Clay samples were collected from three different areas, Abraka River bed, Abraka land river bed and Ugono-Abraka sediment. Chemical classical method of analysis was carried out on them, which include: The titrimetric method of determination of cation exchange capacity of the clays which showed the Abraka inland River Bed Clay with the highest cation exchange capacity of 12.8 meg/100 g, and lowest was that of Abraka River Bed with 2.4 Meg/100. Calcium carbonate determination was carried out using rapid titration method. The result showed that the calcium carbonate content of Abraka Inland River Bed has the highest. Finally the walkley Black method was used in the determination of percentage organic matter content of the clay and result showed that Abraka Inland Clay has the highest content of 0.28% followed by Ugono-Abraka and then Abraka River Bed Clay. And also the plasticity was determined manually and it was found out that the Ugono-Abraka Clay has a very high plasticity, that of Abraka Inland was low and that of Abraka River Bed was very low.

**Keywords:** Cation, Calcium carbonate, Organic, Clay, Soil

---

**INTRODUCTION**

Cation Exchange Capacity (CEC) is the amount of exchangeable cations per unit weight of dry soil. It is measured in milliequivalent of cations per 100 g of soil (Meg/100 g). The cation exchange can be regarded as a single double decomposition

\[ \text{M}^+ + \text{A}^- + \text{M}_2^+ (\text{clay}) \rightarrow \text{M}^- (\text{clay}) + 2\text{A}^+ \]

The functional behavior of (clay) as an anion is considered due largely to the lattice defect of various types which include proxying in the lattice of one ion by another ion of different charge. The property of ion exchange and the exchange reaction are of fundamental importance in all fields in which clay materials are used (Baver, 1940; Tentawe, 1982). For example, in soils the retention and the availability of potash added in fertilizers depend on the cation exchange between the potash salt and the clay mineral in the soil. Although the exchange of cations by double decomposition can occur in variety of
systems, it has become established by convection that the cation exchange capacity is measured by the exchange of cations of neutral salts at pH 7.0. The method described here uses ammonium acetate to saturate the cation exchange site of the clay surface with ammonium ion, and displacement and determination of the ammonium ion retained under these conditions by KJELDAHL distillation. A critical step in this procedure is the complete removal of the entrained and/or absorbed ammonium acetate from the clay particles with, at the same time, complete retention of the cation-exchanged ammonium ion. In the case of acid clays, particularly washing the cation saturated clay with water until the effluent is essentially free of ammonium salt result in a variable degree of hydrolysis of the exchanged ammonium ion.

\[
\text{NH}_4^+\text{(Clay)-} + \text{H}_2\text{O} = \text{H}^+\text{(clay)-} + \text{NH}_4\text{OH}
\]

Washing with 95% ethanol has been recommended (Piper, 1942)

There are two essential requirement for cation exchange (and the less common anion exchange); these include

- An imbalance of electrical charge in the crystals.
- A superficial geometry permitting the absorption of ions of suitable charge onto the crystals.

These requirement are met by some of the clay minerals. These minerals all have a residual charge on their unit cells, i.e., they invariably have a deficiency of positively charged atoms in their structure. The small particle size of clay minerals (generally observed to be less than 2 microns in maximum dimension) is another important contribution to high cation exchange. No ion exchange can take place unless a medium for transfer is available. Almost everywhere clays are associated with water, which serves as the medium for transfer. There is no single rule for ion exchange which holds for all clays and all conditions. In general, the law of mass action will apply, when an ion predominates in the surrounding fluid it will tend to become the dominant exchange ion in the clay.

The carbonate is the most important source of soil calcium. Calcium carbonate occurs in clay minerals as impurities. The presence of calcium carbonate in clay has a number of effect on the properties of the clay and it goes a long way in affecting its uses. The presence of \(\text{CaCO}_3\) impurities affect the refractoriness of fire clay by reducing it. Calcium montmorillonite generally have better decolorizing and absorbent properties than the sodium variety (Peech, 1945; Warshaw and Roy, 1961). Calcium is needed by plant in large quantities for cell division, it is the constituent of the middle lamella in each cell wall. Deficiency of calcium stunt plant growth and give recognizable leaf symptom. Also an insufficiency of calcium permits the accumulation of undesirable ions in plants and apart from any specific calcium effect, there can be no doubt that liming a soil improves crop growth by preventing this (Jackson, 1956). Organic matter are present in clay as impurities, this impurity affects the property and economic use of clay. Clay minerals have the ability to react with organic matter. Those with high absorbing capacity are used in decolorising oil, while other serves as catalyst in the cracking of organic compounds (Talvitie, 1951).

The following parameters percentage organic matter, cation exchange capacity, and calcium carbonate content will be used as indices to
provided basic data in order to access their possible areas of end use application, bearing in mind the conventional uses of crude and modified clay in water treatment as filtration and ion exchange medium, bleaching of oils, and various industrial formulations. This work can also be used to compare the proportion of cation exchange capacity, percentage organic matter, and calcium carbonate content of clay minerals in river beds and those found on ground sediments.

MATERIALS AND METHODS

Collection and Preservation of Clay Samples

Different clay samples were collected from three different sources, viz., Abraka river bed, Abraka inland river bed and Ugono-Abraka sediments. The clay samples were collected into black polythene bags which were then sent to the laboratory for analysis.

Preparation of Samples for Analysis

The samples (clay) in the natural state are labelled and placed in drying trays in the drying room. After 48 h of drying, the lump are broken up in order to expose fresh surface for drying, it was left for another 24 h. The clay is ground to pass through a 2 mm sieve. The materials that could not pass through the sieve are rejected. After sieving, the clay is dried for further 24 h. The clay sample after drying is again ground to pass through a 60-mesh sieve. The finely ground sample is now ready for use for determination of carbonate content, organic matter content, and total cation exchange capacity.

Determination of Cation Exchange Capacity

The method described here uses ammonium acetate to saturate the cation exchange site of the clay surface with ammonium ion (NH$_4$)$^+$, and displacement and determination of the ammonium ion retained under this conditions by KJELDAHL distillation. A critical step in this procedure is the complete removal of entrained and/or absorbed ammonium acetate from the clay particle with, at the same time complete retention of the cation-exchanged ammonium ion.

Procedure

5.0 g of 60 - mesh clay sample was weighed and transferred into 400 mL beaker, 100 mL of N ammonium acetate solution was added to the sample in the beaker and the mixture was well stirred. The suspension was then transferred to a Buchner funnel fitted with a moist Whatman No. 42 filter paper and was then filtered with gentle suction. The clay sample was then leached with an additional 250 mL of N ammonium acetate solution in 50 mL portions, using gentle suction so that the leaching process will require not less than one hour. The sample was washed thoroughly with 50 mL portion of ethanol, this washing was continued until a 200 mL of ethanol was used. This was after the sample in the Buchner funnel and filter paper was transferred to another 500 mL flask. The sample including the filter paper transferred to 800 mL Kjeldahl flask, and was diluted to 350 mL total volume with water and a few boiling chips were added. 20 mL of 40% potassium hydroxide solution was added. Kjeldahl flask was then set in a Kjeldahl distillation unit. The condenser end was fitted into a 300 mL Erlenmeyer flask containing 50 mL of 0.1 N sulphuric acid which contains 5 drops of methyl red indicator. The condenser just dips below the surface of the sulphuric acid. The content of the
Kjeldahl flask was gently shaken and then heat was applied. Distillation was continued until 100-150 mL of distillate was collected. The distillate was then titrated with standardized 0.1 N Sodium Hydroxide solution until the red color of methyl red changes to yellow. Also a blank of 50 mL of 0.1 N sulphuric acids was titrated with the sodium hydroxide.

Determination of Percentage Organic Matter
The Walkley-Black procedure is used in this determination. This procedure measures active or decomposable organic matter in the clay. The carbon in plant residues and humus is oxidized but the carbon present as graphic or charcoal is not. From 90-95% of total carbon in clay is oxidized and measured by this procedure.

Procedure
1.00 g of clay sample was weighed in duplicate and transferred to 200 mL Erlenmeyer flask. 10 mL of 1 N K$_2$Cr$_2$O$_7$ solution was pipetted accurately into each flask and swirled gently to disperse the clay. 20 mL conc. H$_2$SO$_4$ using an automatic pipette was added directing the stream into the suspension. The flask was immediately swirled gently until soil and reagent are mixed. Then the mixture was swirled more vigorously for one minute. The beaker was allowed to stand for about 30 min. Then 100 mL of distilled water was added after standing for 30 min. 3-4 drops of indicator was added and then the solution was titrated to end point with 0.5 N ferrous sulphate solution. As the end point was approached, the solution took on a greenish cast and then changed to dark green. At this point ferrous sulphate was added drop-wise until the color changed sharply from blue to red in reflected light against a white background. A blank titration in the same manner without clay sample but following the same step to standardize the potassium dichromate was made.

Determination of Calcium Carbonate Content (Vogel, 1962; Welcher, 1963)
A rapid routine method of limited accuracy is to decompose the carbonate with excess dilute acid and to titrate the unused acid with standard alkaline. The result is referred to as the calcium carbonate equivalent.

Procedure
1.0 g of dried sample was weighed into a 250 mL beaker and 25 mL of 1 M HCl was pipetted into the flask. The neck of the beaker was washed with a few mL of distilled water. The beaker was covered with a small wash glass and was allowed to stand for one hour. When the clay has settled it was placed on a hot plate and was gently boiled for 5 min, or until all reactions seized. This was allowed to cool. 50 mL of distilled water was added to the sample, washing around the neck and a bar magnet was inserted for stirring. From the beaker 25 mL was pipetted into another conical flask and 66 drops of bromothymol blue indicator was added and this was placed in the magnetic stirrer for 5 min and then titrated to a blue end point with 1 M sodium hydroxide. With each sample a blank was treated in the same manner.

Determination of Plasticity

Procedure
40.0 g of clay sample was mixed with 0.5 mL of distilled water. This was then thoroughly mixed together. After mixing each sample was the milled
into rolls and this was rolled round the finger. The plasticity was then determined by the extent at which the roll goes round the finger without breakage.

Color
The various colors of the samples were determined by visual inspection.

RESULTS
Results got from the experimental work on the various samples are shown below (Tables 1 to 4). The three samples are tagged A, B and C, for Abraka river bed, Abraka inland river bed and Ugono-Abraka clay sediments, respectively.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Initial Burette Reading In (Ml)</th>
<th>Final Burette Reading In (Ml)</th>
<th>Volume Of Naoh Used In Ml</th>
<th>Cecmeq/100g</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.00</td>
<td>58.30</td>
<td>58.30</td>
<td>2.4</td>
</tr>
<tr>
<td>B</td>
<td>0.00</td>
<td>53.40</td>
<td>53.40</td>
<td>12.8</td>
</tr>
<tr>
<td>C</td>
<td>0.00</td>
<td>56.90</td>
<td>56.90</td>
<td>5.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Initial Burette Reading In (Ml)</th>
<th>Final Burette Reading In (Ml)</th>
<th>Volume Of Naoh Used In Ml</th>
<th>% of C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.00</td>
<td>19.97</td>
<td>19.97</td>
<td>0.103</td>
</tr>
<tr>
<td>B</td>
<td>20.00</td>
<td>39.2</td>
<td>39.2</td>
<td>0.28</td>
</tr>
<tr>
<td>C</td>
<td>10.00</td>
<td>29.6</td>
<td>29.6</td>
<td>0.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Initial Burette Reading In (Ml)</th>
<th>Final Burette Reading In (Ml)</th>
<th>Volume Of Naoh Used In Ml</th>
<th>% of CaCo³</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.00</td>
<td>11.60</td>
<td>11.60</td>
<td>74.5</td>
</tr>
<tr>
<td>B</td>
<td>10.00</td>
<td>22.50</td>
<td>22.50</td>
<td>70.0</td>
</tr>
<tr>
<td>C</td>
<td>30.00</td>
<td>40.80</td>
<td>40.80</td>
<td>78.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Colour</th>
<th>Plasticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Light yellow</td>
<td>Very low</td>
</tr>
<tr>
<td>B</td>
<td>Light grey</td>
<td>Low</td>
</tr>
<tr>
<td>C</td>
<td>Ash coloured</td>
<td>High</td>
</tr>
</tbody>
</table>
This determination was done manually and the colour was by visual observation. The result are shown in the table below:

DISCUSSION

Considering the cation exchange capacity of the three clay sample, the sample obtained from Abraka inland river bed has the highest value of about 12.8 Meq/100 g, that of Ugono-Abraka sediment has 5.2 Meq/100 g while that of Abraka river bed has 2.4 Meq/100 g. It can be seen that the inland clay has the highest sites for cation exchange to occur and hence will be more effective for the use as water softener, also it is most suitable as a decolorizer comparative.

The clay have very minute quantity of calcium carbonate. Calcium carbonate is needed in the soil to correct pH of soil. The calcite content of clay also makes it suitable for its use in some fields as in the production of paints, ceramics, plastics, etc.

And its presence as impurities can also be detrimental to its economic value. The Abraka inland river bed clay has the highest organic matter content of about 0.28% followed by that of Ugono-Abraka and then the least was that of Abraka river bed which has 0.009%. Organic matter is needed by plants to get its nutrients, and hence the clay of Abraka inland river bed will be more suitable to support plant life. The Abraka inland clay has a higher absorbing capacity and hence it is more suitable for use as a decolorizer of oil and catalyst for organic compounds.

Considering the plasticity of the three clay samples, that of Ugono-Abraka sediment has the highest, it has a very high ability to undergo permanent deformation in any direction without rupture under stress. Plasticity is a property of clay that makes it suitable for the production of ceramics. Hence the Ugono-Abraka clay will be more suitable for ceramic production. That of Abrakainlandriver has low plasticity and that of Abraka river bed is very low.

CONCLUSION AND RECOMMENDATION

That of clay from land sediment has a very high plasticity and hence contain a higher amount of clay mineral as compared to those of the river bed. This is a pointer to the fact that Ugono-Abraka sediment is more suitable for ceramic use. The inland clay has the highest cation exchange capacity followed by that of Ugono-Abraka sediment and least is that of Abraka river bed. Hence the inland clay is more suitable for application of clay as cation exchange medium. The calcium carbonate content of the clay is very low and it can be considered that the presence of calcium carbonate is very minimal. The use of automatic sieve to determine the clay, silt and fine sand composition of the clay from the various locations. The use of pH meter to determine the pH of the various clays. The use of UV-Visible Spectroscopy for the determination of anion exchange capacity. The study area should be increase in order to have a comprehensive data on the soils from the Niger Delta region.

REFERENCES


11. Piper C S (1942), Soil and Plant Analysis.


18. Workley A and Black L A (1934), Soil Science, Vol. 37, pp. 29 - 38