

## An Investigation on the Effect of Solvent and Heat to Clay Minerals in Shaly Sandstone

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**Abstract:** Core cleaning could be complicated for samples that contain a high amount of clays. Some clays are delicate and exposure to solvent and heat would damage or alter its properties. In this study, we investigated the effect of direct exposure of solvent and heat to clay mineral properties based on petrographical data from X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-Ray (EDX). Experiments were performed on sidewall core samples taken in a shaly sand zone. The FTIR data did not show any changes at the molecular level to the clay mineral after direct contact with the selected solvent. The FESEM images showed some illite floccules collapse in the samples exposed to oven-drying at 60 °C.

**Keywords:** clay minerals; core cleaning; petrography; solvent; heat exposure

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### ■ INTRODUCTION

Core analysis data is an important source of information for understanding formation characteristics as well as for calibrating with down hole well log data. Therefore, the information should be obtained from core samples that are representative of their native states and free from contaminants. Drilling mud and its additives are well-known sources of contamination that occur during drilling. It may alter rock surface chemistry and consequently affected important rock properties. These contaminants must be removed prior to any other measurement. However, the removal of these contaminants could be complicated especially from tight and delicate samples. Unsuitable techniques and solvent used in the cleaning process might lead to undesirable measurements as a result of the alteration of native rock properties. It has been reported that properties such as porosity, permeability and wettability are highly affected by the technique and solvent used in cleaning [1-4]. For samples with high clay content, the usage of solvent and exposure to heat might alter the electrochemical properties of the minerals.

Clay minerals are phyllosilicates with the tetrahedral layer and octahedral layer as the basic building block. The tetrahedral layer consists of either Si or Al bonding with the basal oxygen in tetrahedral coordination while the octahedral layer consists of cations (Si, Al or Mg) bonding with the basal oxygen in octahedral coordination. The structure of the clay determines its physical, electrochemical, rheological and thermal properties [5-6]. The alumino-silicates minerals appear as layering either in 2:1 or 1:1 ratio. In 1:1 clay minerals, the repetition of tetrahedron-octahedron (T-O) sheets in one layer disallows for alkali metal cations or water molecules to exist between them. In 2:1 structure the repetition of tetrahedron-octahedron-tetrahedron (T-O-T) sheets in one layer provides space for cations occupancy [7]. Smectite and illite are examples of 2:1 phyllosilicate (2 tetrahedral and 1 octahedral layer) and kaolinite is a 1:1 phyllosilicate. The 2:1 clay minerals only contain siloxane surfaces while the 1:1 clay minerals contain both the siloxane and hydroxyl surfaces [8]. The siloxane surface allows isomorphous substitutions by cations of lower valence at octahedral

sites, leaving the surface with positive charge deficiency. The charge deficiency is balanced by hydrated interlayer cations, which are easily released in water and exchanged with other cations, which contributes to electrical conductivity. Water can be bonded to the exchangeable cations or directly to the clay mineral surface.

Soxhlet extraction is one of the normal procedures used in core cleaning. In the Soxhlet procedure heat is introduced to vaporize the solvent, which also exposed the samples to heat. The samples were exposed to another heat by oven drying to remove pore water after cleaning. Nevertheless, earlier studies have been reported that exposure to heat during cleaning and drying would have impacted the rock properties. Bush and Jenkins [9] reported increasing errors in dry porosity and permeability for decreasing the values of the parameters. This was due to the removal of adsorbed water on the clay surface when exposed to heat in a Soxhlet procedure. From the study, it was suggested that at least one to two layers of adsorbed water on the clay surfaces should be retained when measuring the permeability and porosity of cores. Soeder et al. [4] claimed that unhumidified drying could cause a significant increase in permeability as a result of hydration water removal and the collapse of clay minerals.

A study by Pallatt et al. [10] exhibited that dehydration and shrinkage of clay minerals due to oven-dried had produced much higher permeability as compared to the wet and preserved state. Since clay minerals is a material that originally has a hydrophilic character due to the presence of the surface hydroxyl ( $-OH$ ) groups that link easily to water molecules, hydration due to heat might affect the bonding to water molecules. This will consequently affect its electrical properties, which is related to the electrical current flow through hydrated clay surfaces. As an alternative, solvent flush cleaning without vapor is recommended for samples with delicate clays but this method incurs high cost and Soxhlet is preferable.

The use of solvent and heat in core cleaning is common to effectively remove mud contamination and pore fluid prior to the measurement of other rock properties. The possible effect of solvent to rock properties is balanced with the need to remove the

contaminants in order to bring back the rock sample to its native state. Other than the effect of heat discussed earlier on, other studies also reported the effect of some organic solvent of varying polarities and dielectric to clay structure at a molecular level [11]. In this study, we analyzed any changes that might occur to the clay mineral structure as a result of the cleaning process. The mineral was analyzed X-Ray Diffraction (XRD), Fourier Transform Infra-Red (FTIR), Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-Ray (EDX).

## ■ EXPERIMENTAL SECTION

### Materials

Laboratory analysis was performed on fresh samples taken in the Malay Basin where high compaction was expected. The sample was cored in the shaly sand zone on top of a gas reservoir and was preserved at low temperatures from the well site to protect from heat and keep the moisture. Gamma Ray from good log shows high reading indicating high shale content. As synthetic oil based mud was used during drilling, high resistivity reading at the near borehole wall as shown by induction log data indicates high mud contamination. The sample was carefully handled and preserved from the well site. Therefore, it was expected that any changes that would be observed after cleaning is due to response to the solvent and heat; and not from the surrounding effects.

### Procedure

#### XRD

Relative mineral content was analyzed using the Empyrean XRD equipment. The mineralogical analysis using XRD was performed in a few steps involving bulk clays, glycolation, and heating at 350 and 550 °C. For first evaluation of the relative amount of bulk clays, a powdered sample was scanned over a  $2\theta$  range of 2–70° with CuK $\alpha$  radiation (1.5406) at a scan step time 148.92 and step width of 0.0260°. The generator was set at 40 mA and 45 kV. The proportion of clay minerals in the sample was further analyzed at clay size < 2  $\mu$ m. 1.5g of the powdered sample was mixed with 3 drops of calgon

in a small tube to further break down the sample particles. Thirty milliliter distilled water was added and the mixture was well shaken before entering the ultrasonic bath for 10 min. Sample slurry was left for 24 h before air-dried on glass slides. The sample was then scanned using the same configuration as for bulk measurement. Ethylene glycol was used to detect the swelling components and estimate the illite-smectite composition. Sample on the glass slide was put side by side with ethylene glycol in a container and put in the oven at 80 °C for 30 min before scanned again. The sample was heated to 350 and 550 °C for 30 min before scanned again to distinguish kaolinite from chlorite.

#### FTIR, FESEM, and EDX

Two types of FTIR equipment were used to analyze the mineral content and structural change. The quantitative analysis was performed using bench top FTIR while Perkin Elmer FTIR Spectrometer was used to generate the spectrum in the range between 400 to 4000  $\text{cm}^{-1}$ . Both types of equipment used the attenuated total reflection (ATR) method. The mid-range of infrared frequency was chosen as many minerals exhibit vibration modes within this range. For sample preparation, four offcuts from the sample were cleaned with four different types of solvent; methanol, toluene, chloroform and azeotrope (70% chloroform and 30% methanol). The effluent was checked every day until no further changes in

the color were observed. The effluent was analyzed using Gas chromatography–mass spectrometry (GCMS) to study the component of contaminants being removed. Three types of drying were used for the samples cleaned with toluene; ambient, 60 °C with 40% humidity and 60 °C oven dry. Samples were ground to fine powder form prior to FTIR analysis. The powdered samples were also analyzed using Quanta FEG 450 FESEM and EDX.

## RESULTS AND DISCUSSION

### XRD Analysis

XRD data indicates the mineral constituents of the sample are consist of illite, kaolinite, chlorite, and quartz (Fig. 1). Characteristic reflection related to 10 Å periodicity that remains unchanged after ethylene glycol treatment indicates the presence of illite. Further confirmation is achieved with unchanged reflection after 350 and 550 °C treatment. Kaolinite and chlorite were identified from the reflection related to 7 Å that remains unchanged following ethylene glycol treatment. There are no changes in the reflection after 550 °C ignition indicates the presence of kaolinite rather than chlorite. Residual reflection identified at 7 Å is corresponding to kaolinite whereas chlorite would be destroyed at 450 °C heat [7]. However, the unchanged reflection after 550 °C heating could also indicate the existence of antigorite together with kaolinite. The presence of chlorite is indicated by the

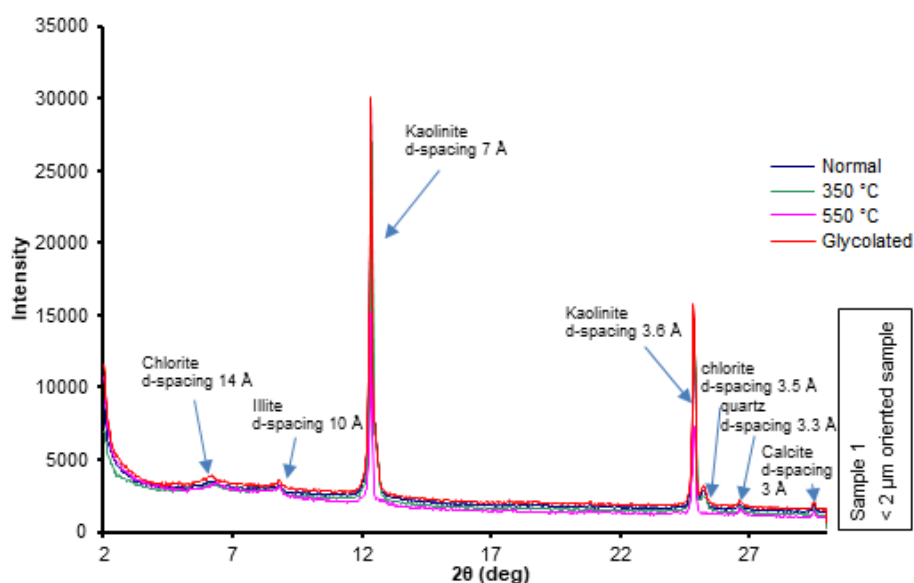


Fig 1. X-Ray Diffractogram of the sample

reflection at 14 Å periodicity that is unaltered following glycolation. The reflection slightly collapsed after 550 °C heating shows the presence of vermiculite alongside with the other minerals. Quartz was identified based on reflection related to 3 Å periodicity in the data.

### EDX

The quantitative EDX analysis (Table 1) suggested O and Si as dominant elements in the sample. These elements are common in both quartz and clay minerals. Al and K, which are common in illite and kaolinite are found in smaller quantities. Fe also found in small quantities, which confirms the presence of illite as indicated by XRD and FTIR data. Minor concentrations of Na and Mg were also found in the sample. Mg is common in illite but Na is usually found in smectite. Since the XRD data did not indicate the presence of smectite, Na found in the EDX data could be attributed to residual impurities.

### FTIR

Using the benchtop FTIR the mineral spectrum of the samples was automatically compared to a spectral library stored in the equipment. The mineral content in the samples was produced as a percentage as in Fig. 2. Consistent with the XRD result, FTIR data also recorded the presence of quartz, illite, kaolinite and chlorite. For the purpose of analysis, 10% tolerance is accepted for comparison of mineral content in each sample. Samples from toluene and chloroform recorded the same amount of quartz, illite, kaolinite and chlorite (within the acceptable tolerance). Samples from methanol and azeotrope recorded more quartz and less illite. Kaolinite

and chlorite also presence in a smaller amount. The difference could be due to inefficient cleaning by methanol as inferred by the effluent's color. It had been observed that the effluent from samples in methanol was clear while effluent from toluene and chloroform were blackish. Effluent from azeotrope showed lighter color as compared to toluene and chloroform. This indicates that toluene and chloroform provide efficient cleaning while methanol is not suitable for this type of mud. This is supported by a study by Gupta et al. [2], who reported that toluene and chloroform have similar cleaning efficiencies. On the other hand, methanol is more suitable for removing polar components and dissipated salt [1]. The presence of mud contamination could have concealed the actual spectrum. The GCMS result indicates an abundance of alkane hydrocarbon (tridecane, undecane, ethyl, cyclopentane) and acid (oxalic and sulfuric) and no traces of components from

Table 1. EDX result

No	Element	Weight %	Atomic %
1	O	56.53 ± 1.54	70.52
2	Na	0.24 ± 0.12	0.21
3	Mg	0.29 ± 0.12	0.24
4	Al	5.44 ± 0.25	4.02
5	Si	32.52 ± 0.95	23.11
6	K	1.39 ± 0.17	0.71
7	Ca	0.36 ± 0.14	0.18
8	Ti	0.27 ± 0.16	0.11
9	Fe	2.37 ± 0.38	0.85
10	U	0.58 ± 0.5	0.05
Total		100	100

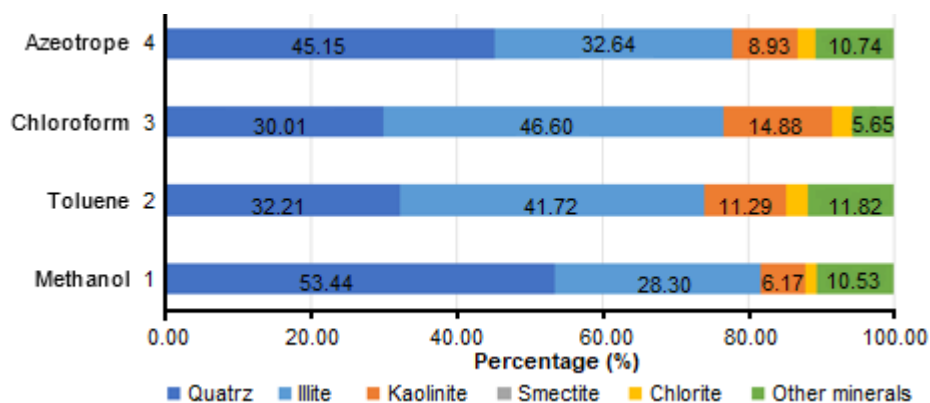
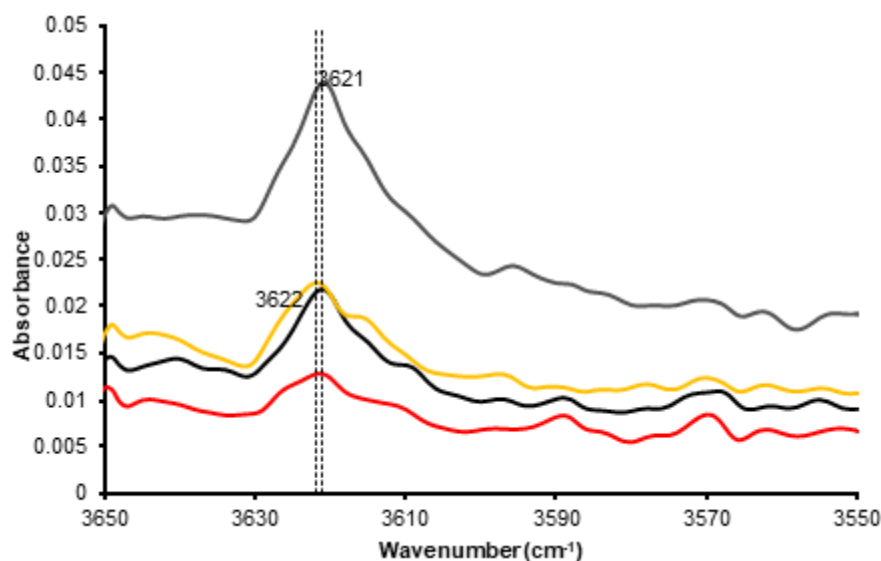


Fig 2. FTIR analysis result on percentage of clay minerals



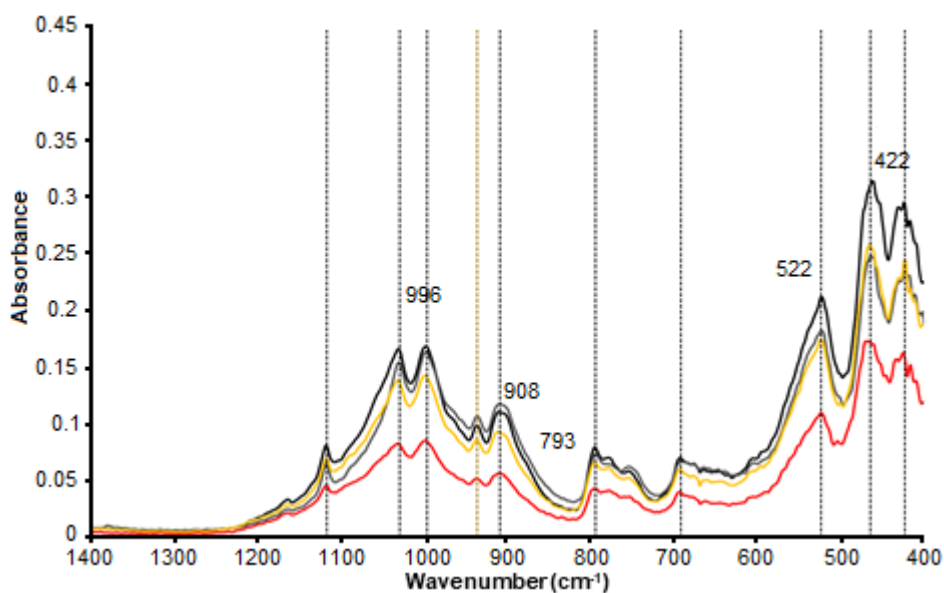
**Fig 3.** From top to bottom; FTIR spectrum for samples cleaned with chloroform, azeotrope, toluene, and methanol for 3600 to 3500  $\text{cm}^{-1}$

quartz minerals (O, Si). This excluded the possibility that quartz has been removed by toluene and chloroform.

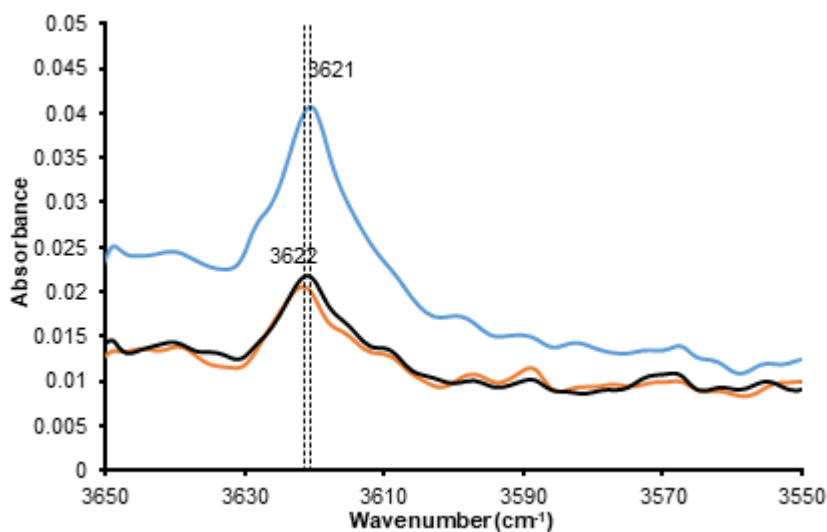
The FTIR spectrum of the samples was further analyzed to study any changes to the mineral structure. FTIR spectrum for all samples shows absorbance in the 1200-400  $\text{cm}^{-1}$  region and vibration at near 3620  $\text{cm}^{-1}$  (Fig. 3 and 4). The 3620  $\text{cm}^{-1}$  bands are corresponding to the stretching vibration of an inner hydroxyl group, lying between the tetrahedral and octahedral sheets [12]. The band is found in pure kaolinite and also in smectite that has a high amount of Al in the octahedral [12-13]. We believed that this energy bend represents kaolinite since smectite was unidentified by XRD analysis. The hydroxyl groups in kaolinite are bonded to octahedral cations, but residing largely within the plane of apical oxygen atoms that link the tetrahedral and octahedral sheets. The stretching region of samples cleaned with toluene, chloroform and azeotrope had shifted to higher energy band by 1  $\text{cm}^{-1}$  while the samples cleaned with methanol had shifted to higher energy band by 2  $\text{cm}^{-1}$  from the common band of pure kaolinite. Methanol is an intermediate polarity organic solvent, which has the ability to interact with clay surface oxygen and structural hydroxyl groups while toluene and chloroform are non-polar molecules that have a low influence on clay structure. Some other solvent with a very high polarity such as formamide had shown very strong nonbonding

interaction with Na-montmorillonite structure that consequently affect its hydraulic conductivity [11]. However, very low energy shifting indicated that the hydroxyl stretching is able to return to its original energy band. The shifting to 3622  $\text{cm}^{-1}$  in methanol exhibits an energy band as in dickite. Dickite is a 1:1 phyllosilicate that has identical chemical composition and structure of the individual layer to kaolinite but differs in the layer stacking arrangement. Kaolinite has a single-layer structure instead of double-layer polytype.

The energy band between 1200-400  $\text{cm}^{-1}$  in the samples are corresponding to stretching and bending of Si-O and bending of OH from several minerals. The vibrations at 1116, 1029, 996, 935 and 908  $\text{cm}^{-1}$  are closed to kaolinite with shifting to lower energy within 3 to 15  $\text{cm}^{-1}$ . These vibrations are attributes to Si-O stretching. The 908  $\text{cm}^{-1}$  energy band is closed to the inner surface OH groups bending region of kaolinite at 913  $\text{cm}^{-1}$ . All samples exhibited the same vibrations pattern that shows all solvent had a similar influence on the clay structure of the sample. 1029  $\text{cm}^{-1}$  energy band is close to Si-O stretching vibrations in illite at 1030  $\text{cm}^{-1}$  and muscovite at 1028  $\text{cm}^{-1}$ . The lower energy bands at 522, 463 and 422  $\text{cm}^{-1}$  carry almost similar patterns to those found in illite. No shifting in energy has been observed from all the samples.



**Fig 4.** From top to bottom; FTIR for samples cleaned with toluene, chloroform, azeotrope and methanol for 1200 to 400  $\text{cm}^{-1}$



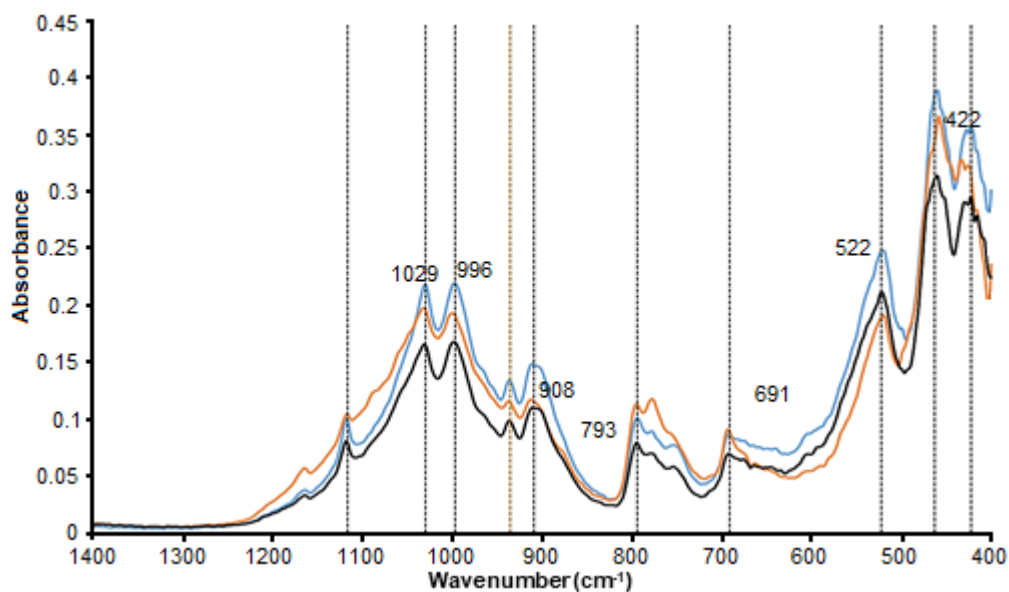
**Fig 5.** From top to bottom; the FTIR spectrum for samples dried at ambient, 60 °C humidity and 60 °C oven-dried for 3600 to 3500  $\text{cm}^{-1}$

The FTIR data for samples dried at ambient, 60 °C humidity and 60 °C oven-dried also shows a slight effect on the clay structure based on energy shifting in Fig. 5 and 6. All samples exhibited the same pattern with insignificant shifting in the energy band between 1200 to 400  $\text{cm}^{-1}$ .

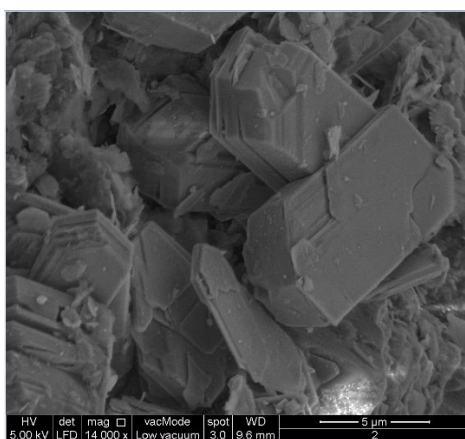
#### FESEM

FESEM images indicate that the clay minerals in the sample are dominated by kaolinite and illite (Fig. 7). The ragged appearance of the flat platelets exhibited that the

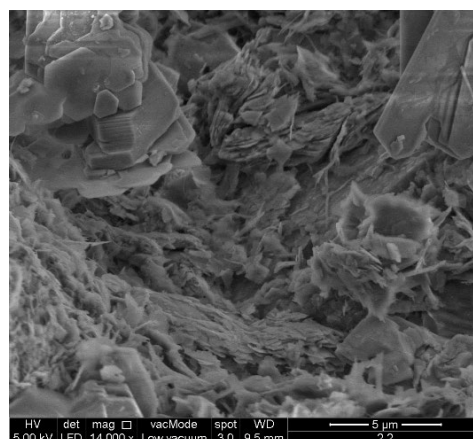
illite is detrital in origin [14]. These two types of clay minerals are common in the Malay Basin. Illite flocculation of typical edge-face cardhouse orientation has been observed in the sample after toluene cleaning and dried at ambient temperature (Fig. 8). Flocculation happens when clumps of electrostatically charged clay flakes sink in ion-enriched salty water and form a “cardhouse” structure of individual edge-face or edge-edge-oriented flakes and/or domains of face-face-oriented flakes. This may generate pores, which when



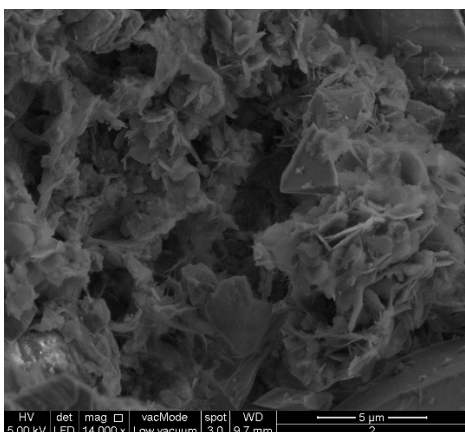
**Fig 6.** From top to bottom; the FTIR spectrum for samples dried at ambient, 60 °C humidity and 60 °C oven-dried for 1200 to 400 cm<sup>-1</sup>



**Fig 7.** Kaolinite surrounded by illite



**Fig 9.** FESEM image of the sample after oven-dried at 60 °C



**Fig 8.** FESEM image of illite flocculation for sample dried at ambient temperature

interconnected will form permeability pathways. The edge-face and face-face flocculation is common in clay aggregates and happens in the presence of either fresh or salt water [15]. The illite floccules and kaolinite structures show that the mineral survived and less affected by toluene cleaning.

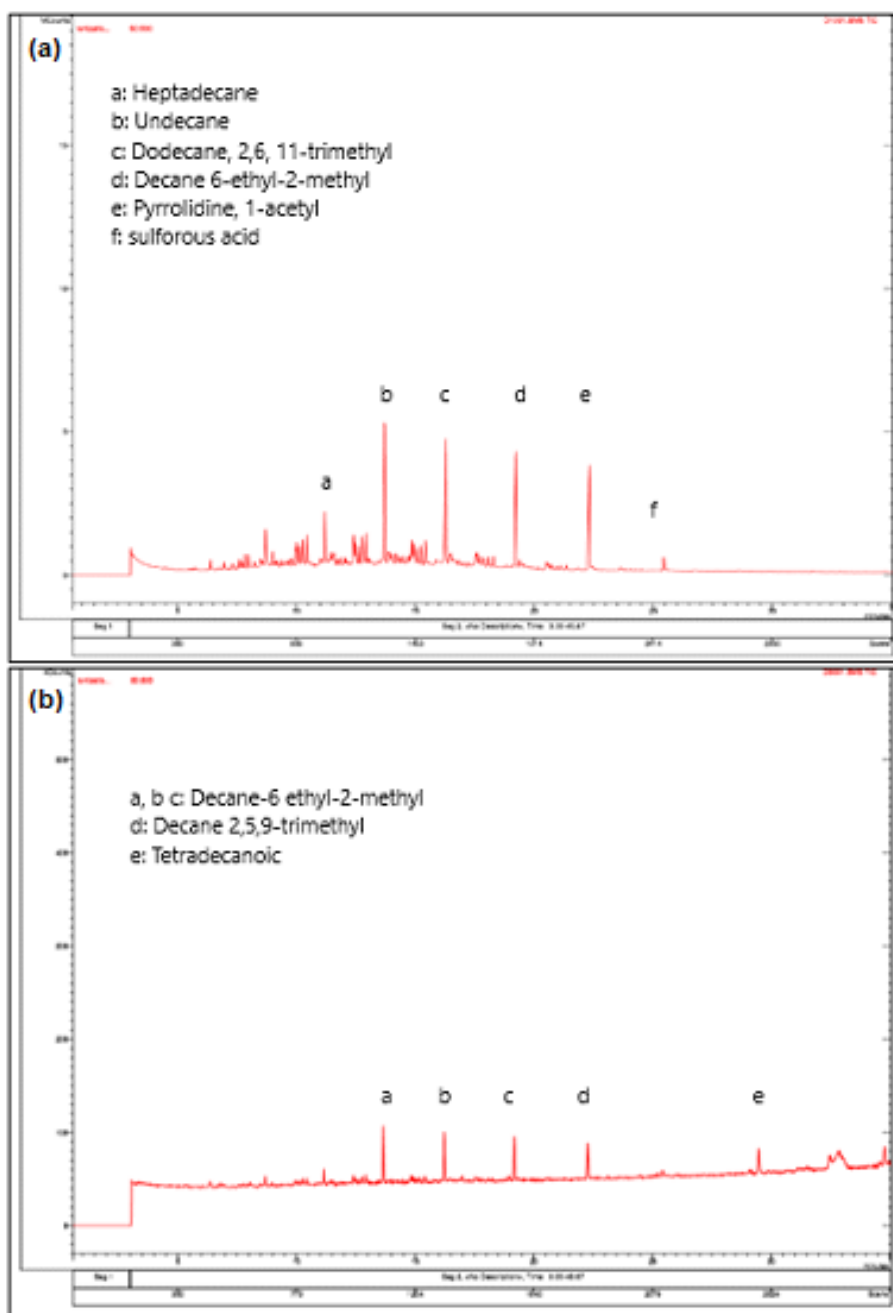
Floccules collapsed (Fig. 9) has been observed in the sample after 60 °C oven-dried. The collapse of the floccules structure might be due to dehydration upon oven-heating. A similar effect in a different type of illite clays had been observed in an earlier study by Pallatt et al. [10]. The SEM photograph of filamentous diagenetic

illite clays in the report showed that the open mesh was compacted against pore walls due to oven-drying. This had created a larger path for fluid to flow and increased permeability.

### GCMS

The Gas chromatography–mass spectrometry

(GCMS) result of effluent from methanol, toluene or chloroform cleaning shows no traces of clay mineral components being removed or dissolved in the solvents (Fig. 10(a) to (b)). The effluent from toluene shows a high amount of hydrocarbon component and acid, which is expected from the drilling mud contamination. This shows that toluene interacts well with hydrocarbon



**Fig 10.** (a) chromatogram for effluent from toluene cleaning and (b) chromatogram for effluent from methanol cleaning



in drilling mud but does not give any effect to the clay mineral. A lesser amount of hydrocarbon component was recorded in the effluent from methanol cleaning showing that methanol alone is less efficient to remove the contaminants but better interaction with water and salt. We did not manage to get the result for effluent from chloroform cleaning due to evaporation prior to the test.

## ■ CONCLUSION

The FTIR result showed that direct contact with the selected solvent does not give any impact at the molecular level to the clay minerals in the sample. Toluene and chloroform are very-low polarity solvents that do not have a strong ability to interact with water or negatively charged clay sheets but only with the hydrocarbon component from the synthetic based mud. Methanol is an intermediate polarity solvent that can interact with water and oxygen on the clay surface but the kaolinite, illite and chlorite constituted in the sample are a type of non-expandable clay minerals, which have a tight crystal structure and low bonding with water. Kaolinite and illite have been reported to release the physically bound water at temperatures 55 and 72 °C respectively [16] but the effect had not been observed from FTIR data in this study.

The illite floccules collapse from the FESEM images could possibly due to the heat exposure during oven-drying. This could lead to enlargement of the fluid flow path and consequently increase porosity and permeability. The impact of these two parameters was not investigated here but should be further studied alongside with the impact of other parameters such as wettability and electrical properties.

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