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Original Article

# Characterization of halloysite from Thung Yai District, Nakhon Si Thammarat Province, in Southern Thailand

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#### Abstract

Halloysite obtained from Thung Yai District, Nakhon Si Thammarat Province, Southern Thailand was characterized by X-Ray fluorescence (XRF), X-Ray diffraction (XRD), Fourier transform infrared (FTIR), a zeta potential analyzer, thermal analysis (TGA and DTA), scanning (SEM), and transmission (TEM) electron microscopy. SEM and TEM analysis showed that it consisted mainly of hollow microtubules and plates with typical dimension of 0.08-0.20  $\mu$ m diameter and lengths of 0.50-4.50  $\mu$ m. XRF analysis showed that it consisted mainly of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.37 indicated that a 1:1 clay mineral was the dominant component. It had a high Fe<sub>2</sub>O<sub>3</sub> (2.27%) and TiO<sub>2</sub> (2.72%) content. XRD analysis showed that the halloysite was mainly in its dehydrated (7Å basal spacing) form with some kaolinite, quartz and anatase. Semi quantification in clay by XRD after formamide treatment showed that it was approx. 70% halloysite. FTIR was used to distinguish between the different types of clay minerals and provided information concerning their structure. TGA and DTA were used to examine the dehydroxylation and other thermally induced caused changes of the halloysite. The charge (zeta potential) behavior of the halloysite was negative over the relevant pH range (>2) and indicated that the material has a potential for binding of cationic drugs or could be used as a coating polymer from solution.

Keywords: halloysite characterisation, clay, southern Thailand

# 1. Introduction

Halloysite is defined as aluminosilicate clay, present in natural deposits, and it is chemically similar to kaolinite, but has a hollow tubular structure. Typically, the inner diameter, outer diameter, and length of the halloysite tubule are 1-30 nm, 30-50 nm, and 100-2,000 nm, respectively (Mingliang

\* Corresponding author. Email address: tripop.b@psu.ac.th *et al.*, 2010). Kaolinite sheets were rolled into tubes because of the strain caused by lattice mismatches closely aligned silicon dioxide and aluminum oxide layers (Nicolini *et al.*, 2009). According to the state of hydration, halloysite occurs mainly in two different groups: the hydrated form (10 Å) with the minimal formula  $Al_2Si_2O_5(OH)_4$ •2H<sub>2</sub>O, and the dehydrated form (7 Å) with the minimal formula of  $Al_2Si_2O_5(OH)_4$ . The 10 Å halloysite is usually found in humid regions. In areas with dry climate, the hydrated halloysite has rarely been reported. In a xeric environment when the surface soil temperatures often exceed 40°C, 10 Å halloysite is likely to convert irreversibly into its 7 Å form. The most common morphology of halloysite is a nanoscale (shaped like a nanotube). Other less common morphologies have also been observed, such as platy and spheroidal crystals.

The main occurrences of halloysite are in weathered or hydrothermally altered rock, saprolites, and soil. Under comparable rainfall condition, soils derived from rhyolitic tephra tend to yield halloysite, while those from basaltic parent material are dominated by allophone and imogolite (Joussein et al, 2005). Halloysite had been reported to form by alteration of feldspars, biotite, and volcanic glass. Halloysite derived from volcanic glass has a spheroidal morphology, whereas the dominant morphology of tubular halloysite derived from crystalline minerals, such as feldspars and micas although other forms had been observed (Yariv and Shoval, 1976). Generally, the relative abundance of halloysite with respect to kaolinite decreases with increasing weathering degree (Joussein et al., 2005). Both halloysite and kaolinite were presented in kaolin deposits in a wide range so that distinguishing of these was difficult because of their structural similarity, especially when the halloysite component appeared in the dehydrated form. Intercalation of formamide was used to differentiate dehydrated halloysite from kaolinite (Nicolini et al., 2009).

Due to the tubular morphology it is interesting to compare halloysite with carbon nanotubes as shown in Table 1. Halloysite has some applications in biocompatible nano-containers. Aluminosilicate chemistry is not toxic and durable with high mechanical strength. In addition, halloysite is inexpensive; the world supply is in excess of thousand tons per year. Accordingly a true mass-scale might be used in industrial applications (Yuri *et al.*, 2008).

Recently, researchers focused on the applications of halloysite as indicated by the rapid growth in related publications. Historically, halloysite was used to produce high quality ceramics in manufacturing of porcelain, bone china, fine china and crucible products, for example, which have been the main application. Currently, scientists and engineers have developed several new applications for this unique, cheap, and abundantly available naturally occurring clay with nanoscale lumens. Applications of halloysite nanotube are for examples: (1) controlled release of anticorrosion agents; (2) sustained release of herbicides, insecticides, fungicides, and antimicrobials; (3) sustained release of drugs (cosmetics, dermatology), fertilizers, and food additive; (4) plastic fillers for strength enforcement and protection (e.g., radiation or ultraviolet stability); (5) catalytic materials and molecular sieves; (6) specific ion adsorbent; (7) encapsulation of hydrogen storage materials and (8) use in advanced ceramic materials (Yuri *et al.*, 2008).

This study aims at characterizing halloysite samples from a newly found deposit in Thung Yai District, Nakhon Si Thammarat Province. The structural changes of halloysite induced by heat treatment were determined using XRD, TGA, and DTA. Other characterizations were performed using XRF, FTIR, SEM, TEM, and zeta potential measurement. These properties are important in terms of applications.

# 2. Materials and Methods

#### 2.1 Study area

Halloysite samples were collected from Thung Yai District, Nakhon Si Thammarat Province as shown in Figure 1. The deposit is found on an alluvial and flood plain of the Tapi River, approximately ¼ km<sup>2</sup> in area (mining lease area). The top surface is brownish yellow clay about 1.0 meter in thickness, overlying dark brown ball clay of 1.0-2.0 meters thick. The bed underneath is white kaolinite of 6.0-10.0 meters thickness. Locally, there have been some reports of pinkish clay deposits occurring as lenses or pockets of a few meters. According to the mining lease the ball clay reserve is estimated to be 126,000 metric tons, and the kaolin reserve is about 480,000 metric tons.

#### 2.2 Mineralogical and chemical analysis

All samples were first desegregated through a 100 mesh sieve shaker (Nitto, ANF -30). The mineralogical analysis of clay samples was carried by XRD. To obtain the pattern of the clay more clearly for XRD analysis,  $a < 2 \mu m$  fraction was first analyzed on a glass slide. The  $< 2 \mu m$  clay sample fraction was obtained by an oriented aggregated specimen prepared using a filter membrane technique (Drever, 1973; USGS, 2001). A 0.45  $\mu m$  membrane filter was placed on a glass slide mounted and placed over a suction flask. A pipetted sample was added to the flask and suction was applied to force the sample onto the membrane filter. The membrane filter was then placed upside down on a glass slide, pressure

Table 1. Comparison of halloysite and carbon nanotubes (Yuri et. al., 2008).

	halloysite nanotubes	carbon nanotubes
Inner diameter $\times$ length	15 nm × ca. 1,000 nm	$2 \text{ nm} \times \text{ca.} 1,000 \text{ nm}$
biocompatibility	biocompatible	toxic
Price <sup>a</sup>	\$4 per kg	\$500 per kg
Availability	thousand tons	grams

<sup>a</sup> Average value based on information from several companies.



Figure 1. Map and photograph of the sampling locality of the clay deposit in Thung Yai District, Nakhon Si Thammarat Province; modified from DMR. Note: Maenam = river.

was applied and the membrane filter was removed, leaving the extract adhering to the slide. For clay mineralogical analysis samples of these were dried at room temperature. Others were glycolated overnight at 65°C for detection of expandable minerals, and others heated for 3 hrs at 400°C and 550°C (Baccour *et al.*, 2009). The crystalline phases present in the materials were examined by XRD (Phillips X'Pert MPD) Cu-K $\alpha_1$  radiation ( $\lambda$ =1.5406 Å) tube 40 kV and a current of 30 mA, and the diffraction pattern from 5°-90 (2 $\theta$ ) at a step size of 0.02° (2 $\theta$ ). Quantification of the different phases was carried out using the computer program X'-pert High Score Plus. The chemical composition was determined by WDXRF in a Phillips PW2400 apparatus.

### 2.3 Scanning electron microscope

Microstructures were examined by SEM, after coating with gold using a JEOL, model JSM-5200.

#### 2.4 Thermal analysis

DTA (DTA7, Perkin Elmer) and TGA (TGA7 Perkin Elmer) were used to study the kinetics of any phase transformation processes and chemical reaction mechanisms up to 1,300°C with a heating rate of 10°C/min. The finely ground sample was introduced into a platinum crucible and placed in the furnace along with the reference sample.

#### 2.5 Transmission electron microscope

TEM images were obtained by a JEM 2010, JEOL microscope operating at 160 kV. The samples were suspended in ethanol deposited drop-wise and evaporated on 200 mesh copper grids covered with amorphous Formvar carbon.

# 2.6 Zeta potential analyzer

Zeta potential measurements of dilute halloysite suspensions (0.1 mg/ml) in an aqueous electrolyte solution (0.001 M KCl), with pH adjustment using 0.1 M HCl or 0.1 M NaOH, were performed using a Model ZetaPALS, Brookhaven, USA. The operating conditions were checked and adjusted using a calibrated latex solution (zeta potential =  $-50\pm5$  mV) supplied by the instrument manufacturer.

# 2.7 Fourier transform infrared spectroscopy

The characterization by FTIR was performed in an Equinox 55, Bruker spectrophotometer, using pellets obtained by pressing mixtures containing approximately 1 mg of sample and 99 mg of KBr. Each spectrum was obtained in the transmission mode, with a resolution of 2 cm<sup>-1</sup>, in the region of 4,000-400 cm<sup>-1</sup>.

#### 3. Results and Discussion

# 3.1 SEM and TEM study

SEM studies indicated that the sample was uniform in content, containing many tubules with the presence of occasional particle agglomerates (Figure 2). Figure 3 shows the transmission electron micrographs of halloysite. The majority of the sample consists of cylindrical tubes of 0.08-0.20  $\mu$ m diameter and length of 0.50 to 4.50  $\mu$ m. The results for the determinations of the mean size and size distributions using TEM images are presented in Figure 4. The mean diameter and length are 0.13 and 2.48  $\mu$ m, respectively. TEM images clearly indicate that the lumen of the halloysite was empty.

# 3.2 Mineralogical and chemical analysis

#### 3.2.1 XRF study

The chemical analysis and the loss on ignition at 900°C are present in Table 2. The major compositions are  $SiO_2$  and  $Al_2O_3$  because of the presence of clay minerals and quartz. The ratio  $SiO_2/Al_2O_3$  is 1.37 and indicates that the dominant component of the clay was a 1:1 mixture. The SiO<sub>2</sub>/



Figure 2. Scanning electron micrographs of the representative clay sample.



Figure 3. Transmission electron micrographs of the representative clay sample.



Figure 4. Actual size and size distribution pattern of clay obtained from transmission electron micrographs: diameter (left) and length (right).

Table 2. Chemical composition of the representative sample.

Conc. (%)							LOI (%)		
Na <sub>2</sub> O	MgO	$Al_2O_3$	$SiO_2$	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	900°C
0.05	0.08	34.10	46.86	0.80	0.13	2.72	2.27	1.37	12.6

 $Al_2O_3$  is slightly greater than 1.0 because of the presence of some quartz. This is supported by the low concentrations of Na, Mg, K, and Ca. The Fe and Ti contents are relatively high. Newman and Brown (1987) noticed that high Fe concentration is occasionally present in halloysite.

# 3.2.2 XRD study, intercalation of formamide into halloysite and heat treatment

Figure 5 shows the XRD pattern of the studied clay. The following mineralogical phases were identified: halloysite (H), kaolinite (K), quartz (Q), and anatase (A). XRD is used to characterize halloysite and to determine it in dehydrated or hydrated form. The plot for the halloysite shown in Figure 6 shows the basal spacing reflections indicating a sharp peak at  $12^{\circ}(2\theta)$  which translate to a (001) basal spacing of 7 Å. There is also an absence of a peak at 8.8° (2 $\theta$ ) indicating the absence of the 10 Å form, which is indicative of hydrated halloysite.

Churchman and Theng (1984) found that formamide can be intercalated into halloysites of varying composition. By contrast, kaolinite intercalates formamide very slowly and then only incompletely. They use this difference in the behavior of kaolinite and halloysite toward formamide to provide a rapid and simple test to distinguish between the two mineral types. These procedures can be used for the semiquantitative estimation of halloysite and kaolinite. The X-ray diffraction patterns of the set of samples obtained by the intercalation of formamide into halloysite are shown in Figure 7. The dehydrated halloysite shows a characteristic first



Figure 5. XRD of the representative clay sample; H=halloysite; K=kaolinite; Q=quartz; A=anatase.



Figure 6. XRD diffraction patterns of the representative clay sample



Figure 7. XRD patterns of clay sample after air dried and treated with formamide for 1 hour.

peak at 7 Å. It was observed that after the intercalation halloysite moves from 7 to 10 Å.

The degree of intercalation was assessed from the ratio of the intensity of the appropriate basal reflections. The degree of intercalation is given by the ratio  $a = I_{10}/(I_7+I_{10})$ where  $I_7$  and  $I_{10}$  denote the intensity of the peak near 7 and 10 Å, respectively. The halloysite proportions were refined by subtracting the respective peak ratio of the sample. Figure 8 shows a plot of the percentage halloysite in synthetic mixtures with kaolinite vs. the peak ratio of the respective values after expansion with formamide. Each ratio as obtained on the basis of either the peak intensity or the peak area (Theng et al., 1984) corresponded closely to the respective percentage of halloysite in the mixture. The results indicated that there was a general equivalence from the intensity and area for estimating the percentages of the halloysite forms. The percentage of halloysite in a given sample was obtained by multiplying the corrected ratio by 100. In this experiment  $I_{10}=2168$  count,  $I_7=275$  count calculating  $\alpha = 0.7$ . The estimated percentage of halloysite from Figure 8 is approx. 70%. After heat-treatment, the intensity of all reflections increased and the (001) reflection became sharp at 400°C. In the 550 °C

heat-treated specimens the reflections apparent in the original sample were not observed. Halloysite is considered to increase its crystalinity as the temperature is increased up to 400 °C. This is because the residual inter-layer of water between the kaolin layers is lost with the rise of treatment temperature that causes the arrangement of kaolin unit layers to be the same order as that in the metakaolin. At 550 °C the structure of halloysite begins to disintegrate due to the slow disappearance of the lattice water. Then the lattice water completely disappears. Therefore, its crystallinity drops.



Figure 8. Variation in basal peak ratio with percentage halloysite in synthetic mixtures with kaolinite, ratios refer to complexes with formamide obtained on basis of either peak (Theng *et al.*, 1984)



Figure 9. XRD diffraction patterns of sample after air dried and heat-treated 400°C and 550°C

# 3.3 Differential thermal analysis

The TGA and DTA curves of the clay sample with heattreatment are shown in Figure 10. The endothermic reaction  $(E_n)$  caused by the loss of the lattice water in the halloysite, changes the peak height and the area of this reaction reduces in the specimen heated to 471°C, this fact seems to indicate the rearrangement of ions in the metakaolin state. In the exothermic reaction (*Ex*) taken place at 1002°C associated with the mullite nucleation the features of this reaction were the same as those for kaolinite.

# 3.4 FTIR study

Figure 11 shows the FTIR spectra of the halloysite. The absorptions bands at 3,695 and 3,620 cm<sup>-1</sup> in the FTIR spectrum were assigned to the stretching vibration due to the inner-surface of O-H groups of halloysite, respectively. The interlayer water is indicated by the vibration at 1,647 cm<sup>-1</sup>. The 1,111 cm<sup>-1</sup> peak was assigned to the stretching mode of



Figure 10. TGA and DTA graphs of the representative clay sample.



Figure 11. FTIR spectra of the representative clay sample.

Si-O, while the band at 1,030 cm<sup>-1</sup> was caused by the stretching vibration of Si-O-Si. The band observed at 538 cm<sup>-1</sup> was due to the vibration of Al-O-Si. The vibration of the innersurface hydroxyl group at 912 cm<sup>-1</sup> and Si-O-Si at 470 cm<sup>-1</sup> confirm the existence of corresponding groups. The bands observed in the halloysite showed no significant changes, since the majorities are assigned to Si-O and Al-O bonds.

# 3.5 Zeta potential study

The zeta potential curve for halloysite was determined over a wide pH range (Figure 12). It is apparent from the plot that the surface charge of the mineral is only slightly negative at a low pH, but as the pH value increased from pH 3 to 8 the surface charge fell to reach a plateau at  $\sim 20$  mV. The reason for the negative surface charge with increasing pH is that in its curved structure, the silica is mainly positioned on the outer surfaces of the tubule, whereas the alumina is present mainly on the inner surface and edges of the tubules. Exposure of both oxides to water caused the formation of the surface hydroxyl group (sur-OH). Since the surface is mainly silica, the surface charge will be negative over a wide range of pH, as being evident in the zeta potential plot.

#### 4. Conclusion

The morphology of halloysite was observed to have tubular, a few microns long particles with cross-sections of the order of 0.08-0.20  $\mu$ m. The clay was rich in structural Fe<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub>. The distribution between the kaolinite and halloysite forms was identified by XRD and SEM. The clay was composed mainly of halloysite with some kaolinite, quartz and anatase. The FTIR was used over 400 to 4,000 cm<sup>-1</sup> region to study of the vibrational spectrum of the clay mineral structure. The various vibration modes were attributed to the O-H, Si-O and Al-O bonds. The structural changes of the halloysite with heat treatment were also studied. Three processes were identified. The first process was accompanied by the loss of the inter-layer and adsorbed water, and the second process by the loss of the lattice water. The third process induced an amorphous state similar to that of metakaolin with a re-arrangement of ions taking place for the mullite



Figure 12. Zeta potential curves of the representative clay sample.

nucleation. Over a wide range of pH, the clay has a negative electrical zeta potential, which allows for medium dispersibility. At a pH above 3, halloysite should bind cationic drugs or could be used as a polymer for coating from solution.

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