Effect of Acid Treatments on the Physicochemical Properties of Kaolin Clay

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ABSTRACT

Improvement on the quality of kaolin has been conducted by treatment with different concentrations of hydrochloric acid. The raw and treated clays were analysed for SiO2, Al2O3, TiO2, K2O, Fe2O3, and MgO using energy dispersive x-ray fluorescence. The physical change in colour from pink to white as the concentration increased to 2mol/dm3 was a removal of metallic compounds, like Fe2O3 which stained the clay. The experiments showed that treatment of kaolinite in dilute hydrochloric acid clean the clay minerals by removing iron oxides and other metallic compounds from the surface of the clay.

Keywords: acidification, colour, density, metallic compounds.

INTRODUCTION

Kaolin is one of the clay materials widely used for a large number of applications such as in ceramics, paper coating, paper filling, paint extender, rubber filler, cracking catalyst or cements, oil refinery and water treatment [1], [2], [3], [4]. Kaolinite is the major mineral component of kaolin, which may usually contain quartz and mica and also less frequently feldspar, illite, montmorillonite, anastase, haematite, bauxite, zircon, rutile, kyanite, sillimanite, graphite, attapulgite and halloysite [1], [2]. Kaolinite is a clay mineral with chemical composition Al2Si2O5(OH)4. It is a layered silicate mineral, with one tetrahedral sheet of being linked through oxygen atoms to one octahedral sheet of alumina [5]. Rocks that are rich in kaolinite are called kaolin. Kaolinite has a low shrink-swell capacity and a low cation exchange capacity. It is a soft, earthy material, usually white mineral produced by chemical weathering of aluminium silicate minerals like feldspar. In many parts of the world, it is coloured pink, orange or red by iron oxide giving it a distinct rust hue.

Kaolinite like other clays are composed of fine grained minerals which are plastic at appropriate water content and hardens up when fired [6]. They have varying chemical composition depending on both physical and chemical changes in the environment where they are found. The industrial utilization of kaolinite is closely related to its reactivity and surface properties and depends strongly on surface modification. Several methods have been suggested in literature to improve the properties of clay materials with thermo-chemical treatment [1], [2] or chemical activation [7], [4].

Acid activation has been widely studied as chemical treatment methods for improvement of the surface and catalytic properties of fibrous clays [1] and has been noted to induce changes in crystal structure of aluminosilicate minerals.
due to the dissolution of structural ions and/or rearrangement of the structure [7]. In this work the authors have studied the effect of acid treatment on kaolinites with much focus on the removal of colouring pigments and other metallic impurities. This paper reports the effects of acid treatment on colour, density and metallic composition of kaolin clay.

**MATERIALS AND METHODS**

Kaolin clay was collected from a local mine in Abia State, Nigeria and grinded to powder with a laboratory mortar and pestle and stored in a polyethylene bag for subsequent use. A portion (20g) each of the clay was measured into 2 different 250ml beaker containing 200ml each of 1mol/dm$^3$ and 2mol/dm$^3$ HCl respectively. The suspension was stirred for 1 hour and allowed to stand for 48 hours with occasional stirring. The suspension was filtered and the residue washed with distilled water and allowed to dry at room temperature. The raw and treated clays were labelled and subsequently analysed using energy dispersive x-ray fluorescence.

The bulk density of the clay were carried out using the laboratory methods as described in the European committee for standardization, CEN/TS 15103, [8], colour was determined by visual comparison and loss of mass on ignition was determined by subjecting a known quantity of the clay in a muffle furnace at 600oC for 2 hours.

**RESULTS AND DISCUSSION**

Characterization of the sample with X-ray fluorescence showed that the clay consists mainly of silica and alumina, with metallic compounds like Fe$\text{O}_3$ and Ti$\text{O}_2$ occurring as minor. Other compounds including K$\text{O}$, CaO, MgO, ZrO$_2$ and other s were detected in traces. Analysis gave SiO$_2$ (65.89%), Al$2$O$_3$ (24.32%), Fe$2$O$_3$ (3.79%), Ti$\text{O}_2$ (3.29%), K$\text{O}$ (0.776%) MgO (0.47%), Zr$\text{O}_2$ (0.147%), P (0.13%), Na$2$OO (0.095%), V$2$O$5$ (0.078%), Ce$\text{O}_2$ (0.078%), SrO (0.070%), Cr$\text{O}_3$ (0.057%), BaO (0.048%), La$\text{O}_3$ (0.040%), S (0.029%), Ga$\text{O}_3$ (0.016%), Mn$\text{O}$ (0.014%), Y$2$O$3$ (0.014%), NiO (0.011%), PbO (0.01%), Re$2$O$_7$ (0.007%), Mo$\text{O}_3$ (0.006%), Rb$2$O (0.006%), X$2$O$_3$ (0.005%), ZnO (0.005%), Th$\text{O}_2$ (0.005%)

Loss of mass on ignition

The results obtained by weight loss on ignition of the sample showed that the average percentage of 9.3%. This may be as a result of the presence of organic matter lost during the roasting and/or some non-metals like sulphur which could have been removed from the clay in the form of SO$_2$.

**Table 1: Results of the treatment of kaolinite on the physical properties of the clay**

<table>
<thead>
<tr>
<th></th>
<th>Colour</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sample</td>
<td>Pink</td>
<td>4.64g</td>
</tr>
<tr>
<td>1mol/dm$^3$</td>
<td>Slightly pink</td>
<td>4.56g</td>
</tr>
<tr>
<td>2mol/dm$^3$</td>
<td>White</td>
<td>4.47g</td>
</tr>
</tbody>
</table>

The treatment of kaolinite in different concentrations of hydrochloric acid proceeded with a change in colour and density as the concentration of the acid increased (Table 1). The result of the treatment of the kaolinite showed a slight reduction in colour from pink to slightly pink. This may be attributed to the slight removal of iron oxide which stained the clay, the percentage removed increased as the concentration of the acid increased from 1mol/dm$^3$ to 2mol/dm$^3$ as shown in Table 1. The same effect was seen in the result of the density analysis. This may be as a result of the removal of metallic compounds as shown in Table 2. Further increase in the concentration of the acid (2mol/dm$^3$) increased the % removal of the metallic compounds and subsequently reduced the density of the clay.

**Table 2: Dissolution of the studied minerals under dilute HCl treatment (the data show the % removal of the metallic compounds)**

<table>
<thead>
<tr>
<th></th>
<th>%MgO</th>
<th>%Fe$2$O$_3$</th>
<th>%K$2$O</th>
<th>%Ti$\text{O}_2$</th>
<th>%Al$2$O$_3$</th>
<th>%SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1mol/dm$^3$</td>
<td>32.34</td>
<td>44.59</td>
<td>28.73</td>
<td>28.87</td>
<td>3.16</td>
<td>1.44</td>
</tr>
<tr>
<td>2mol/dm$^3$</td>
<td>56.38</td>
<td>51.98</td>
<td>47.55</td>
<td>44.38</td>
<td>7.85</td>
<td>3.54</td>
</tr>
</tbody>
</table>

The treatment of kaolinite in different concentrations of HCl proceeded with the release of structural elements in solution. Table 2 showed the percentage of Al$2$O$_3$, Fe$2$O$_3$, MgO, Ti$\text{O}_2$, Si$2$O$_3$, K$2$O removed during the treatment of...
kaolinite in 1mol/dm$^3$ and 2mol/dm$^3$ HCl solutions. Treatment with 1mol/dm$^3$ produced 32.87% K$_2$O, 28.87% TiO$_2$, 44.59% Fe$_2$O$_3$, 3.16 % Al$_2$O$_3$ and 1.44% SiO$_2$ removal from the clay, with order of relative removal as Fe$_2$O$_3$ > MgO > TiO$_2$ > K$_2$O > Al$_2$O$_3$ > SiO$_2$. The difficulty in leaching of alumina and silica may be as a result of the position (central position in the structure) alumina and silica occupies in the clay structure. This is in line with the reports of [9] and [10] while studying the dissolution of palygorskite clay in acidic solution. Si and Al ions are being removed from the octahedral sheet into the solution and at the same time additional bonds are being formed (Al-OH and Si-OH) without disturbing the structure [11]. This shows the reason for the reduction in percentage of silica and alumina because in the process of bond breaking and formation some ions of Si and Al are lost in the solution. While the ease in reduction of ferric oxide, magnesium oxide and titanium oxide from the clay may be as a result of migration of metal ions from lattice position to exchange position followed by their removal. Increasing the acid concentration from 1mol/dm$^3$ to 2mol/dm$^3$ increases the acid attack on the structure which results in more bond breaking and formation and subsequently more alumina and silica are leached from the clay. This also causes a rapid migration of other metallic ions which are in lattice positions to exchange positions and this leads to greater loss into the solution causing more reduction of metallic ions from the clay. This is strongly evidenced in MgO which the extent of removal increased from 32.34%-56.38% from 1mol/dm$^3$-2mol/dm$^3$ HCl solution.

CONCLUSION

A clear influence of the effect of HCl treatment of kaolinite was observed in the colour, density and concentration of metallic compounds. The result of the analysis showed that HCl is a good solvent for the removal of impurities in kaolin clay. Elemental analysis by EDXRF showed a slight removal of metallic compounds in 1mol/dm$^3$ HCl solution which subsequently increases as the concentration was increased to 2mol/dm$^3$. The difficulty in removal of alumina and silica was as a result of the position they occupy in the structure.

REFERENCES