, which indicates flocculation at that pH. In a dilute suspension such as a TEM sample, the hysteresis might occur also in the direction from dispersion to flocculation. Secondly, the intersection angles of fibers also reflect the stability. In well-dispersed systems, the intersection angles tend to be close to a right angle. Thirdly, the uniformity or evenness of the clay distribution on the collodion film of TEM mesh reflects the colloidal stability. Although the clay concentrations prepared were all the same, Figures 3c and 3d look more dense than the others, because each shows a part of flocs. Figures 3a, 3b and 3h also look relatively dense compared to the well-dispersed ones. These clays also flocculated and their densities or distributions on the collodion films were uneven.

Usually, the imogolite sample separated under acidic condition looks thin, and after deferration or Na_2CO_3 treatment it looks thick with TEM due to the pH of the suspension. At the same time, the uniformity of the density varies also with the pH. This suggests that tests for imogolite identification should be made under acidic conditions with sonication.

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Figure 3. TEM of imogolite adjusted to different pHs, showing morphological hysteresis of colloidal stability. a–d) initial pH was 9.6; e–h) initial pH was 3.9.