

# Effect of Bentonite on the Properties of Liquid Insulating Oil

Loai Nasrat, Mervat S. Hassan

**Abstract**—Bentonitic material from South Aswan, Egypt was evaluated in terms of mineralogy and chemical composition as bleaching clay in refining of transformer oil before and after acid activation and thermal treatment followed by acid leaching using HCl and H<sub>2</sub>SO<sub>4</sub> for different contact times. Structural modification and refining power of bentonite were investigated during modification by means of X-ray diffraction and infrared spectroscopy. The results revealed that the activated bentonite could be used for refining of transformer oil. The oil parameters such as; dielectric strength, viscosity and flash point had been improved. The dielectric breakdown strength of used oil increased from 29 kV for used oil treated with unactivated bentonite to 74 kV after treatment with activated bentonite. Kinematic Viscosity changed from 19 to 11 mm<sup>2</sup>/s after treatment with activated bentonite. However, flash point achieved 149 °C.

**Keywords**—Dielectric strength, unactivated bentonite, X-ray diffraction, SEM image

## I. INTRODUCTION

TRANSMISSION and distribution transformers form a critical, highly loaded and expensive part of the electricity generation and distribution network. The potential consequences of transformer failure can be quite damaging [1],[2]. The widespread use of transformer oil for high voltage insulation and power apparatus cooling has led to extensive research work aimed at enhancing both its dielectric and thermal characteristics [3].

Power transformers represent very important equipment in production and distribution of electric power. Since the liberalization of the electric energy market the cost pressure to the utilities increased, which has forced a change in management strategy in several business segments. Taking a look to the technical and economical aspects of operating a distribution grid the length of life in correspondence to the drop out risk of electric power equipment is coherence.

For the estimation of the technical condition of a power transformer the following parameters have to be considered: life cycle characteristics, overload times, maintenance strategies and measures. The coherence between life cycle characteristics and temperature excursions of the oil insulation system due to overloads has been studied [4]-[6].

Transformer oil is prone to undergo irreversible changes in its chemical and dielectric properties due to ageing. Factors, such as temperature, oxygen, humidity, copper electrical field and electrical discharges may accelerate the ageing process [7],[8]. Moreover, transformer oil may act as an information carrier whose condition may be related to condition of the power transformer.

Now after a life period of 40 to 60 years many transformers must be replaced or respectively retro filled in the next five to ten years. After a century of oil use, starting with vegetable oil via PCB's leading to conventional transformer oil, improvement with some additive like TiO<sub>2</sub>, Bentonite or fullerenes and nanotubes, there is the question for a further improvement. The following are available on the market and some of the alternative fluids are already in common use in transformers and reactors at voltage levels up to several tens of kilovolt [9],[10].

The generic name of active or activated clay is used to indicate a variety of argillaceous silicates, with similar behavior under certain conditions, but more or less different in composition and structure. These silicates can be modified in several ways to obtain the desired properties associated with activated clay.

Smectite clays (bentonite, montmorillonite) do not have sufficient activity to be commercially interesting, therefore must undergo the activation process in which clays are either put through a severe treatment with mineral acid or thermal treatment and/or grinding followed by acid leaching. These processes involve the distortion of the mineral structure and the removal of metallic ions through acid leaching, leaving pores within the structure. Porous materials prepared via this technique show potential industrial applications [11]-[15].

In this study, the relationship between enhancement of liquid insulating oil properties and changes in textural and structural properties of bentonite from south of Aswan through heat and acid treatment were investigated.

## II. MATERIALS AND METHODOLOGY

Egyptian bentonite was selected for this study. This particular bentonite is mined in South Aswan. About 85 percent of the crude clay is Ca- montmorillonite, which has some substitution of Al<sup>3+</sup> for Si<sup>4+</sup>. The principle exchangeable cation is calcium, and the cation exchange capacity is 93 meq/100g. Main impurity in this bentonite is kaolin in addition to quartz as non-clay mineral. Purified Ca-montmorillonite, sample was calcined at 600 and 700°C for 2 hrs. The calcined samples were treated with 25 wt. % sulfuric acid for one hour at 98°C. Another aliquot of Ca-montmorillonite subjected to acid treatment using 4 M HCl for 4 hrs. The activated samples were washed several times until trace of aluminum sulfate ion was removed. The samples were dried overnight at 60°C.

### A. Characterization

A Philips PW 1730 powder X-ray diffractometer with Fe-filtered Co K $\alpha$  run at 30 kV and 20mA was used to examine Ca- montmorillonite and activated products. The infrared vibrational spectra were recorded on Jasco Fourier transform spectrometer at University of Cairo. For each sample, 128 scan were accumulated in the spectral region 4000-400 cm<sup>-1</sup> with the transmittance mode and a resolution of 4 cm<sup>-1</sup>. The

Loai Nasrat is with the Electrical Eng. Dept., Faculty of Engineering, South Valley Univ., Aswan, Egypt, (Tel: +2-01005135520, e-mail: loaisaad@yahoo.com)

Mervat S. Hassan is with the Central Metallurgical R & D Institute, Cairo, Egypt, (e-mail: hassan\_mervat@yahoo.com)

KBr presses disk was prepared with 0.4 mg of sample and 200 mg of KBr. Selected samples were observed on fractured surface under a Philips S-2400s SEM at the Geological Survey of Egypt. The samples coated by Au. N<sub>2</sub> adsorption-desorption isotherms were measured with Nova-1200 from Quantachrome after a degassing overnight at 100°C. The specific surface areas were calculated from nitrogen adsorption isotherms at 77 K. The BET equation was used for corresponding calculation, SBET, was calculated using the N<sub>2</sub> adsorption data in the relative pressure region between 0.01-0.1. The external surface area (*S<sub>ext</sub>*), mainly of the surface of mesopores and micropore volumes (*V<sub>t</sub>*), were calculated by the t-plot method [16]. The difference between the specific surface area (SBET) and the external surface area is referred to as the surface area of micropores (*S<sub>t</sub>*). The total pore volume of the pores < 500 Å (*V<sub>p</sub>*) was obtained from the adsorption data at a relative pressure of 0.98, calculated with the B.J.H. method [17].

#### B. Oil Specimen

During this study all oil specimens have been obtained from power transformer of 40 MVA, 132/33/6 kV and 25 Tons of mineral oil manufacturing year 1978, for EL-PROM-Bulgarea. Table I shown the symbol codes of used and refining oil before and after treatment with unactivated and activated bentonite. Dielectric breakdown strength (kV) measurements are carried out under alternative current (AC) voltage for used and refining oil samples. In the AC breakdown experiment, the AC 50 Hz voltage which is linear increased is applied to the electrodes until the breakdown occurs [11]. The increasing speed of the voltage is 2 kV/s.

The instrument being used in the AC breakdown voltage measurement is a vessel for transformer oil AC breakdown voltage measuring. Physical properties such as; kinematic viscosity (mm<sup>2</sup>/s) and flashpoint (°C) have been carried out to different oil specimens according to ASTM D445 and D92 respectively.

TABLE I  
UNITS FOR MAGNETIC PROPERTIES

Oil Specimens	Symbol Codes
Used Oil	A
Oil treated with unactivated Bent.	B
Oil treated with acid activated Bent.	C
Oil treated with activated Bent.(600°C followed by acid leaching)	D
Oil treated with activated Bent.(700°C followed by acid leaching)	E

### III. RESULTS AND DISCUSSION

#### A. Sample composition

The mineralogical composition of the studied sample obtained by XRD is showing in Figure 1. Ca-montmorillonite is the principal clay minerals phases present in this sample (15.04 Å) followed by kaolinite (7.14 Å) and illite (9.87 Å). Quartz (3.33 Å) is the main non-clay minerals followed by feldspar (3.21 and 3.18 Å). Montmorillonite was identified by its expansion from about 15.04 Å to 17.10 Å after glycol treatment (Fig.2). Upon heating up to 600 °C for 2 h. d001 of montmorillonite shifted to 9.74 Å due to collapsing of montmorillonite structure. However, characteristics peaks of kaolinite disappeared upon heating process due to transformation of kaolinite to metakaolinite.

The X-ray diffraction patterns of dealuminated montmorillonite (acid activation, 600 and 700°C followed by acid leaching) is given by Fig. 3. The montmorillonite d001 shifted from 15.04 Å to 9.74 Å at 600 °C to 9.81 Å at 700 °C. Meanwhile, acid activation of montmorillonite using 4M HCl for 4 h. causing reduction in intensity and broadening of the d001.

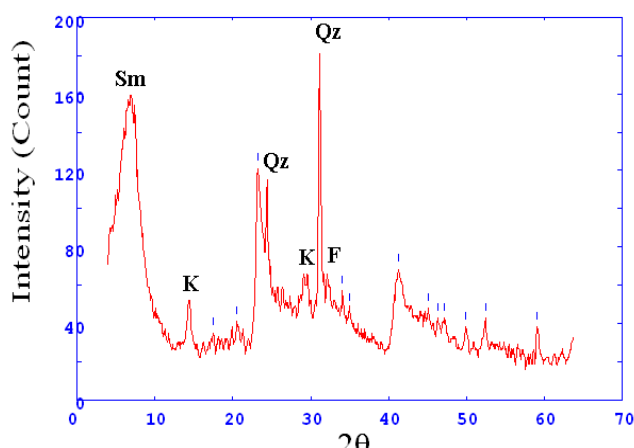


Fig. 1 X-ray diffraction pattern of Ca-montmorillonite

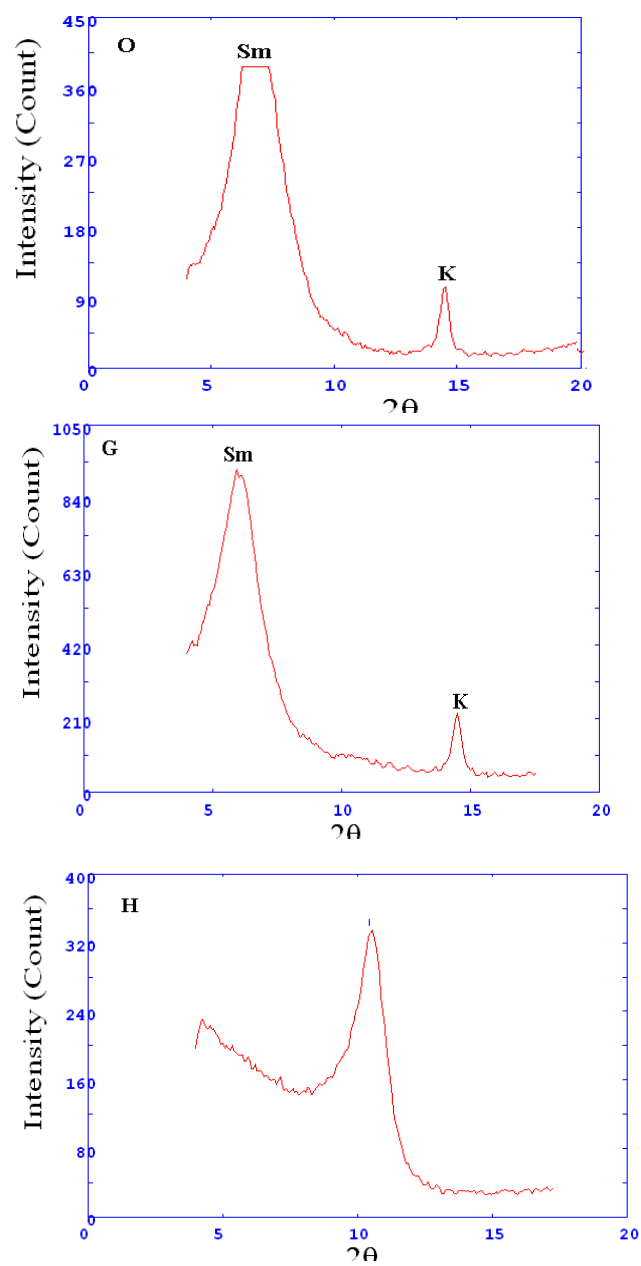


Fig. 2 X-ray diffraction pattern of < 2μm clay frac  
 O=Oriented <2μm clay fraction; G=Glycolated <2μm clay fraction; H=heated <2μm clay fraction at 600 °C for 2h

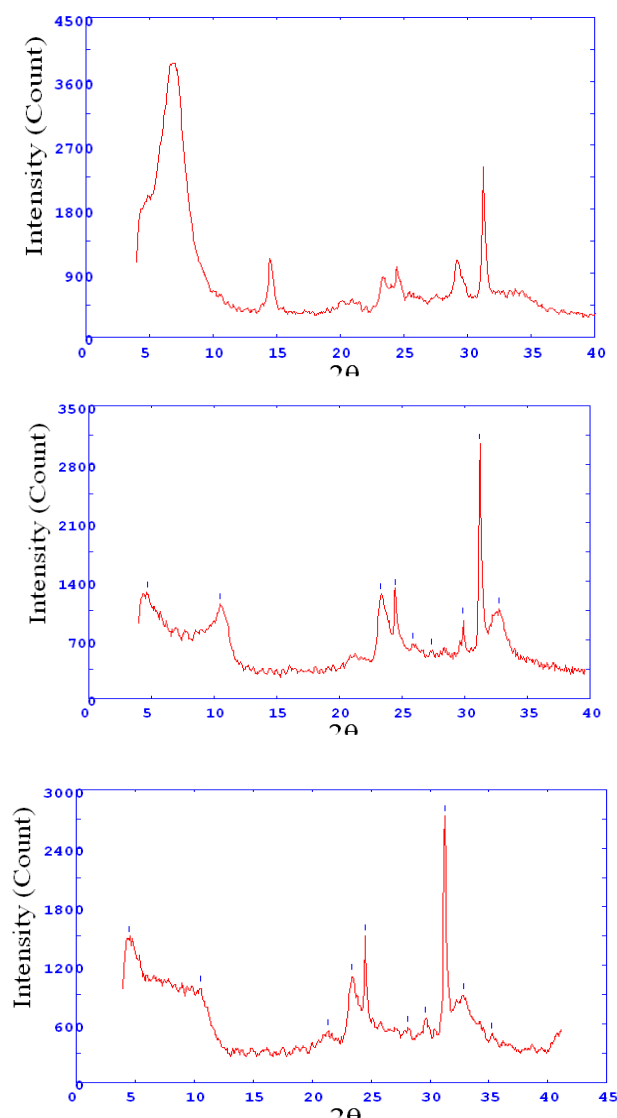


Fig. 3 XRD patterns of activated bentonite ; A= Acid activated bentonite; B= 600 °C+ acid leaching; C= 700 °C+ acid leaching

Table II is showing the chemical data of the bentonite. Alumina and silica are the main components followed by Fe<sub>2</sub>O<sub>3</sub>, MgO and Na<sub>2</sub>O in abundance. Fe could be attributed to either “free” iron (iron oxide or oxyhydroxide) and “structural” iron. Meanwhile, MgO and Na<sub>2</sub>O could be located within montmorillonite structure. K<sub>2</sub>O could be attributed to feldspar.

TABLE II  
CHEMICAL ANALYSIS OF BENTONITIC CLAY

Oxides	Symbol Codes
SiO <sub>2</sub>	55.4
Al <sub>2</sub> O <sub>3</sub>	14.87
K <sub>2</sub> O	0.72
CaO	0.63
TiO <sub>2</sub>	0.83
SO <sub>3</sub>	0.13
Fe <sub>2</sub> O <sub>3</sub>	5.00
MgO	2.28
Na <sub>2</sub> O	1.08
MnO	0.012
Cl	0.85
LOI	18.85

The most prominent feature of the FTIR spectra of studied bentonite (Fig.4) was a wide band at  $1050\text{ cm}^{-1}$ , which corresponds to the Si-O stretch of the phyllosilicate clay structure [18]. This band was not fully resolved because of the considerable thickness of the clay film. Other structural vibrations were also observed. Bands at  $3646$  and  $3703\text{ cm}^{-1}$  corresponded to stretching vibrations of structural OH groups. The  $3703\text{ cm}^{-1}$  band is characteristic of kaolinite and the  $3646\text{ cm}^{-1}$  band is commonly found in many different phyllosilicate minerals [19]. The  $692\text{ cm}^{-1}$  band is a structural OH libration, and a band at  $930\text{ cm}^{-1}$  corresponds to a deformation mode of the  $\text{Al}_2\text{OH}$  group. The shoulder near  $880\text{ cm}^{-1}$  is assigned to  $\text{AlFeOH}$  vibrations, proving the presence of iron in the octahedral sheets of montmorillonite [18]. The  $\text{AlMgOH}$  vibrations are not observed in the spectra homoionic montmorillonite, thus proving relatively low Mg content in the octahedral sheets [20]. The remaining bands were assigned to water vibrations. Bands at  $3473\text{ cm}^{-1}$  are stretching vibrations (3 and 1 modes). Meanwhile, the bands at  $3933$ ,  $2891$ ,  $1469$ ,  $1415\text{ cm}^{-1}$  are attributed to the organic component of the oil.

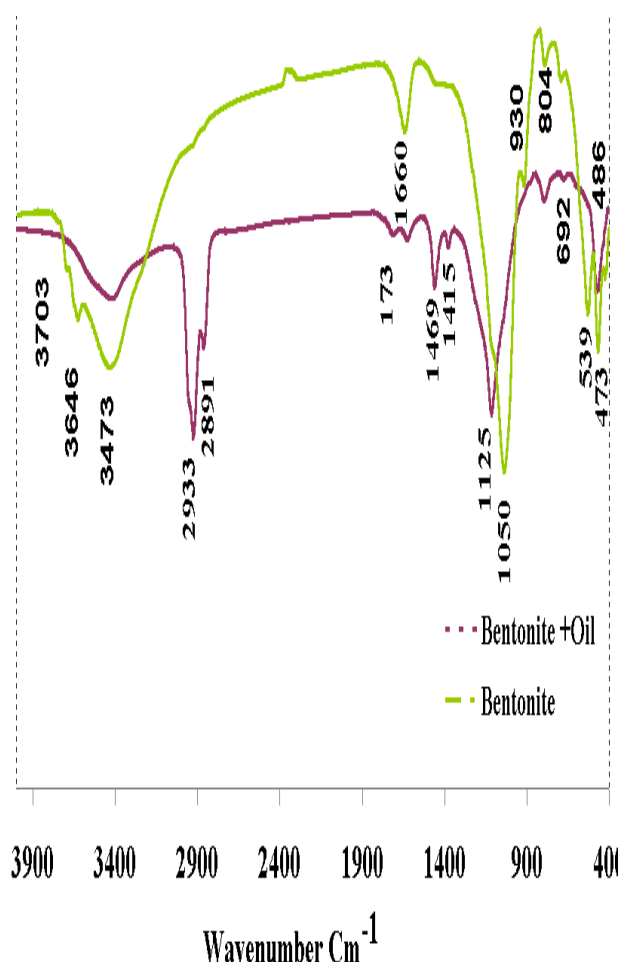


Fig. 4 FTIR of Ca-montmorillonite before and after refining of oil

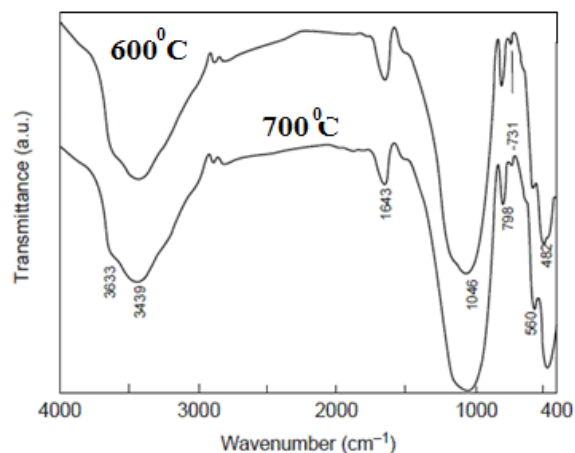


Fig. 5 FTIR of montmorillonite calcined at 600 and 700 °C and leached by  $\text{H}_2\text{SO}_4$

On heating Ca-montmorillonite at 600 and 700 °C, the broad band at ca.  $1050\text{ cm}^{-1}$  assigned to complex Si-O stretching vibrations in the tetrahedral sheet moved to  $1046\text{ cm}^{-1}$  (Fig. 5). Meanwhile, treatment of calcined montmorillonite with  $\text{H}_2\text{SO}_4$  increases the intensity of Si-O vibration band of amorphous silica at  $1100\text{ cm}^{-1}$ . Further, increase intensity of the bands at  $800$  and  $469\text{ cm}^{-1}$ . Meanwhile, acid leaching of montmorillonite causes reduction in intensities of all the characteristics bands of montmorillonite that revealed partial distortion of the structure. The calcium montmorillonite sample (Figure 6A) exhibited the typical morphology for this mineral, consisting of complex aggregates of grains of a few microns in size. The edges of these grains were sharp and rugged. Calcination and acid leaching of montmorillonite led to a loosening of this morphology, with the complex aggregates (Fig. 6 B).

TABLE III  
CHEMICAL ANALYSIS OF BENTONITIC CLAY

Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{ext}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{t}}$ ( $\text{m}^2/\text{g}$ )	% $S_{\text{t}}$	$V_{\text{t}}$ (cc/g)	$V_{\text{t}}$ (cc/g)
Ca B	89.89	70.72	19.17	21.32	0.008	0.167
C	137.04	88.89	48.14	35.12	0.02	0.21
D	245.90	111.78	134.11	54.53	0.06	0.3
E	250.2	115.35	135.8	55.2	0.062	0.32

$S_{\text{BET}}$  = BET surface;  $S_{\text{ext}}$  = external surface area by t- de Boer;  $S_{\text{t}}$  = open surface area by t-de Boer method;  $S_{\text{t}}$  = % surface area contributed by micropore;  $V_{\text{t}}$  = t-de Boer micropore volume.  $V_{\text{p}}$  = average pore volume.

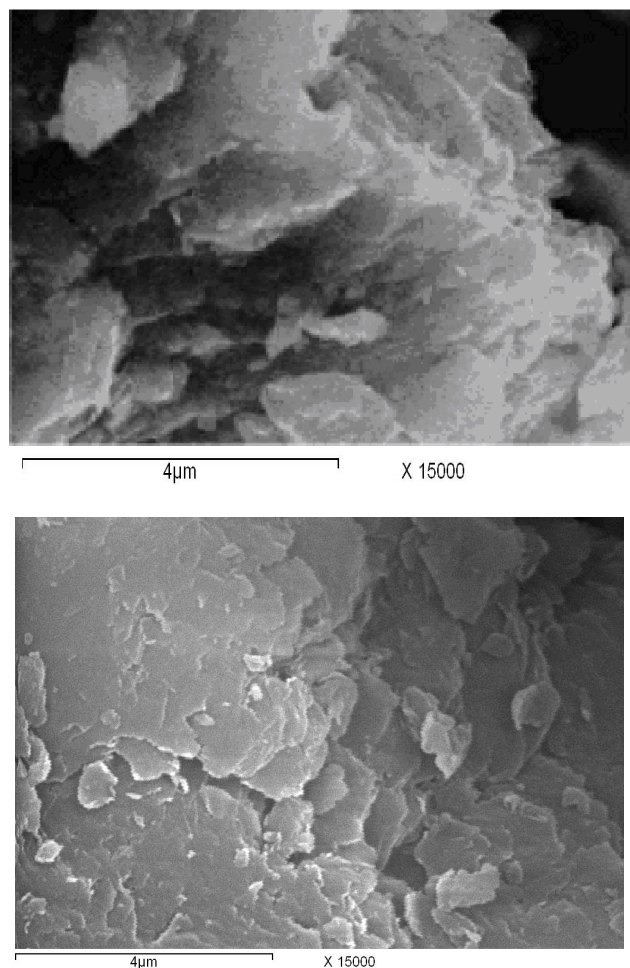


Fig. 6 SEM images of Ca-montmorillonite (a) modified montmorillonite; (b) 600°C

The shape of adsorption isotherms of Ca-montmorillonite resembles types II and IV isotherms, with a large uptake observed when close to the saturation pressure, where capillary condensation in the large voids between the aluminosilicate sheets starts. Desorption isotherms exhibited obvious capillary condensation at an intermediate pressure. The adsorption and desorption branches of the isotherms were steeply sloped in the relative pressure range of 0.98-1.00 suggesting presence of macropores, which are not filled with nitrogen. The sample contained broad and asymmetrical pore size distributions. Ca-montmorillonite has pores with a broad size distribution between 100 and 370 Å, although the narrow mesopores between 35 and 55 Å are predominant (Table III). The isotherms for CaB and activated bentonite were not significantly influenced by acid leaching following thermal treatment. The enlargement of the hysteresis loop upon acid leaching indicates a slight change in the average pore width. This enlargement in the pore width is expected to be due to destruction of the original structure as a result of acid attack. The effect of acid leaching following thermal treatment on the micropore/mesopore distribution of selected samples is shown in Table III.

Acid activation and thermal treatment followed by acid leaching led to a significant increase in amount of pores in the size range 13–38 Å, with a corresponding significant increase in surface area. Most of this increase arose from the contribution of micropores, i.e. open surface area of CaB increased significantly.

The considerable changes in the textural parameters observed during acid activation and acid leaching following heat treatment were caused by removal of cations from the octahedral holes in the layer sheets.

#### B. Physico-chemical properties of oil

From Table 2 it can be observed slight enhancement of dielectric break down strength of used oil (A) after treatment with unactivated bentonite (B). A pronounced improvement in breakdown strength was achieved after treatment of used oil with activated bentonite. This improvement moves in the direction E>D>C. The improvement percentage is almost 61.4%. On the other hand, kinematic viscosity decreased from 19 mm<sup>2</sup>/s (A) to 18 mm<sup>2</sup>/s (B). However, kinematic viscosity decreased greatly during treatment of oil with activated bentonite. The improvement of kinematic viscosity follows the same direction as the breakdown strength (E>D>C). Also, the improvement of flash point of used oil achieved but only during treatment of this oil with activated bentonite (Table 4). The previous effects of bentonite on the physicochemical properties of used oil can be explained by the changes that happened to the structure and texture of montmorillonite during thermal treatment followed by acid leaching and acid activation processes.

The enhancement in used oil properties increased as a function of the specific surface area (mainly specific micropore surface). The degree of enhancement of used oil properties greatly influenced by the degree of destruction of montmorillonite. The degree of montmorillonite structure distortion moves in the direction E>D>C.

TABLE IV  
ELECTRICAL AND PHYSICAL PROPERTIES OF USED OIL BEFORE AND AFTER TREATMENT WITH BENTONITE

Specimens	A	B	C	D	E
Property					
Dielectric Breakdown Strength [kV]	27	29	70	73	74
Kinematic Viscosity [mm <sup>2</sup> /s]	19	18	14	12	11
Flash Point [°C]	147	147	148	149	149

#### IV. CONCLUSION

This paper aimed to outline the proposed methodology for improving properties of the aged transformer oil. Mineral transformer oil was developed by adding bentonite to enhance electrical and physical properties. The results show that bentonite can enhance the dielectric breakdown strength, viscosity and flash point of aged transformer oil.

The data obtained from the characteristics tools e.g. XRD, FTIR, SEM and surface area and microporosity revealed the

destruction of montmorillonite structure and this destruction increased by increasing severity of treatment ; thermal treatment followed by acid leaching acid activation.

The degree of enhancement of used oil properties greatly influenced by the degree of destruction of montmorillonite. The degree of montmorillonite structure distortion moves in the direction  $E > D > C$ .

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