

## ULTRASONIC VELOCITY MEASUREMENT IN IMOGOLITE-BASED COLLOIDAL SOLUTION AND THIXOTROPIC HYDROGEL

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### ABSTRACT

The ultrasonic velocities in a colloidal solution and a thixotropic hydrogel containing imogolite are measured. Our original experimental setup can detect the change of ultrasonic velocity caused by the mixing of imogolite and maleic acid in pure water. Using this setup, the ultrasonic velocity is found to remain unchanged during the macroscopic solid/liquid transition and viscoelastic change of a thixotropic hydrogel consisting of imogolite and maleic acid, which is consistent with previous literatures. Thus, the ultrasonic velocity measurement proves to be effective for the detection of well-dispersed clay minerals in diluted state, regardless of the phase and viscoelastic change of substances.

Key words: imogolite, ultrasonic waves, hydrogel, thixotropy, phase transition

### INTRODUCTION

Ultrasonic testing, which is one of the most frequently used nondestructive testing techniques, has been extensively employed for internal flaw detection and material characterization (Krautkrämer and Krautkrämer, 1990). In particular, evaluation of ultrasonic velocities has been widely used to investigate material properties such as elastic constants, porosity, and grain size in solids (Hübschen, 2016), and density and compressibility in liquids (Povey, 1997). Consequently, this technique has been used for the characterization of clays. To date, the properties of shale (e.g., pore size distribution) containing different types of clay minerals (Kuila and Prasad, 2010) have been measured using dry samples (Vanorio *et al.*, 2002 and Gong *et al.*, 2018).

On the other hand, since clay minerals are utilized as components in functional solutions and hydrogels (Shikinaka *et al.*, 2014a, b), the measurement of their properties in diluted state is also essential. However, the current techniques, which include transmission electron microscopy and synchrotron X-ray scattering, are complicated to perform and induce denaturation of the samples (Bergaya *et al.*, 2006). To solve these problems, we propose an easy and noncontact technique for the detection of clay minerals in diluted state that is based on ultrasonic velocity measurement, which is able to estimate the presence of substances in its solution.

In this study, we demonstrate this idea by measuring the ultrasonic velocity in a colloidal solution and a hydrogel containing imogolite. Imogolite is an aluminosilicate clay mineral that consists of rigid single-walled cylindrical nanotubes of composition  $(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH}$  (Farmer *et al.*, 1977, 1983). Due to the presence of many hydroxyl groups such as alminol (outer) and silanol (inner) on its surface, imogolite nanotubes disperse well in polar solvents such as water. The imogolite nanotube has a high aspect ratio, i.e., its external diameter is about 2 nm and its length is several tens of nanometers to several micrometers. Recently, imogolite nanotubes were cross-linked by hydrogen bonding *via* dicarboxylic acids, causing gelation of an imogolite-based colloidal solution (Shikinaka

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*et al.*, 2014a). Moreover, a homogenous gel consisting of imogolite and maleic acid showed hysteresis-free thixotropic nature, owing to the characteristics of imogolite as perfectly rigid polyelectrolyte (Donkai *et al.*, 1985) at a certain mixing ratio of aluminol groups in imogolite to carboxyl groups in maleic acid such as 1 : 1. Herein, we measure the change of ultrasonic velocity in a colloidal solution and a hydrogel containing imogolite to detect well-diluted clay minerals in solvent in a noncontact manner.

## MATERIALS AND METHODS

Deionized water further purified using a Milli-Q® Advantage A10® system (Millipore™, Eschborn, Germany) was used throughout the experiments. Other reagent-grade chemicals, except for imogolite, were purchased from Tokyo Kasei Chemicals and Wako Pure Chemical Industries and used as received.

Imogolite was synthesized and purified according to the method described in Farmer *et al.* (1983) and Shikinaka *et al.* (2015) as follows. Aqueous solutions of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (9.96 g in 369 mL of purified deionized water; Kanto Chem. Co. Inc., Japan) and  $\text{Na}_4\text{SiO}_4$  (6.90 g in 362 mL of purified deionized water; Junsei Chem. Co. Ltd., Japan) were mixed to prepare a solution containing 12.5 and 2.5 molL<sup>-1</sup> of Al and Si, respectively. The pH of the mixture was adjusted to 6.0 by rapidly adding ca. 26 mL of 1.0 molL<sup>-1</sup> NaOH aqueous solution (the solution was stirred to avoid the occurrence of locally high pH). The resulting solution was stirred for 1 h. The resultant white precipitates were collected by centrifugation and were then redispersed in 400 mL of water under stirring. After adding further 2400 mL of water, the solution pH was adjusted to 4.5 by adding 7–8 mL of 1.0 molL<sup>-1</sup> HCl. The solution was then carefully and continuously heated for 4 days at 100°C under gentle stirring. The as-prepared imogolite solution was then cooled to room temperature, and a fine powder of sodium chloride (16.4 g) was added under stirring. The resulting gel was collected by centrifugation (5000 rpm, 30 min) and was subsequently washed portionwise with 500 mL of water using a 100 nm Millipore filter under suction. The wet products (caution should be taken to stop the samples from drying out) were added to 1800 mL of tetrahydrofuran (stabilizer-free grade) under stirring, and the fluffy precipitates were collected by filtration and dried *in vacuo*, resulting in a yield of 42%. For the preparation of the imogolite-based colloidal solution, a calculated amount of imogolite in pure water (for preparing 6.4 wt% colloidal solution) was sonicated for 4 h at 100 W (FU-21H, SDUltra Ltd., Korea), while maintaining room temperature by intermittent addition of ice to the sonicator bath. Through this procedure, slightly opaque solutions of 0.2 molL<sup>-1</sup> aluminol functional groups were obtained, and the average length of imogolite nanotubes in the solution was shortened to 131 nm, which was confirmed by transmission electron microscopy (Shikinaka *et al.*, 2015). For the 0.08 molL<sup>-1</sup> imogolite aqueous solution (1 equivalent with respect to the  $-\text{Al}(\text{OH})_2$  group), the same volume of aqueous solution of 0.08 molL<sup>-1</sup> maleic acid was added under stirring to obtain a hydrogel (Shikinaka *et al.*, 2014a).

The ultrasonic velocity in a solution was measured using

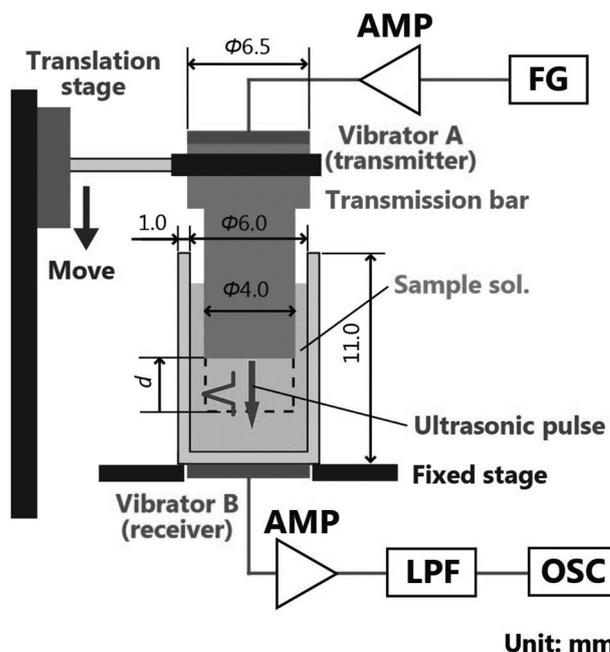


Fig. 1. Sketch of the experimental setup for measuring ultrasonic velocity. AMP: amplifier, FG: function generator, LPF: low-pass filter, OSC: oscilloscope.

our original setup shown in Figure 1. This setup is an improved version of our previously reported setups (Hayashi *et al.*, 2011, 2012, Minakawa *et al.*, 2013). Using a pipette, the sample solution was injected into an acrylic cylindrical container with a height of 11.0 mm, an inner diameter of 6.0 mm, and a thickness of 1.0 mm. The room temperature was 20°C. Before a thixotropic gel (i.e., imogolite–maleic-acid gel) was employed as the sample, it was well shaken to ensure it maintained its liquid state. Using a function generator and an electrical amplifier, a rectangular pulse voltage (peak voltage: 10 V, repetition rate: 100 Hz, duty ratio: 0.3%) was generated and applied to a vibrator A (transmitter; resonance frequency: ca. 357 kHz) attached to an aluminum bar (with a step horn used to amplify the vibration). The vibration generated at the vibrator A was transmitted to the bottom of the bar, and the ultrasonic wave was emitted and propagated in the solution. When the ultrasonic wave reached a vibrator B (receiver) attached to the bottom of the container, the corresponding voltage was output from the vibrator B. After noise suppression by low-pass filtering (cut-off frequency: 1.59 MHz), the output signal was observed using an oscilloscope. The propagation time  $t_a$ , which is defined as the time required for the ultrasonic wave to reach the vibrator B, is not influenced by the multiple reflections inside the solution and the bottom of the container. Therefore, by measuring  $t_a$  while changing the relative position  $d$  of the vibrator A (note that  $d$  was defined to be positive when the vibrator A was far from the vibrator B), the ultrasonic velocity in the solution can be determined as  $\Delta d / \Delta t_a$ , where  $\Delta d$  and  $\Delta t_a$  indicate the changes in  $d$  and  $t_a$ , respectively.

## RESULTS

Figure 2 shows the output waveforms obtained when

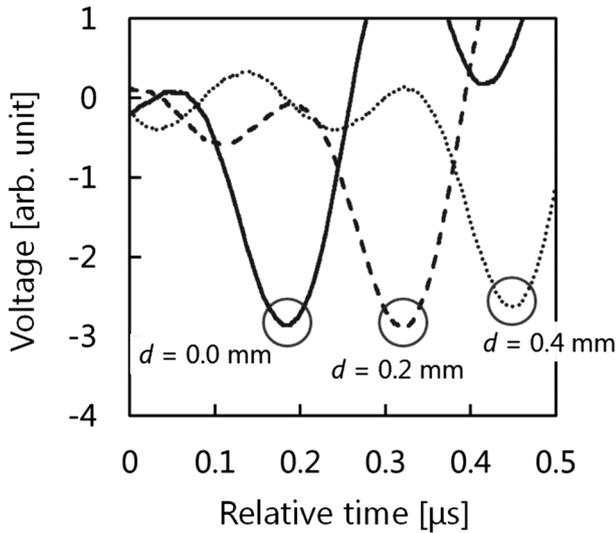


Fig. 2. Output waveforms of the receiver obtained at different vibrator positions  $d$  when the ultrasonic pulses transmit through the imogolite–maleic-acid gel.

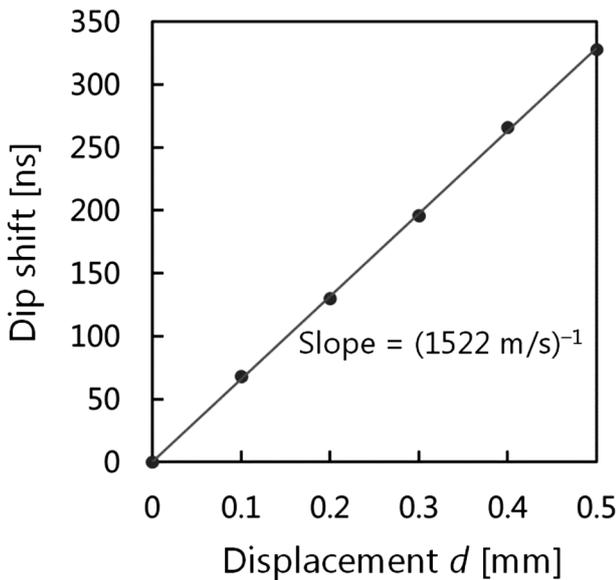


Fig. 3. Calculation of ultrasonic velocity from the dip shift dependence on the vibrator displacement  $d$  by linear fitting.

the relative positions  $d$  of the vibrator A were 0.0, 0.2, and 0.4 mm, respectively, when using the imogolite–maleic-acid gel (Shikinaka *et al.*, 2014a) as the sample. Clear dips (indicated by red circles) indicated the first detection of the ultrasonic wave. As expected, the appearance of the dip was delayed as  $d$  increased. The dependence of the dip shift on the displacement  $d$  was well fitted by a linear trend (Figure 3), and the inverse of the slope of this trend gives the ultrasonic velocity in the solution. Thus, the ultrasonic velocity  $V$  in the imogolite–maleic-acid gel (liquid state) was calculated to be  $1,522 \text{ ms}^{-1}$ .

In the same manner, the ultrasonic velocities  $V$  of pure water, imogolite-based colloidal solution, maleic acid solution, and imogolite–maleic-acid gel were measured, and the corresponding results are summarized in Table 1. The measured  $V$

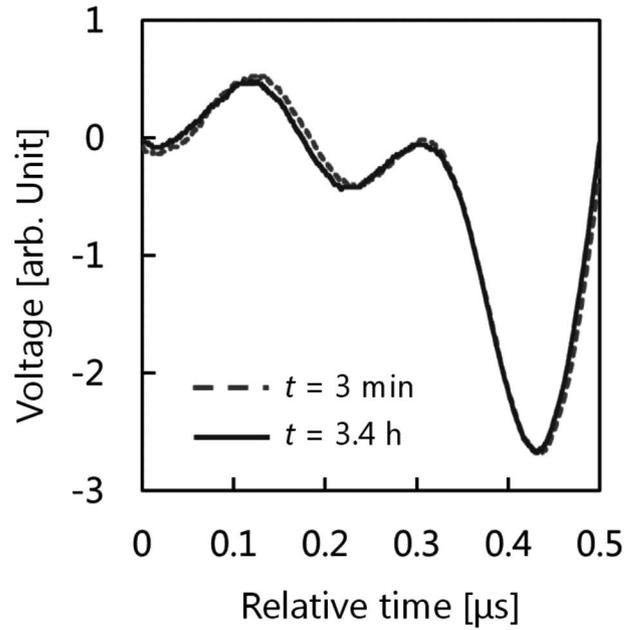


Fig. 4. Output waveforms of the receiver when ultrasonic pulses transmit through the imogolite–maleic-acid gel at liquid state ( $t=3 \text{ min}$ , dashed curve) and gelled state ( $t=3.4 \text{ h}$ , solid curve).

Table 1. Measured ultrasonic velocities  $V$  of various solutions.

Solution	$V$ [ $\text{ms}^{-1}$ ]
Pure water	1,499
Imogolite colloidal solution	1,460
Maleic acid solution	1,603
Imogolite–maleic-acid gel	1,522

value of pure water ( $1,499 \text{ ms}^{-1}$ ) was in good agreement with the theoretical and measured values found in the literature (Lubbers and Graaff, 1998), which proves the correctness and accuracy of our setup for measuring the ultrasonic velocity. After imogolite was mixed,  $V$  decreased ( $1,460 \text{ ms}^{-1}$ ) probably because of the high crystallinity of imogolite relative to water. In contrast, the maleic acid water solution exhibited a higher  $V$  value ( $1,603 \text{ ms}^{-1}$ ) than pure water and the imogolite–based colloidal solution, which may originate from the hydration of maleic acid molecules by water molecules. In addition, it is reasonable that the  $V$  value of the imogolite–maleic-acid gel (liquid state) fell between those of the imogolite–based colloidal solution and the maleic acid solution.

Finally, we measured the temporal change in the ultrasonic velocity of the imogolite–maleic-acid gel ( $0.04 \text{ mol L}^{-1}$  in this experiment), which shows gelation within 1 h [Shikinaka *et al.*, 2016]. Figure 4 shows the output waveforms of the receiver when the ultrasonic pulses transmitted through the thixotropic gel at liquid state ( $t=3 \text{ min}$ ) and gelled state ( $t=3.4 \text{ h}$ ). The two output waveforms were almost identical, which indicates that the ultrasonic velocity in the thixotropic gel is not largely affected by the liquid/solid transition. This result is in good agreement with that previously reported (Norisuye *et al.*, 2006).

## CONCLUSION

The ultrasonic velocities in imogolite-based colloidal solution and thixotropic hydrogel were measured in this study. The velocity of pure water was found to change after imogolite was mixed. In contrast, the ultrasonic velocity did not show any dependence on the gelation of the imogolite-based colloidal solution caused by its crosslinking *via* maleic acid. The obtained results pave the way for the detection of diluted clay minerals in solvents using ultrasonic waves. Furthermore, the experimental results show that the ultrasonic velocity differs depending on the molecular species (i.e., imogolite or maleic acid) and the mixing of several molecules (i.e., hydrogel consisting of imogolite and maleic acid). This feature provides a new possibility for the detection of species and the amount of clay minerals by ultrasonic velocity measurement even in coexistence with other organic molecules, which cannot be performed by other noncontact measurement techniques such as dynamic light scattering in the diluted state of clay minerals.

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