

## Validity of the New Method for Imogolite Synthesis and Its Genetic Implication

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**Abstract**—In this study, we validated the dialysis membrane method to produce orthosilicic acid. Solid silica material, orthosilicic acid source was used for the synthesis of imogolite. The mineralogical analysis showed that imogolite, allophane and an amorphous material are formed during synthesis. The products in the precipitate depend on the purity of solid silica sample source, the orthosilicic acid. Our proposed method is easily applicable without pre-treatment, for the source materials containing high purity silica. On the other hand, silica material with low purity also can be used for imogolite synthesis after pre-treatment with acid. The occurrence of imogolite and allophane as a weathering product from basaltic saprolite in the soil environment can be explained from the present results. Acceleration of leaching of impure materials will give more homogeneity to the parent weathered material.

**Keywords:** dissolution, selective, separation, imogolite, synthesis

### INTRODUCTION

Imogolite was first identified as a fibrous acid-dispersible clay component of weathered pumice in Japan (Yoshinaga and Aomine, 1962). Imogolite is frequently found together as main clay components in soils derived from pyroclastic materials such as volcanic ash and pumice. They have occasionally been found to occur in soils developed from other parent materials such as basalt and tills derived from various types of rock, and also in association with basaltic saprolite. In particular, imogolite and allophane have also been recognized as major components of the B horizon clays of many podzolized soils worldwide (Parfitt and Henmi, 1980; Farmer *et al.*, 1980; Wada, 1989).

Imogolite has nano-tubular structure having an inside diameter of 1.0 nm and outside diameter of 2.0 nm with a well-defined fibrous electron-diffraction pattern indicating that the tubes are uni-dimensional crystals. These tubes may be several hundred nanometers in length. The basic structure of imogolite is built up largely of a gibbsite sheet, with orthosilicic acid coordinated from inside via

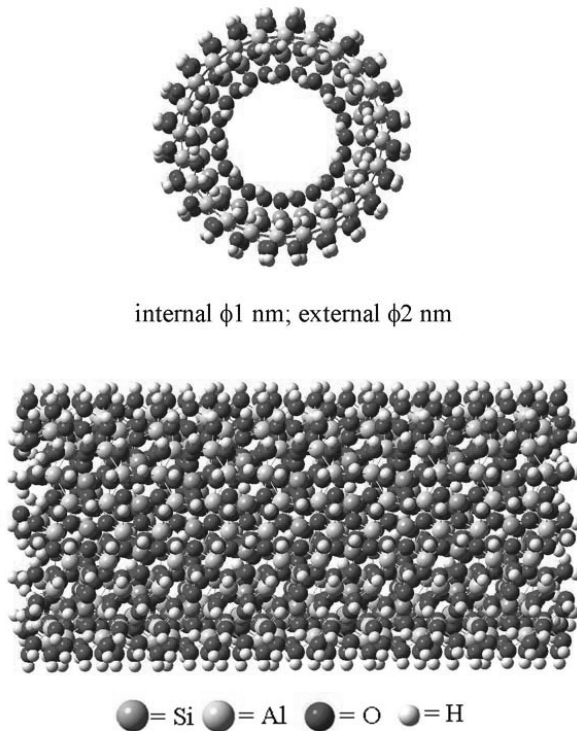


Fig. 1. Chemical structure of nano-tube imogolite.

oxygen of the three Al atoms with a Si/Al ratio of 0.5 (Cradwick *et al.*, 1972). The structure of imogolite is shown in Fig. 1.

Imogolite have considerable control on the physical and chemical characteristics of soil environment. Because of its reactive surface, imogolite has high surface area and acid reactivity. It can also form strong chemical bonds along its outer parts with heavy metal cations, phosphate, arsenate, sulfate and organic materials, as surface-adsorbed species in solution (Wada, 1989). It has a unique chemical structure through which gases can be easily adsorbed both inside and outside the particle. Therefore, imogolite has wide range of uses in industry, e.g. as catalysts, deodorizers and humidity control material.

In our previous reports, we proposed a new method for imogolite synthesis by using polysilicic acid as orthosilicic acid source (Abidin *et al.*, 2008). By adding concentrated polysilicic acid as colloidal silica in the dialysis membrane, soluble form of silica ion species will pass through the dialysis membrane into the solution. These applications seem to be promising for further development in the industrial field because of the combination between batches with flow system. It is expected that this method will give large yields in the synthesis of imogolite.

However, we need validation of this method for using other silica material as orthosilicic acid source.

## MATERIALS AND METHODS

### *Materials*

Silica gel for adsorbent (labeled as SG-1, Wakogel DX), silica gel for chromatography (labeled as SG-2, Merck 60), and silica gel for drying (labeled as SG-3, Nacalai tesque chemical) were selected as orthosilicic acid source for imogolite synthesis. We used natural imogolite samples from Choyo Kumamoto Prefecture as reference material (labeled as CiG). The dialysis membrane used in this experiment had a pore diameter size 50 Å (Sanko, Japan).

### *Dissolution of silica*

Solid silica was mixed with distilled water and put in to the dialysis membrane tube. Then, the membrane was immersed into the bottle containing distilled water adjusted to a pH of 8.0 and aged at 70°C for two days. The amount of silicon in the solution was measured using Polarized Zeeman Atomic Absorption Spectroscopy (Hitachi Z-5000, Tokyo Japan) in nitrous oxide-acetylene flame. After the amount of soluble silicon species in the supernatant was measured the solution was diluted and used for the synthesis process. The pH of the solution after aging process was in the range of 6.2 and 6.4. At the same time, the concentration of sodium ion in the solution was almost not detectable.

### *Synthesis of imogolite*

Aliquots of  $\text{AlCl}_3$  solution were simultaneously mixed with orthosilicic acid to yield Si/Al ratio of 0.5. The solution mixtures were titrated with NaOH at a rate of about 0.5 mL NaOH  $\text{min}^{-1}$  to an OH/Al molar ratio of 2. The Si concentration of the resulting solution was 1.6 mM. All the parent solutions had pH in the range of 3.98 to 4.03. The solution mixtures were heated in an autoclave at 110°C for 48 hours. After the collected precipitates were flocculated by sodium chloride, the sample was dialyzed using cellulose tubes against distilled water until they were free of sodium and chloride ions.

A portion of each colloidal precipitate was put on a glass slide and then dried under room temperature. X-ray diffraction was performed by a Rigaku Miniflex X-ray diffractometer with Cu-K $\alpha$  radiation generated at 30 kV and 10 mA. X ray diffraction pattern was determined by oriented film method. The imogolite sample gel was placed on a glass slide and dried at room temperature to form oriented films. The glass slide containing the sample was mounted in the holder and its X-ray pattern was measured from 3.0° to 60.0° of  $2\theta$ , at a step interval of 0.01 and a scanning rate of 2°  $\text{min}^{-1}$ .

The morphology of the sample was examined by means of scanning electron microscopy (SEM). Hitachi High Technology S-800 electron microscope at an accelerating voltage of 20 kV was used to observe the morphology of precipitate.

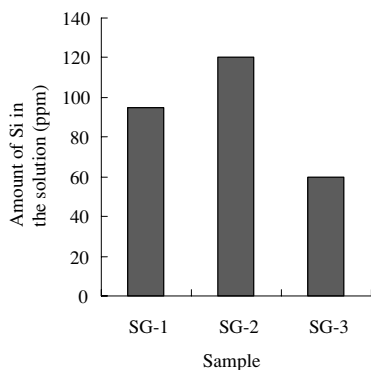


Fig. 2. Dissolution of solid silica at 70° for 2 days.

A drop of a diluted suspension of the precipitate was spread on micro cover glass and then dried under room temperature.

## RESULTS AND DISCUSSION

### *Dissolution of silica*

Solid silica samples are easily dissolved to form the soluble form of silica ion species in a solution at pH 8.0. Figure 2 shows the amount of soluble silicon in the solution after heating at 70°C for 2 days. Amount of soluble silicon in the solution was different among the three solid silica samples after heat treatment. SG-2 sample was easily soluble than SG-1 and SG-3 samples. The SG-2 sample had smaller sized articles compared to SG-1 and SG-3 samples. The fine particles adhering to the surface, such as the particles after sample grinding normally has higher surface free energy, and hence should dissolve more rapidly than large grains.

The solubility of silica depends on pH and formation of alkali metal salts. Silica can easily be dissolved in the high pH solution. The hydroxyl ion is considered as playing an important role in the dissolution reaction via nucleophilic attack. Hydroxyl ion increases the coordination number of silicon atom to form a five-fold coordination as transition state complexes. These complexes will result in weakening the oxygen bonds connecting the underlying silicon atoms and dissolve these parts from silica to form monomeric silica or low polymeric silicic acid. A part of silica is dissolved to soluble form of silica ion species and pass through the dialysis membrane. By diluting the concentration of soluble silica to a concentration of about 2 mM the polymer decomposes with time into the monomeric form, which is the stable silica species in solutions (Iller, 1979).

### *Precipitate products*

Determination of the precipitated reaction products by X-ray diffraction

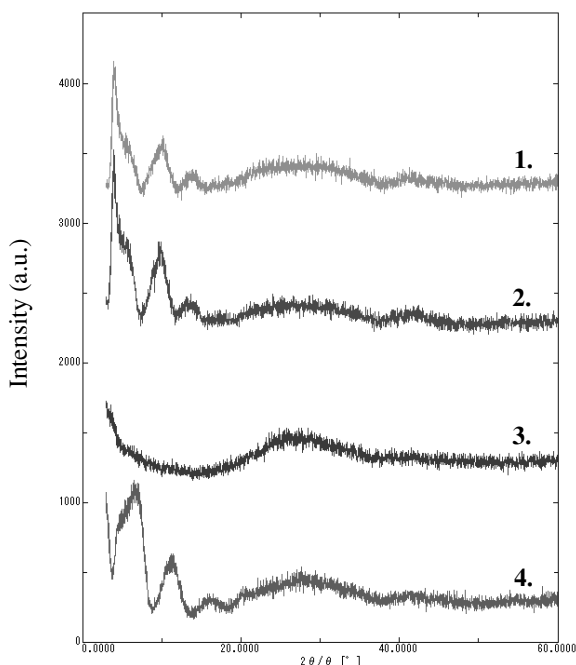


Fig. 3. X-ray pattern of synthetic and natural imogolite (1. SG-1; 2. SG-2; 3. SG-3; 4. CiG).

indicates that the solution containing orthosilicic acid and  $\text{AlCl}_3$  at a Si/Al molar ratio of 0.5 and an OH/Al molar ratio of 2.0 were imogolite and allophane or amorphous materials. While imogolite could be detected and confirmed by X-ray diffraction peaks at 2.30, 0.92, and 0.62 nm, allophane or amorphous materials products were poorly crystalline to non-crystalline and so difficult to be identified by X-ray (Fig. 3).

Imogolite was synthesized by using orthosilicic acid solution from dissolution of SG-1 and SG-2 samples. The reactions involved in hydrolysis and polymerization of hydroxy-Al ion and the interaction of the hydroxy-Al ions with orthosilicic acid resulted in the formation of imogolite. This pattern is similar to that obtained for the natural imogolite, showing a narrow reflection peak at a  $d$  value of about 2.0 nm. In X-ray diffraction patterns of films, natural samples exhibit a sharp peak at 1.80 nm. It indicates that the synthesis tubes had greater diameter than natural imogolite. On the other hand, allophane or amorphous materials result from dissolution of SG-3 sample.

From these results, we could see the purity of solid silica sample depends on the purity of the orthosilicic acid source. For example, the orthosilicic acid from high purity silica gel sample can be easily used in the imogolite synthesis. On the other hand, allophane or amorphous materials are easily formed by **SG-3 sample**. Impurity in this silica sample will inhibit the growth of nano-tube shape material

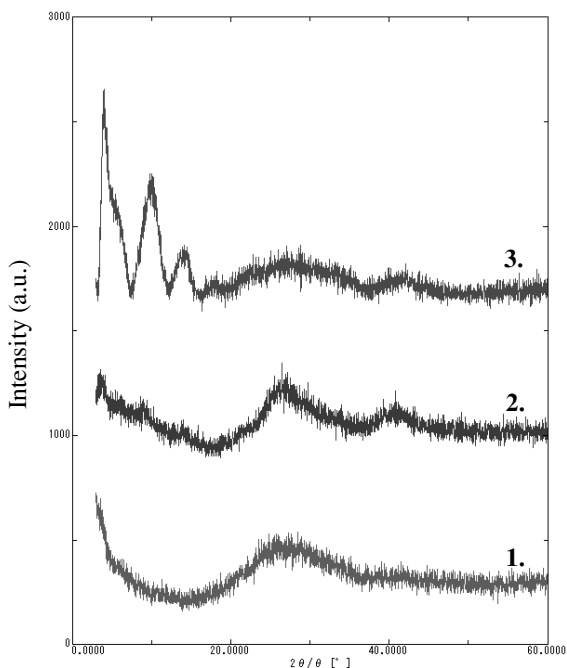


Fig. 4. X-ray pattern of product on SG-3 with several treatments (1. Treated with water for 2 days; 2. Treated with water for 2 months; 3. Treated with acid).

and shift to amorphous product during synthesis.

There are two kinds of mechanisms inhibiting the growth of nano-tube shape material. First, the impurity will affect in the orthosilicic acid form. For example, some alkali and alkali-earth metal ions can accelerate dissociation of orthosilicic acid (Abidin *et al.*, 2007). Second, the impurity will affect in the aluminum ions. These impurities usually come from phosphate or organic species which react with aluminum ions. The complexes of Al with phosphate or organic species will block and inhibit further polymerization of Al to form gibbsite sheet part in the imogolite structure (Inoue and Huang, 1984; Henmi and Huang, 1987).

Interesting phenomena could be observed during the formation of orthosilicic acid from dissolution of SG-3 sample. The intensity of the 2.3 nm imogolite peak on precipitate production increased after washing process for 2 months (Fig. 4). Thereafter, the crystallinity of the product improved with increasing washing period, indicating the transformation of allophane or amorphous materials to imogolite. The impurities in the silica sample decreased gradually during the washing process. Then, we tried another method to remove impurity in the SG-3 sample by using acid treatment. After treatment with acid, orthosilicic acid from this sample could be used easily to produce imogolite (Fig. 4).

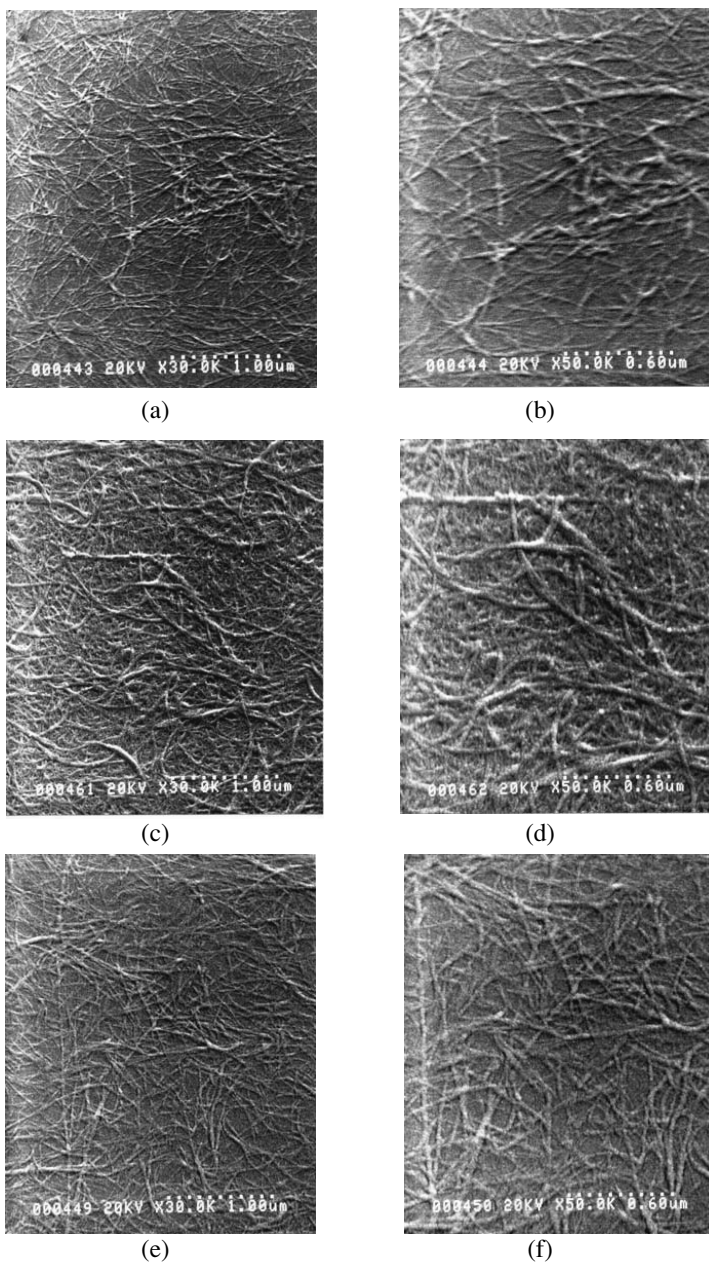


Fig. 5. Scanning Electron Microscopic image of SG-1 (a and b); SG-2 (c and d) and acid treated SG-3 (e and f).

### *Morphology of imogolite*

Scanning electron microscopy of the reaction products of orthosilicic acid and  $\text{AlCl}_3$  at a Si/Al molar ratio of 0.5 and an OH/Al molar ratio of 2.0 showed similarity in the morphology for SG-1, SG-2 and acid treated SG-3 samples (Fig. 5). The precipitate consisted mostly long threads of several micrometers length. Imogolite threads appeared in the electron microscope as assemblies of tubular structure unit in nearly parallel alignment. Fiber units on imogolite with the random twisting of tube bundles can be described as a hexagonal close packing of the tubular structure units.

The diameter of synthetic imogolite thread was larger than that of naturally occurring imogolite. Natural and synthetic imogolite threads had diameters of 10–30 nm and of 40–90 nm, respectively (Yoshinoga *et al.*, 1968; Tani *et al.*, 2004). The diameter of imogolite threads depend on the number of imogolite threads twisting together and the diameter of imogolite tube. Electron microscopy, electron diffraction, and X-ray diffraction indicate that synthetic and natural imogolite are not identical, the synthetic tubes having larger diameters compared to natural one (Farmer and Fraser, 1978). Therefore, there are variations in the diameter of imogolite threads.

X-ray diffraction and porosity data showed that three different pores exist in imogolite and can be termed inter thread, inter-tube structure unit and intra-tube structure unit pores (Wada and Henmi, 1972). Hexagonal close packing of the tubular structure can accommodate water in the inter-thread and intra-tube structure-unit pores larger than in the inter-tube structure unit pore. Water adsorbed on the inter-thread and the inter-tube structure unit pores also will affect the diameter of imogolite threads. The temperature, length of drying treatment and high vacuum treatments can remove water adsorbed on imogolite and results in reduced diameter of imogolite threads.

### *Selective dissolution separation*

In previous experiments, we have succeeded in using dialysis membrane to produce orthosilicic acid for synthesis of imogolite (Abidin *et al.*, 2008). We used colloidal silica as orthosilicic acid source. Colloidal silica upon dissolution produces soluble form of silica ion species and will pass through the dialysis membrane into the solution outside the membrane. The present study shows that imogolite can be synthesized by orthosilicic acid obtained from solid silica materials as orthosilicic acid source. The dialysis membrane method can be applied easily also for solid silica materials with high purity. However, it is difficult to use this method for silica material with low purity, because impurities will disturb imogolite formation. Therefore, pretreatment with acid or alkali is needed to remove the impurities in the silica samples before use as orthosilicic acid source.

Understanding the silica dissolution process and its mechanism is complicated because of the structural, compositional and variability of non crystalline solids involved in the process (Elliott, 1991). However, by using scheme, we have

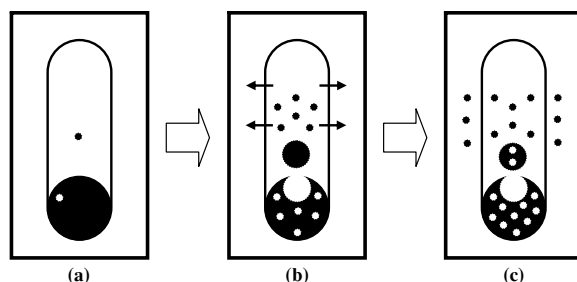


Fig. 6. Scheme of selective dissolution separation on silica by dialysis membrane (a) initial rapid dissolution (b) part of silica dissolved with size variations in the membrane (c) small part of silica dissolved will through pass into the outer part of membrane solution. However, the bigger one still remains in the membrane and continue dissolution process until equilibrium reached.

developed a picture on how silica could undergo dissolution in two ways into the solution through the dialysis membrane. Dialysis is the selective separation of species through a semi-permeable which separates two fluids. In a batch dialysis process with two compartments separated by a semi-permeable system, the process is normally allowed to develop until mass transfer equilibrium is reached.

The diameter of the pore size of the dialysis membrane used was about 50 nm. First, the part of silica will dissolved into solution with variation of soluble form of silica ion species size in the dialysis membrane tube. The soluble form of silica ion species with size less than 50 nm will pass directly into the solution outside the membrane. Second, the part of dissolved silica with size more than 50 nm still remains in the dialysis membrane. We used the term “selective dissolution separation” on this process as described in Fig. 6. By using this method, the most soluble silicic acid dominantly obtained from dissolution of solid silica material was the monomeric form with high purity than low polymeric silicic acid species.

The dissolution of silica will progress in the inner and outer part of dialysis membrane until the equilibrium concentration of monomeric silica form is reached. However, this dissolution process will continue to produce more monomeric silica in the solution and cause significant polymerization of the monomeric silica to form oligomeric silica form. Therefore, it is important to control orthosilicic acid concentration in the solution to less than 5 mM to avoid polymerization reactions. There are some important points to be considered for optimization of the dissolution process by a combination of batch and flow systems. The particles size and purity of samples, heat treatment, aging time and pH of the solutions play important roles in the kinetic dissolution of silica.

#### *Genetic implication*

The relationship between the origin of imogolite and allophane is indicated by their association in the weathered parent materials and similar chemical composition. Since the first description of imogolite by Yoshinaga and Aomine

(1962), its occurrence in weathered pumice grain has been reported from several countries, especially in Japan. The fairly pure imogolite as gel films was found in the pumice beds in Kitakami, Japan and in the basaltic saprolites in Maui, Hawaii (Yoshinaga and Aomine, 1962; Wada *et al.*, 1972).

The important factor in the formation of imogolite and allophane in soil is the sufficient Si and Al ions in the solution. Thus, suitable conditions such as high rainfall, temperate and low pH that leads to rapid weathering of parent mineral aids in their easy formation. The weathering commences in the differential weathered crusts from the un-weathered cores within the pumice sub surface that exist in the pumice grain. The outward diffusion may leach some elements from the pumice grain by rainwater or groundwater. Field and microscopic observations on Kitakami pumice showed that imogolite is often found in the outer part of pumice, whereas allophane is in the inner part (Wada and Matsubara, 1968).

Abidin *et al.* (2007) already explained the differences in the mechanism of formation imogolite and allophane in experimental and theoretical methods. By assuming that the alkaline- and alkaline-earth metal ion is concentrated more in the inner part of pumice than in the outer part, the formation of imogolite is easier in the outer part of pumice and allophane formation is easier in the inner part of pumice. Addition of alkali and alkaline-earth metal ions inhibit imogolite formation and on facilitate allophane formation more in presence of Ca and Mg than Na and K. These metal ions affect dissociation of the silanol group of orthosilicic acid. The dissociation or non-dissociation of orthosilicic acid causes differential formations of imogolite and allophane.

Molecular orbital calculation (*ab initio*) showed that the model with non-dissociated orthosilicic acid induces the formation of imogolite with tubular morphology. The shape of cluster model was asymmetrical in molecular configuration. The calculation, on the other hand, showed that the model with dissociated orthosilicic acid gives rise to the formation of allophane with hollow spherical morphology because of the symmetrical configuration of cluster model. Both experimental and molecular orbital calculation results proved that the dissociation of the Si–OH has an important role in the differential formation of allophane and imogolite.

The present study revealed important information on the mechanism of genetic formation of imogolite and allophane in basaltic saprolites in Maui, Hawaii. By assuming that parent weathered materials in the environment is heterogeneous with some impurity. During early weathering process, the dissolution of silicate and aluminum or aluminate ions or suspended hydrous silica and alumina derived from the parent weathered material include dissolved impurities. In such conditions, allophane or proto-imogolite or amorphous materials are formed earlier than imogolite formation.

With increasing time, exceptionally high rainfall, tropical, temperate and humid climatic conditions accelerate leaching of impurities and make the parent weathered materials more homogenous. The dissolution of silicate and aluminum ion with less impurity will be more favorable for imogolite formation. Other possibility of pathway reaction in imogolite formation is a change from the solid

allophane or proto-imogolite or other amorphous materials to the hydrous gel. In this case, allophane or proto-imogolite or other amorphous materials are intermediate products during early weathering process and will be transformed to imogolite because these intermediate products have unstable structures. Transformation to imogolite from allophane or proto-imogolite processes seems much more likely to result from periodicity in deposition controlled by climatic cycles such as high rainfall, tropical, temperate and humid conditions.

## REFERENCES

- Abidin, Z., N. Matsue and T. Henmi (2007): Differential formation of allophane and imogolite: experimental and molecular orbital study. *J. Comp. Aid. Des. Mat.*, **14**, 5–18.
- Abidin, Z., N. Matsue and T. Henmi (2008): A new method for nano-tube imogolite synthesis. In *Proceedings of the 2007 International Microprocesses and Nanotechnology Conference Kyoto, Japan. Jpn. J. App. Phys.*, **47**(6), 5079–5082.
- Cradwick, P. D. G., V. C. Farmer, J. D. Russell, C. R. Masson, K. Wada and N. Yoshinaga (1972): Imogolite, a hydrated aluminum silicate of tubular structure. *Nat. Phys. Sci.*, **240**, 187–189.
- Elliott, S. R. (1991): Medium-range structural order in covalent amorphous solids. *Nature*, **354**, 445–452.
- Farmer, V. C. and A. R. Fraser (1978): Synthetic imogolite, a tubular hydroxyaluminium silicate. In *International Clay Conference 1978, Proceedings of the VI International Clay Conference 1978*, organized by the Clay Minerals Group, Mineralogical Society, London. *Developments in Sedimentology*, **27**, 547–553.
- Farmer, V. C., J. D. Russell and M. L. Berrow (1980): Imogolite and proto-imogolite allophane in spodic horizons: evidence for a mobile aluminum silicate complex in podzol formation. *J. Soil Sci.*, **31**, 673–684.
- Henmi, T. and P. M. Huang (1987): Effect of phosphate on the formation of imogolite. p. 231–236. In *Proceedings of the International Clay Conference 1985, Denver*, organized by the Clay Minerals Society, Bloomington, Indiana.
- Iller, R. K. (1979): *The Chemistry of Silica*. Wiley, New York, 866 pp.
- Inoue, K. and P. M. Huang (1984): Influence of citric acid on the natural formation of imogolite. *Nature*, **308**, 58–60.
- Parfitt, R. L. and T. Henmi (1980): Structure of some allophanes from New Zealand. *Clays Clay Miner.*, **28**, 285–294.
- Tani, M., C. Liu and P. M. Huang (2004): Atomic force microscopy of synthetic imogolite. *Geoderma*, **118**, 209–220.
- Wada, K. (1989): Allophane and imogolite. p. 1051–1087. In *Minerals in Soil Environment*, 2nd ed., ed. by J. B. Dixon and S. B. Weed, Soil Science Society of America, Madison, Wisconsin, U.S.A.
- Wada, K. and T. Henmi (1972): Characterization of micropores of imogolite by measuring of quaternary ammonium chlorides and water. *Clay Sci.*, **4**, 127–136.
- Wada, K. and I. Matsubara (1968): Differential formation of allophane, imogolite and gibbsite in the Kitakami pumice bed. *Trans. 9th Int. Congr. Soil Sci.*, **3**, 123–131.
- Wada, K., T. Henmi, N. Yoshinaga and S. H. Patterson (1972): Imogolite and allophane formed in saprolite of basalt on Maui, Hawaii. *Clays Clay Miner.*, **20**, 375–380.
- Yoshinaga, N. and S. Aomine (1962): Imogolite in some Ando soils. *Soil Sci. Plant Nutr.*, **8**, 22–29.
- Yoshinaga, N., H. Yotsumoto and K. Ibe (1968): An electron microscopic study of soil allophane with an ordered structure. *Am. Mineral.*, **53**, 319–323.