

## Effect of calcination on the physico-chemical properties of calcined spent oil-base drilling mud organoclay

<sup>\*1</sup>Nnamdi Chibuikwe Iheaturu

<sup>\*1</sup>Department of Polymer & Textile Engineering, Federal University of Technology, Owerri, Imo, Nigeria  
Corresponding Author: Nnamdi Chibuikwe Iheaturu

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**Abstract:** Spent oil-base drilling mud (SOBM) was subjected to calcination. The effect of calcination on the physico-chemical properties of the calcined SOBM is hereby studied. Properties such as colour, pH, moisture content and regain, specific gravity (Sp. Gr.), total petroleum hydrocarbons (TPH), oil and grease (O/G) on cuttings, microstructure, and chemical composition of SOBM clay before and after calcination were investigated. Results from atomic absorption spectroscopy (AAS), indicate the presence of heavy metallic elements and their oxides in the fly ash. However, after calcination, it contained 0% TPH and 0% O/G, 43,910 mg/kg or 66.51% calcium and 19,805 mg/kg or 30% barium as major heavy metals and 61,439 mg/kg or 66.72% and 26,905 mg/kg or 29.22% as their oxides content respectively. Scanning electron micrograph reveals that the end product is an insoluble, egg-yolk-yellow, nanoporous hydrocalcite organoclay with average pore size measured as 809.65 nm. SOBM clay physico-chemical properties were significantly affected by calcination and remained stable in weight after 72 hrs.

**Keywords:** Fly ash, Metallic oxides, Clay, Incineration, Calcination, Nanoporous

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### I. Introduction

Calcination is a process of subjecting clay to very high temperature for prolonged hours in order to effect a thermal decomposition and / or phase transition, other than melting. The main purpose is to drive off volatile matter from the clay material and to completely modify its lattice structure. Rather than altering a single functional group, or ligand attached to a molecule, the clay is modified or built into a giant compound (Weller, 1994). Clays form the major constituent of drilling mud.

#### 1.1 Spent oil base drilling mud

Spent oil-base drilling mud which comprises a multicomponent dispersion of additives in an oil-base; polyaromatic hydrocarbons, asphaltene and / or crude oil, has lost its qualities and has become waste. Additives such as bentonite clay, calcium carbonate, barites, fluid loss reducers, defloculants, defoamers, surfactants, bactericides, shale control inhibitors, emulsifiers, dispersants, corrosion inhibitors, viscosifiers, have been used in mud formulation during drilling operation. However, clays picked up at different underground formations gradually lead to increased solid content of the mud. In that case, partially hydrolysed polyacrylamides (PHPA) are used to balance rheological properties of the fluid while subjecting the fluid to high shear rate (Chilingarian and Vorabutr, 2000). At the end of drilling operations, it becomes difficult to dispose of the huge solid content resulting from spent oil base drilling mud after thermal desorption. Thermal desorption effect on polychlorinated bisphenyl (PCB) contaminated soils has been investigated (Qi *et al.*, 2014), however the effect of calcination on SOBM, PCB and polyaromatic hydrocarbons contaminated clays have not been dealt with.

#### 1.2 High temperature reaction between clay particles in fly ash

Most clay particles contain more than one metal in addition to oxygen forming ternary and quaternary oxides. It is a fact that increasing the temperature of a solid state reaction reduces the activation energy between particle surfaces and speeds up reaction process between particles as the rates of diffusion of the various ions across contacting particle surfaces increase. The effectiveness of this process is seen when the mixture of clay particles melt and the ions become highly mobile. This process may lead to formation of microporous, nanoporous clays or fused inorganic solid particles in the form of zeolites. Iwayama *et al.*, (1987), synthesized crystal zeolites by the reaction of a mixture containing SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>, alkali and tartaric acid. A solution was prepared with SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O:SiO<sub>2</sub>, OH-SiO<sub>2</sub> and tartaric acid:Al<sub>2</sub>O<sub>3</sub> at ratios of 30:1, 20:1, 0.17 and 2.5 respectively. However, an amorphous zeolite crystal was formed in the absence of tartaric acid. Chemical precursors such as metal carbonates, hydroxides and nitrates, are used to effectively reduce particle size further

in order to enhance reaction rates at a particular temperature. The crystallites of these precursors disintegrate with the loss of gaseous species thereby breaking down the material to yield fine, porous, very reactive particles that may be used in catalysis, reactive fillers in polymer reinforcement.

### 1.3 Aim of study

This study highlights the effect of calcination on the physico-chemical properties of clay particles from spent oil base drilling mud.

## Materials and Methods

### 2.1 Sample collection and preparation

Spent oil-base drilling mud (SOBM) which has lost its rheological properties and lie as waste, were collected from a rig site in Rivers State, Nigeria. The samples were carefully collected in 2 plastic bottles.

#### 2.1.1 Preliminary Mud Test

The American Petroleum Institute (API) recommended practice 13B (2014) for field-testing oil-base drilling fluids was used to test the spent oil-base drilling mud sample for percentage oil and water contents, percentage solids by volume, weight of oil, weight of water, weight of solids, weight of mud, average specific gravity of solids, percentage solids by weight, chloride content in grams per litre, and alkalinity.

#### 2.1.2 Mud Rheology

Viscosity, gel strength and yield point were the mud rheological properties determined.

**The gel strength** is the shear stress measured at low shear rate after a mud has set gently for a period of 10 seconds and then 10 minutes. A direct-reading cone and plate viscometer was the apparatus used for this purpose.

**Viscosity of the mud** was determined using a Marsh funnel, conical-shaped funnel, fitted with a small-bore tube at the bottom through which mud flows under acceleration due to gravity. Large particles that may block the tube, are screened out using a sieve on top of the conical funnel. The rate of flow of the mud through the small-bore at the bottom of the conical funnel into a graduated mud-cup is used to calculate the viscosity of the mud.

### 2.2 Incineration of SOBM and Extraction of Solid Content

SOBM was incinerated to yield the solid content from its liquid base. The recovered solids which now appear in dark brown coloured crumbs were crushed in a ceramic mortar.

### 2.3 Tests for Moisture Content and Regain

Hygroscopy test was carried out using a laboratory size oven, with maximum permissible heating temperature of 250 °C. The experiment was carried out at 28 °C and 98.2 % relative humidity. 50g of the sample was kept in the laboratory at room temperature for 24 hours and re-weighed. The sample was then put in the oven and heated at 150 °C. Sample was re-weighed at 15 mins interval after being allowed to cool in a desiccator for 5 mins. The process was repeated until a constant weight of the sample was measured. Equations 1 and 2 were used to calculate the percentage moisture content and regain respectively.

$$\% \text{ Moisture content} = \frac{\text{Wt. of Moisture} \times 100}{\text{Wt. of wet clay}} \quad (1)$$

$$\% \text{ Regain} = \frac{\text{Wt. of Moisture} \times 100}{\text{Wt. of dry clay}} \quad (2)$$

### 2.4 Calcination

SOBM sample was calcined in a laboratory size potclay kiln (Model: GK 4 3215), with maximum permissible temperature of 1200°C. Heating was done at 500°C, 600°C, 700°C, 800°C, 900°C, 1000°C, 1100°C and 1200°C. Each heating temperature was maintained for 2 hrs.

### 2.5 Determination of calcined clay microstructure

The Zeiss Scanning Electron Microscope (SEM) (Model: Evo 60) at 7.56Kx magnification was used to determine the microstructure of the calcined clay.

### 2.6 Determination of specific gravity of SOBM clay

Specific gravity was carried out with a density bottle before calcination according to ASTM D792. Equation 3 was used to calculate the specific gravity of the sample.

$$D = \frac{M_2 - M_1}{(M_4 - M_1) + (M_3 - M_2)} \quad (3)$$

Where;

D = Density at 28°C (68°F)

M<sub>1</sub> = Mass of density bottle

M<sub>2</sub> = Mass of density bottle + material

M<sub>3</sub> = Mass of density bottle + H<sub>2</sub>O + Material

M<sub>4</sub> = Mass of density bottle + H<sub>2</sub>O

After calcination, the material was also tested for specific gravity, using a pycnometer according to ASTM C329 – 75, because the mass of the material that met the meniscus mark on the density bottle became heavier than the density bottle earlier used for this measurement. The average of 3 different readings was calculated as the specific gravity of the calcined SOBM.

## 2.7 Analysis for oil and grease (O/G) and total retained petroleum hydrocarbon (TPH)

ASTM D 3921 was used to determine O/G and TPH on SOBM.

### 2.7.1 Calculation of O/G

The concentration of oil and grease was calculated to the nearest 0.1 mg/kg of dissolved SOBM solids in 100 mls of water using equations 4 and 5;

$$\text{Oil and grease (mg/kg)} = \frac{R \times D}{W} \quad (4)$$

Where;

$$\begin{aligned} R &= \text{Oil and grease in 100 ml of untreated extract (mg)} \\ D &= \frac{\text{Wt. of diluted extract}}{\text{Wt. of undiluted extract}} \\ W &= \text{Wt. of extracted water (kg)} \end{aligned} \quad (5)$$

### 2.7.2 Calculation of TPH

The concentration of TPH was calculated to the nearest 0.1 mg/kg of dissolved SOBM in 100 mls of water using equations 6 and 7;

$$\text{TPH (mg/kg)} = \frac{R \times D}{W} \quad (6)$$

Where;

$$\begin{aligned} R &= \text{TPH in 100 mls of treated extract (mg)} \\ D (\text{Dilution factor}) &= \frac{\text{Wt. of diluted extract}}{\text{Wt. of undiluted extract}} \\ W &= \text{Wt. of extracted water (Kg)} \end{aligned} \quad (7)$$

### 2.7.3 Particle size distribution / analysis

The clay particles were dry sieved into discrete sizes using the Retsch Sieve Shaker (Model: AS 200) with standard sieves based on ISO 3310 / ASTM E11. The discrete particle sizes were weighed on a digital weighing balance. The particle size distribution of the clay was plotted on a cumulative frequency curve.

## 2.8 Chemical analysis of SOBM filler

The procedure for the determination of heavy metals and their oxides in brackish and sea waters as elucidated in APHA 3111B/ASTM D3561 for soluble potassium (K<sup>+</sup>) and sodium (Na<sup>+</sup>) ions. The procedure for other metallic elements as stated in APHA 3111D/ASTM D3561 using the direct air-acetylene flame atomic absorption spectroscopy (F-AAS), was used to determine the presence of heavy metals and their oxides in the uncalcined and calcined SOBM. The following metals and their oxides were investigated; potassium (K<sup>+</sup>), sodium (Na<sup>+</sup>), iron (Fe<sup>3+</sup>), calcium (Ca<sup>2+</sup>), barium (Ba<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), silicon (Si<sup>4+</sup>), aluminium (Al<sup>3+</sup>).

## 2.9 Solubility and pH determination of SOBM

The calcined SOBM was tested for solubility, colour and heat change in both organic and inorganic solvents. This was done by placing 1g of the calcined SOBM clay in various beakers containing 50mls of carbon tetrachloride (CCl<sub>4</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>), paraffin wax, acetone (C<sub>3</sub>H<sub>6</sub>O), methanol (CH<sub>3</sub>OH), formic acid (HCOOH), acetic acid (CH<sub>3</sub>COOH), ethanoic acid (C<sub>2</sub>H<sub>5</sub>COOH), tetraoxosulphate VI acid (H<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), and water (H<sub>2</sub>O). The determination of pH of both uncalcined and calcined SOBM solids was done according to APHA 4500H<sup>+</sup>B.

## Results and Discussion

### 3.1 Preliminary mud test

Results of mud test carried out on SOBM sample are presented in Table 1.

**Table 1:** Results of mud test

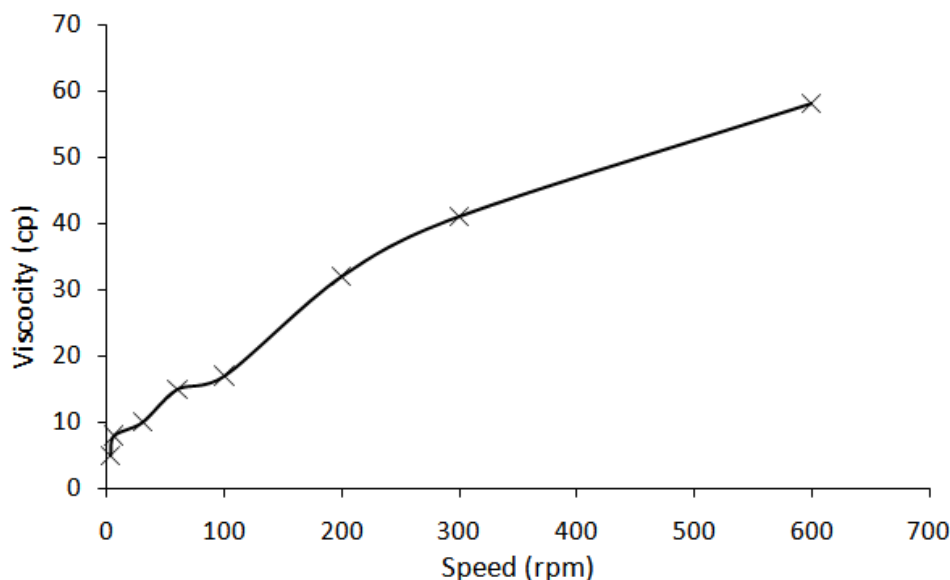
Property	Result
Percentage oil content	30.82%
Percentage water content (%)	17.95%
Percentage of solid by volume (%)	51.23%
Weight of oil in grams (g)	37.94g
Weight of water (g)	22.1g
Weight of solids (g)	63.07g
Weight of mud (g)	123.11g
Average specific gravity of solids (gcm <sup>-3</sup> )	2.52gcm <sup>-3</sup>
Percentage solids by weight	52.15
Chloride content in grams per litre	35,000 g/l
Alkalinity	8.5

#### 3.1.1 Rheology test

Results of rheology tests on the SOBM sample for viscosity, gel strength and yield point are presented in Table 2. Viscosity in centipoise against spindle speed of the cone and plate viscometer in rotations per minute is plotted in Figure 1.

**Table 2:** Results of rheology measurements

Viscosity (centipoise)	Speed (rpm)
58	600
41	300
32	200
17	100
15	60
10	30
8	6
5	3



**Figure 1:** Viscosity in centipoise plotted against speed in rpm

The rheology test of the SOBM shows that the sample has a high gel strength associated with initial viscosity. The spent mud being non-newtonian, exhibited shear-thickening (dilatancy) with increase in shear rate associated with high spindle speed in rpm. This is an indication of high solids content in SOBM sample (Oltedalet *et al.*, 2015). The gel strength was high with an initial viscosity of 5 cp and final viscosity of 7 cp as against initial viscosity of 3 cp and 5 cp for virgin mud. However, viscosity increased gradually with increase in rheometer screw speed. At screw speeds of 6 to 30 rpm and 60 to 100 rpm, the viscosity remained almost constant, and then increased before reaching breaking point.

### 3.2 Mud solids content recovery

Results of solid content recovered from SOBM is shown in Table 3.

**Table 3:** Results of mud solids recovery

Beaker	Wt. of SOBM (g)	Wt. of recovered solids (g)	Percentage solid content per 100mls	Wt. of liquid content (g)	Percentage liquid content (%)
A	127.12	82.05	66.91	45.07	35.45
B	125.60	64.03	50.98	61.57	49.02
C	123.11	63.07	51.23	60.04	48.77
<b>Average</b>	<b>125.28</b>	<b>69.72</b>	<b>55.65</b>	<b>55.56</b>	<b>44.35</b>

Mud solids constituted about 69.72 g per or 55.65% per 100 mls of the spent oil-base mud from 125.28g (100%) of spent drilling mud collected from the rig site. Liquid content which includes oil and water constitute 55.56g or 44.35% of the spent drilling mud sample. More than half of the spent drilling mud sample is composed of mud solids. High solid content in drilling mud causes stock pipe during drilling and is a health risk both to the operatives on the rig site and to the environment to which spent mud is to be disposed of.

### 3.3 Hygroscopy test

The recovered sample having been left for 24 hrs at room temperature became heavier than it was the previous day. The sample attracted moisture from the atmosphere but remained insoluble in it. Results of hygroscopy test is given in Table 4.

**Table 4:** Results of hygroscopy test

Sample size (µm)	Initial weight of sample (g)	Weight of sample after 24 hrs exposure (g)	Weight of attracted moisture (g)
0.075	54.60	57.91	3.31
0.100	52.96	56.34	3.38
0.300	37.01	39.21	2.20
0.425	27.48	28.60	1.12
0.600	29.22	30.81	1.59
0.850	26.20	27.31	1.11
1.000	41.61	44.44	2.83
<b>Total</b>	<b>269.08</b>		<b>15.54</b>

Moisture content of 269.08g SOBM was 15.54 g. A closer look of the moisture content distribution based on sample size shows that the smaller samples of 0.075 µm and 0.1 µm attracted the highest moisture content of 3.31 g and 3.38 g respectively. It may be inferred that the sample size is indirectly related to the surface area of the particles which may be directly related to the adsorbed moisture.

### 3.4 Moisture content

The sample having been dried in the oven at 150°C to a point when a constant sample weight was attained after three consecutive weighings at intervals of 15 mins and 5 mins to cool in a desiccator gave the following results as shown in Table 5.

**Table 5:** Results of moisture content and regain

Time (mins)	SOBM final wt. (g)
0	148.35
15	147.74
30	142.19
45	139.12
60	138.26
75	138.22
90	138.16
105	138.10
120	138.07
135	138.07
150	138.07
165	138.09
180	138.10

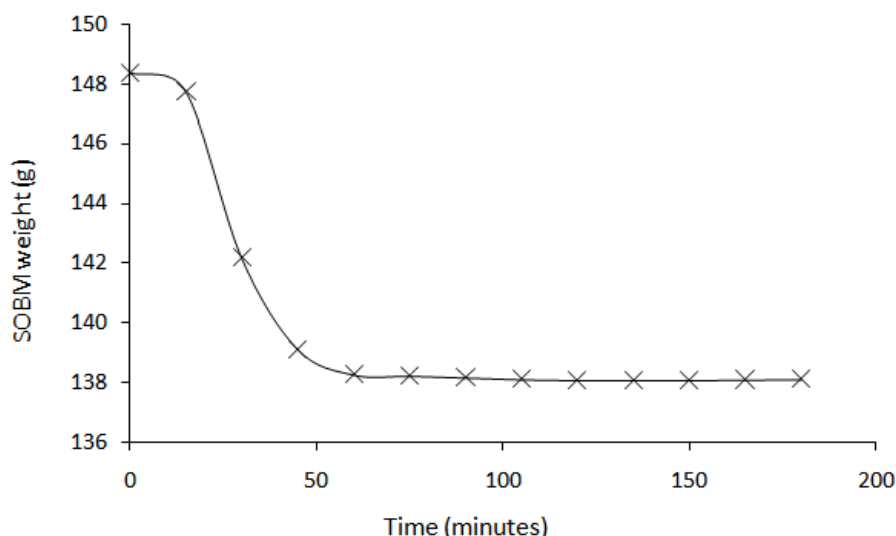


Figure 2: SOBM weight vs drying time at 150C

The final weight of the sample was found to be 138.066 g at 120 mins (2 hrs) of drying time. The material is hygroscopic which is natural for all clays. After 120 mins of drying, the sample weight remained almost constant. Therefore, moisture content and regain were calculated based on sample wet and dry weights respectively. Sample wet weight was found to be 148.34 g, while sample dry weight is 138.066g. The sample contained 6.9297% moisture while sample percentage regain is 7.4457%.

### 3.5 Results of particle size analysis

The data generated from dry sieving SOBM core clay sample and particle size distribution, is given in Table 6.

Table 6: Cumulative frequency and mass fraction of particle size distribution of SOBM core clay sample.

Sample size (µm)	Mass (g)	Mass fraction	Percentage (%)	Cumm. Frequency
0 - 63	2.47	0.0045	0.45	0.45
64 - 75	34.9	0.0634	6.34	6.78
76 - 100	22.88	0.0415	4.15	10.94
101 - 150	35.06	0.0636	6.36	17.30
151 - 300	331.51	0.6018	60.18	77.48
301 - 425	7.18	0.0130	1.30	78.78
426 - 600	87.57	0.1590	15.90	94.68
601 - 850	7.2	0.0131	1.31	95.99
851 - 1000	22.11	0.0401	4.01	100.00
<b>Total solids</b>	<b>550.88</b>	<b>1.0000</b>	<b>100.00</b>	

Graph for the cumulative frequency showing particle size distribution is shown in Figure 3.

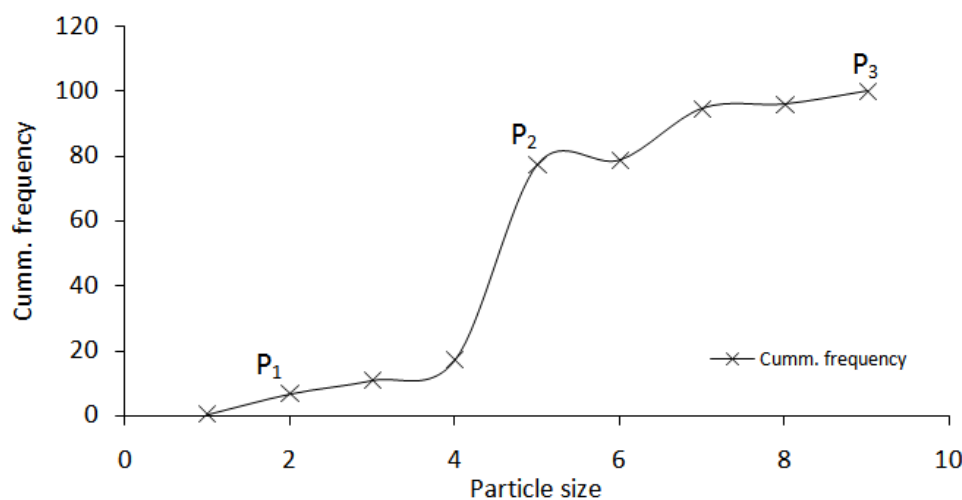


Figure 3: Cumulative frequency of plot for particle distribution of SOBM clay

Particles of size between 0 to 63µm represents 0.45% by mass of recovered SOBM, 64 – 75µm constitutes 6.18%, 76 – 100µm constitutes 4.15%, 101 – 150µm constitutes 6.36%, 151 – 300µm constitutes 60.18%, 301 – 425µm constitutes 1.30%, 426 – 600µm constitutes 15.90%, while the rest or very coarse particles of size between 601 – 1000µm constitutes 5.32% by mass of recovered SOBM. The result of the particle size distribution show that recovered spent mud sample contains about 10.94% of particles with size less than 100µm. Points P<sub>1</sub> on the graph, represents the effective particle size and maximum size of the smallest 6.78% particle content. Point P<sub>2</sub> represents maximum size of the smallest 77.48% of the particle content, while P<sub>2</sub> to P<sub>3</sub> represents coarse particles.

## 1.6 Results of calcination

### 3.6.1 Effect of calcination temperature on colour and physical state

During and after calcination, the following observations on SOBM clay colour and physical state were made at different temperatures as shown in Table 7.

**Table 7:** Effect of temperature on the colour and physical state of SOBM solids

Calcination temperature (°C)	Time (hrs)	Observations	
		Colour	Physical state
500	2	Brown	Powder
600	2	Brownish yellow	Powder
700	2	Olive yellow	Powder
800	2	Banana yellow	Powder
<b>900</b>	<b>2</b>	<b>Egg yolk yellow</b>	<b>Powder</b>
1000	2	Pure yellow	Brittle ceramic solid
1100	2	Pure yellow	Fused ceramic solid
1200	2	Dark yellow	Fused ceramic solid

From Table 6, there was noticeable changes in physical state of the SOBM powder as it was fired in the kiln from 500°C to 1200°C. The microstructural were also associated with changes on colour of sample from its original very dark brown powder at 500°C to egg yolk yellow nanoporous powder at 900°C to fused ceramic solid at 1200°C. With the observable changes in powder microstructure and colour as firing temperature increased, it can be adduced that there may have been high temperature solid state reactions involving more than one metal in addition to oxygen, precursor metallic oxides, ternary and quaternary oxides, metal carbonates, hydroxides, sulphates and nitrates of the clay sample. At calcination temperature above 800°C, the crystallites of the precursor metallic oxides contained in the SOBM clay material, disintegrated with the loss of carbon IV oxide (CO<sub>2</sub>) and structural water, further breaking down the clay powder to fine, very reactive particles. The limit of this reaction may have been reached above 1000°C, when the mixture of clay solids melt and the metallic ions become highly mobile at the melting point of the SOBM material. Above 1100°C, the particles begin to crystallize and recrystallize into an entirely new material while deepening in colour. Obviously, the associated colour changes is a confirmation of the physical and chemical changes that may have taken place during firing. Above the calcination temperature of 1100 °C, gradual cooling led to the formation of a fused ceramic solid. With the observable changes on the fired SOBM clay, 900°C was adduced the process temperature to obtain egg-yolk-yellow powder that could serve as plastic filler/ reinforcement. The formation of coloured clay-organic complexes in the case of egg-yolk-yellow SOBM, may be attributed to either acid – base interactions, oxidation – reduction reactions or charge transfer when polyaromatic compounds are adsorbed on Brønsted and Lewis acid clay platelets. Ligand to metal charge transfer (LMCT) between cyclohexadienyl ligand cation otherwise a protonated benzene and the octahedral aluminium ion or metal to ligand charge transfer (MLCT) as the case may be, could have been responsible for the colour transformation of the clay to egg yolk yellow.

### 3.7 Calcined SOBM clay microstructure

Figure 4 is micrograph of calcined SOBM clay taken at 7.56 kx magnification. SEM micrograph show clearly a porous particle. Porosity of the clay was probed at 6 pore locations Pb 1: 323.1°, Pb 2: 322.9°, Pb 3: 56.3°, Pb 4: 26.1°, Pb 5: 90.0°, and Pb 6: 105.3°. Table 8 presents measurements of approximate pore size in nanometre. Estimated average pore size is given as 809.65nm.

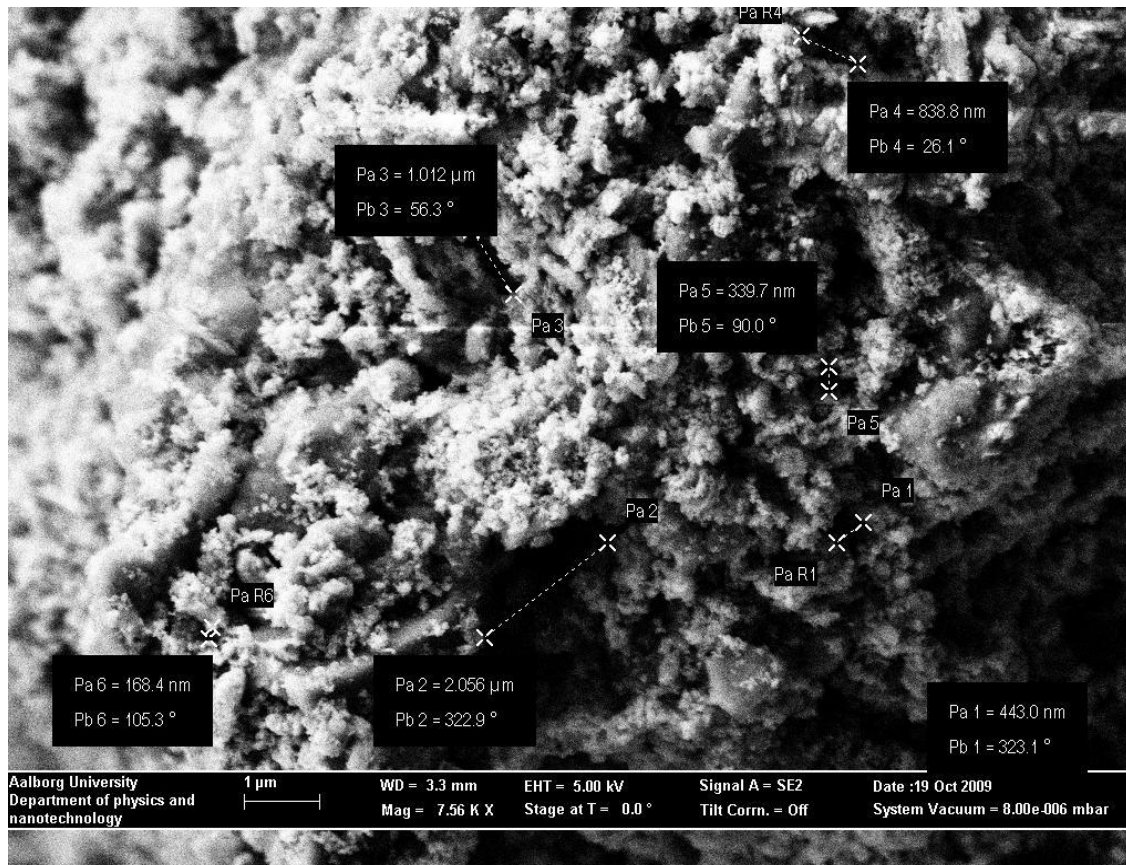


Figure 4: SEM measurement of pore dimensions at different points on the SOBM clay sample

Table 8: Point-to-point pore size measurements on synthesized SOBM clay

Pore location	Approx. Pore Size (nm) in one dimension
Pa 1	443.0
Pa 2	2,056
Pa 3	1,012
Pa 4	838.8
Pa 5	339.7
Pa 6	168.4
Average pore size	<b>809.65</b>

However, overall pore size is usually measured by gas adsorption, BET – Brunauer Emmett and Teller in  $m^2/g$  or using the Envelope Surface Area Analyzer (ESA). By so doing, accurate overall particle surface area, pore size, and pore size distribution in the bulk structure can be obtained.

### 3.7.1 Results of specific gravity

The specific gravity of the recovered SOBM was measured at 28 °C (68 °F) by substituting for  $M_1(10.994g)$ ,  $M_2(25.14g)$ ,  $M_3(79.953g)$  and  $M_4(77.37g)$  in equation 3 to obtain the specific gravity of the recovered SOBM clay as  $1.22g/cm^3$ . The recovered SOBM sample has specific gravity comparable to excavated earth, loamy soil with specific gravity of  $1.24g/cm^3$ , pulverized feldspar with specific gravity of  $1.233g/cm^3$ , broken slate with specific gravity of  $1.29g/cm^3$  and ¼ inch crushed slag with specific gravity of  $1.185g/cm^3$ .

Specific gravity results obtained using the pycnometer are as follows;  $2.750g/cm^3$ ,  $2.795g/cm^3$  and  $2.77g/cm^3$ . Average specific gravity is  $2.77g/cm^3$ . The calcined SOBM clay has specific gravity comparable to that of solid andesite with specific of  $2.771g/cm^3$ , talc and solid slate with specific gravity  $2.691g/cm^3$ , and gypsum with specific gravity of  $2.787g/cm^3$ .

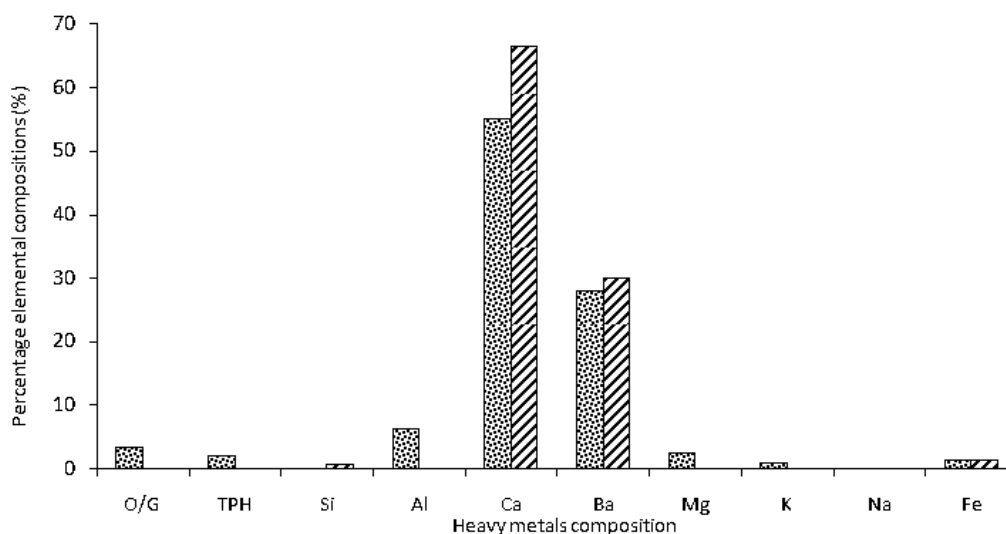


### 3.8 Results of chemical analysis by Direct Air-Acetylene Flame-Atomic Absorption Spectroscopy (FAAS)

Results of chemical analysis are presented in Tables 9 and 10. Figures 5 and 6 show bar chart plots of percentage elemental and metallic oxides composition in the recovered and calcined SOBM organoclay.

**Table 9:** Elemental chemical composition of heavy metals present in recovered and calcined SOBM

Elemental chemical composition	Test method	Elemental composition in recovered SOBM solids (mg/kg)	% composition	Elemental composition in calcined SOBM solids (mg/kg)	% composition	% expelled / reacted matter
O/G	ASTM D3921	3,147	3.26	0	0	100.00
TPH	ASTM D3921	1,917	1.99	0	0	100.00
Si	APHA 3111D	443	0.46	443	0.67	0.00
Al	APHA 3111D	6,025	6.24	215	0.33	96.43
Ca	APHA 3111D	53,110	55.02	43,910	66.51	17.32
Ba	APHA 3111D	27,022	27.99	19,805	30.00	26.71
Mg	APHA 3111B/ASTM D3561	2,296	2.38	341	0.52	85.15
K	APHA 3111B/ASTM D3562	770	0.80	136	0.21	82.34
Na	APHA 3111B/ASTM D3563	496	0.51	253	0.38	48.99
Fe	APHA 3111B	1,300	1.35	920	1.39	29.23
<b>Total</b>		<b>96,526.00</b>	<b>100</b>	<b>66,023.00</b>	<b>100</b>	<b>559.46</b>



**Figure 5:** Elemental composition of recovered and calcined SOBM organoclay

▨ Elemental composition in recovered SOBM solids (mg/kg) ▨ Elemental composition in calcined SOBM solids (mg/kg)

**Table 10:** Chemical composition of heavy metal oxides present in recovered and calcined SOBM

Chemical composition	Test method	Chemical composition of recovered SOBM solids (mg/kg)	% composition	Chemical composition of calcined SOBM (mg/kg)	% composition	% expelled / reacted matter
SiO <sub>2</sub>	APHA 3111B/ASTM D3563	948	0.71	948	1.03	0.00
Al <sub>2</sub> O <sub>3</sub>	APHA 3111B/ASTM D3563	11,384	8.49	406	0.44	0.96
CaO	APHA 3111B/ASTM	74,312	55.45	61,439	66.72	0.17

	D3564					
BaO	APHA 3111B/ASTM D3564	40,113	29.93	26,905	29.22	0.33
K <sub>2</sub> O	APHA 3111B/ASTM D3565	928	0.69	164	0.18	0.82
MgO	APHA 3111B/ASTM D3563	3,807	2.84	565	0.61	0.85
NaO	APHA 3111B/ASTM D3561	669	0.50	341	0.37	0.49
Fe <sub>2</sub> O <sub>3</sub>	APHA 3111B/ASTM D3563	1,859	1.39	1,315	1.43	0.29
<b>Total</b>		<b>134,020</b>	<b>100</b>	<b>92,083</b>	<b>100</b>	<b>3.92</b>

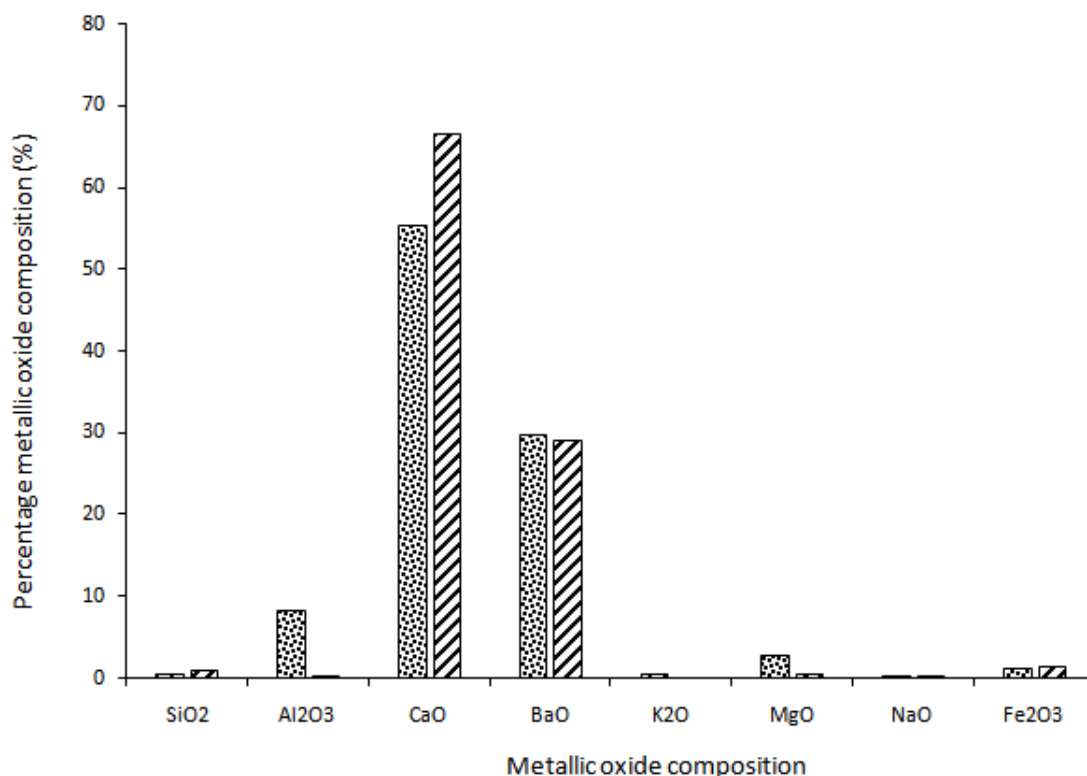


Figure 6: Metallic oxides composition in recovered and calcined SOBM solids

▨ Chemical composition of recovered SOBM solids (mg/kg) ▨ Chemical composition of calcined SOBM solids (mg/kg)

SOBM contained a mixture of calcium carbonate hydrates and carbonate minerals, barites, silica and aluminosilicates with traces of oxides of potassium, magnesium, sodium and iron. Silica and barite content varied marginally before and after calcination, while iron and its oxide reacted little or remained less volatile. 559.46g of metals and 3.92g of their oxides reacted or were expelled during calcination in the kiln. An exception is seen in the case of calcium and calcium oxide wherein there was an apparent increase in the percentage content of the calcined clay. The end product of calcination may be either a mixture of organically modified clays comprising of binary, ternary, quaternary oxides or complex inorganic compounds of aluminosilicates, hydrocalcites or highly insoluble oxalates. This may have caused the increase in specific gravity from 1.22g/cm<sup>3</sup> to 2.77g/cm<sup>3</sup> for the calcined SOBM.

3.8.1 Solubility, pH and moisture content tests  
Results of solubility test is presented in Table 11.

**Table 11: Solubility test results**

Solvent	Solubility by observation	Colour change by observation	Heat change by feel
Organic	Carbon tetrachloride (CCl <sub>4</sub> )	Nil	Nil
	Benzene (C <sub>6</sub> H <sub>6</sub> )	Nil	Nil
	Toluene (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )	Nil	Nil
	Paraffin wax	Nil	Brown
	Acetone (C <sub>3</sub> H <sub>6</sub> O)	Partial	Brown
	Methanol (CH <sub>3</sub> OH)	Partial	Yellowish Brown
	Formic acid (HCOOH)	Nil	Nil
	Acetic acid (CH <sub>3</sub> COOH)	Nil	Nil
	Ethanoic acid (C <sub>2</sub> H <sub>5</sub> COOH)	Nil	Nil
Inorganic	Tetraoxosulphate VI acid (H <sub>2</sub> SO <sub>4</sub> )	Nil	Nil
	Hydrochloric acid (HCl)	Nil	Nil
	Sodium Hydroxide (NaOH)	Nil	Nil
	Sodium chloride (NaCl)	Nil	Nil
	Water (H <sub>2</sub> O)	Nil	Nil

The calcined SOBM was insoluble in almost all the organic and inorganic solvents used for this study. There was neither heat change nor colour change. As expected, the mild cold experienced with acetone and methanol was expected. However, while the recovered SOBM gave a pH of 8.50, the calcined SOBM clay gave a pH of 8.87 in the alkaline range. However, the calcined SOBM organoclay remained stable without increase in weight after 3 consecutive weighings in 72 hours at 24 hrs interval. No moisture was attracted from the atmosphere by the nanoporous SOBM organoclay after 72 hrs.

#### IV. Conclusion

Spent oil-base drilling mud solids have been subjected to calcination. Physical and chemical properties of the calcined SOBM solids have been characterized. Before calcination, the solids have been shown to contain heavy metallic elements as silicon, aluminium, calcium, barium, magnesium, potassium, sodium, iron and their oxides. After calcination, oil and grease, total petroleum hydrocarbons and elemental compositions were reduced leading to a complex fused but porous glass. SOBM solids have been calcined into nanoporous egg-yolk-yellow clay powder with associated increase in specific gravity from 1.22g/cm<sup>3</sup> before calcination to 2.77g/cm<sup>3</sup> after calcination. The microstructure of the material was porous with average pore size measured as 809.65nm. Therefore, end product of spent oil-base drilling mud calcination maybe either a mixture of organically modified clays comprising of binary, ternary, quaternary oxides or complex inorganic compounds of aluminosilicates, hydrocalcites or highly insoluble oxalates. In application, the egg-yolk-yellow nanoporous powder may be used in thermoset polymers, plastics and rubber compounds as filler or reinforcement. Since the maximum size of the smallest 77.48% is 300µm, the particles may require further processing like ball or jaw milling in order to reduce the particles for effective mechanical reinforcement function, otherwise they may just play the role of filler for the purpose of cheapening their host polymer, plastic or rubber material.

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#### Conflict of Interest

The author declares that there is no conflict of interest in publishing this scholarly research article.

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