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Conditions for Thermal Activation of Ngwo Clay as an Alternative Resource for Alumina

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Abstract

The thermal activation of Ngwo clay from southeastern Nigeria for optimal leaching of alumina was investigated. The clay assayed 24.63% Al_2O_3 and 52.15% SiO_2, comprising mainly kaolinite mineral and free silica or quartz. The alumina locked up in the clay structure was rendered acid-soluble by thermal activation which transformed the clay from its crystalline nature to an amorphous, porous phase or metakaolinite. The clay samples were heated at calcination temperatures of 500°C, 600°C, 700°C, 800°C, and 900°C at holding times of 30, 60, and 90 minutes. Uncalcined clay samples and samples calcined at 1000°C (holding for 60 minutes) were used in the control experiments. After leaching the resulting clay calcines in 1 M hydrochloric acid solution at room temperature, it was observed that the clay calcines produced at 700°C (holding for 60 minutes) responded most to leaching. Samples calcined for 60 minutes also responded better than those held for 30 or 90 minutes. Based on activation energy studies, it was observed that calcines produced at 700°C (for 60 minutes) had both the highest leaching response (51.84% after 1 hour at leaching temperature of 100°C) and the lowest activation energy of 25.03 kJ/mol. It is concluded therefore that Ngwo kaolinite clay should be best calcined for alumina dissolution by heating up to 700°C and holding for 60 minutes at that temperature. The clay deposit has potential for use as alternative resource for alumina production in Nigeria where bauxite is scarce.

Keywords

Ngwo Clay, Bauxite, Kaolinite, Alumina, Calcination, Thermal Activation, Leaching
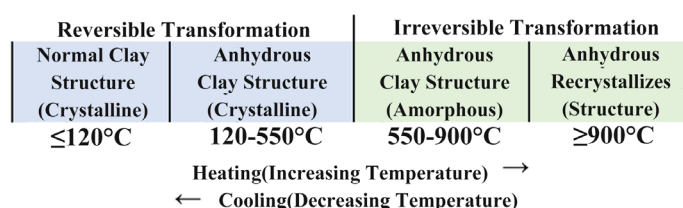
1. Introduction

Primary aluminium is produced by the electrolytic reduction of alumina (Al_2O_3)

in the Hall-Héroult process [1] [2] [3] [4]. The alumina used is usually refined from bauxite, which has remained the most important ore for aluminium [5] [6]. About 90 percent of the world production of bauxite is used for making alumina, most of which is consumed in the manufacture of aluminium. The rest is used in the production of abrasives, refractories, chemicals used chiefly in water purification and in the manufacture of paper, petroleum catalysts, aluminous cements, materials for the purification of kerosene and other petroleum products, and for other purposes [7] [8] [9] [10]. West Africa holds the largest bauxite resources in the world [11] [12] [13]. The U.S. Geological Survey put the world bauxite reserve at about 55 billion tonnes with West Africa having the highest share of 32% [10]. It was reported that countries in the sub-region (Nigeria's neighbours) hold about one-third of the world's bauxite reserves, and the resource is sold at locally unfavorable, internationally competitive prices [10]. Bauxite deposits are found in Guinea, Sierra Leone, Ghana, Mali, Cameroon, and Gabon [11] [13] [14]. However, no such deposits have been discovered in Nigeria [13] [15]. Only minor occurrences with low concentrations of bauxite minerals are reported from some regions like Ekiti province [15] [16] [17] and the Jos Plateau [11]. Again, only the occurrence of bauxitic clay is reported from the Mambilla Plateau (the western extension of the Adamawa Highland, near the border with Cameroon) [11] [13] [18]. This shows that the raw material for manufacture of alumina (*i.e.* bauxite) is very scarce in Nigeria.

The high-volume consumption of aluminium in Nigeria [19] [20] and the establishment of an aluminium smelter plant at Ikot-Abasi [20] [21] call for the development of methods for producing alumina from nonbauxite alumina/aluminium bearing raw materials. The plant was shut down mainly due to challenges of procuring the feed stock [19] [20]. The kaolinitic clays are aluminous raw materials and are well distributed on a large scale in Nigeria [12] [13] [18] [22].

Kaolinite clay has the structural formula in which the silica tetrahedral layer, represented by $\left(\mathrm{Si_2O_5}\right)^{2-}$ is made electrically neutral by an adjacent aluminium octahedral layer, $\mathrm{Al_2\left(OH\right)_4^{2+}}$ [23] [24]. Taking one silicon tetrahedral unit and one aluminium octahedral unit, the structural formula of kaolinite can be written as $\mathrm{Al_2\left(OH\right)_4\cdot\left(Si_2O_5\right)}$ or $\mathrm{Al_2Si_2O_5\left(OH\right)_4}$ or in terms of oxides as $\mathrm{Al_2O_3\cdot 2SiO_2\cdot 2H_2O}$. In its pure form, kaolinite has the theoretical composition of 46.54% $\mathrm{SiO_2}$, 39.50% $\mathrm{Al_2O_3}$, and 13.96% $\mathrm{H_2O}$ (equivalent to loss on ignition or LOI). This makes kaolinite the clay mineral with the highest content of alumina [25] [26]. Kaolinite clays are therefore potential sources of alumina where bauxite is scarce or depleted. In view of Nigeria's situation, the abundant reserve of kaolinitic clays is thought as a suitable substitute for bauxite from which alumina of high purity can be obtained [27].

However, the alumina content of kaolinite (and other clay minerals) is locked up in the clay structure. It can only be released or leached out after proper thermal treatment or activation [28]. As illustrated in **Figure 1**, four temperature ranges are important in the transformation of clays [29], namely: the drying

Reversible Transformation		Irreversible Transformation	
Normal Clay Structure (Crystalline)	Anhydrous Clay Structure (Crystalline)	Anhydrous Clay Structure (Amorphous)	Anhydrous Recrystallizes (Structure)
≤120°C	120-550°C	550-900°C	≥900°C

Heating(Increasing Temperature) →
← Cooling(Decreasing Temperature)

Figure 1. Effect of temperature on the physical state of clay minerals ([29], p.174).

range or free-water dehydration range (50˚C - 120˚C); the clay stability range (120˚C - 600˚C); the anhydrous clay range (600˚C - 900˚C); and the recrystallization range (above 900˚C).
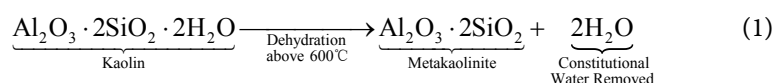
For example, kaolinite is reported to change from hydroplastic condition to leather hard, then stone hard and finally to anhydrous condition or metakaolinite as it is heated between room temperature and about 600˚C [30] [31]. This is because of drying, dehydration and dihydroxylation, as follows:

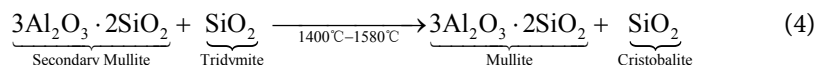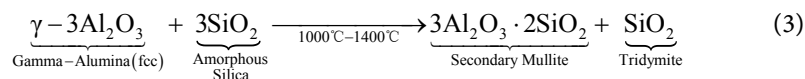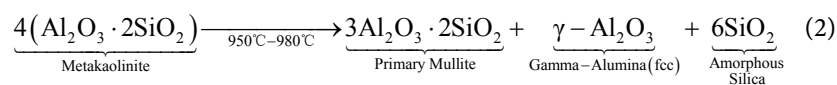1) Drying or loss of wetness or physically adsorbed water by evaporation occurs at temperatures below 120˚C. The loss of physically attached water is endothermic and results in measurable weight loss. For kaolinite, the weight loss is usually minor, and the changes due to loss of physical water do not alter the crystalline structure of the clay [30]. Within the drying range, liquid water is removed from the clay, and the resulting material is referred to as *leather dry* or *leather hard clay* [31].

2) Dehydration is further loss of any remaining physically held water between 120˚C and about 550˚C. The resulting material after this transformation is referred to as *bone-dry* or *stone hard clay*. Throughout the drying and dehydration temperature range (where physical water is removed), the expulsion of water is reversible as shown in **Figure 1** [29] [31].

3) De-hydroxylation is loss of constitutional or chemically combined water (the OH water). Around 550˚C, the chemically combined water in clays begins to be released. This transformation continues until all chemically combined water is expelled resulting in the formation of *metakaolin*, an *anhydrous form* of kaolin. As with the loss of physically adsorbed water, the loss of the chemically combined water is an endothermic process that is accompanied by weight loss. The magnitude of the weight loss depends on the amount of chemically combined water in the clay. After de-hydroxylation, metakaolin appears amorphous on X-ray diffraction, but the short-range ordering of the cations within the sheets that make up the kaolinite structure is retained. Metakaolin is a homogeneous molecular-level mixture of non-crystalline alumina and silica and does not spontaneously rehydrate when it is exposed to water and it remains stable up to approximately 980˚C [30] [31].

The thermal changes of kaolinite heated above 600˚C can be outlined in accordance with the following sequence of reactions [28] [32]:

$$\underbrace{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O}_{\text{Kaolin}} \xrightarrow[\text{above 600℃}]{\text{Dehydration}} \underbrace{Al_2O_3 \cdot 2SiO_2}_{\text{Metakaolinite}} + \underbrace{2H_2O}_{\substack{\text{Constitutional} \\ \text{Water Removed}}} \quad (1)$$

3

$$\underbrace{4\left(Al_2O_3 \cdot 2SiO_2\right)}_{\text{Metakaolinite}} \xrightarrow[950°C-980°C]{} \underbrace{3Al_2O_3 \cdot 2SiO_2}_{\text{Primary Mullite}} + \underbrace{\gamma - Al_2O_3}_{\text{Gamma-Alumina(fcc)}} + \underbrace{6SiO_2}_{\substack{\text{Amorphous} \\ \text{Silica}}} \quad (2)$$

$$\underbrace{\gamma - 3Al_2O_3}_{\text{Gamma-Alumina(fcc)}} + \underbrace{3SiO_2}_{\substack{\text{Amorphous} \\ \text{Silica}}} \xrightarrow[1000°C-1400°C]{} \underbrace{3Al_2O_3 \cdot 2SiO_2}_{\text{Secondary Mullite}} + \underbrace{SiO_2}_{\text{Tridymite}} \quad (3)$$

$$\underbrace{3Al_2O_3 \cdot 2SiO_2}_{\text{Secondary Mullite}} + \underbrace{SiO_2}_{\text{Tridymite}} \xrightarrow[1400°C-1580°C]{} \underbrace{3Al_2O_3 \cdot 2SiO_2}_{\text{Mullite}} + \underbrace{SiO_2}_{\text{Cristobalite}} \quad (4)$$

Thus, the thermal changes of kaolinite heated above 600°C progress in four major steps, namely: endothermic dehydration by de-hydroxylation of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) to metakaolinite ($Al_2O_3 \cdot 2SiO_2$); sudden exothermic crystallization at about 980°C resulting to the formation of primary mullite ($3Al_2O_3 \cdot 2SiO_2$), γ-alumina and amorphous silica; further recrystallization to secondary mullite and tridymite; and then transformation of tridymite to cristobalite. Whereas reaction (1) or the first transformation is associated with loss in weight (due to LOI); all four transformations are accompanied by considerable volume and enthalpy changes [28].

The temperatures at which these transformations (phase changes) begin and end depends on 1) degree of crystallinity of the kaolinite, 2) its impurity oxides contents, 3) particle sizes, rate of heating, and duration of heating at a given temperature. Therefore, clays from different localities vary considerably not just in mineralogy and chemical composition, but in degree of crystallinity and purity [28] [33]. There is need to investigate the characteristics of each clay deposit. The current investigation is focused therefore on determining the thermal treatment required to transform Ngwo clay found in south-eastern Nigeria to an anhydrous amorphous phase or metakaolinite. The response of the clay calcines to alumina leaching in hydrochloric acid solution vis-à-vis the thermal treatments was also studied.

2. Experimental Methods

Ngwo clay deposit (Lat. 6°25'0"N, Long. 7°26'0"E) in Udi Council of Enugu state, Nigeria was sun-dried, crushed and ground. The ground clay sample was placed on a 300 μm ASTM sieve and shaken for 5 minutes. The oversize was further ground and sieved on the same sieve. The procedure was repeated until the entire clay sample passed through the 300 μm sieve (50 standard Tyler mesh).

2.1. Mineralogical and Chemical Analyses

Representative sample of the sieved clay was analysed using Pananalytical XRD (Empyrean model) to determine the constituent minerals. Optimally calcined sample of the clay was also analysed with XRD to determine the effect of thermal transformation on the clay. Similarly, the chemical composition (amounts of Al_2O_3, SiO_2, TiO_2, etc.) was determined by means of Buckscientific AAS (model 210 VGP). The loss on ignition (LOI) was determined by placing one gramme of dry clay sample (dried at 105°C for 12 hours in an oven) into a platinum crucible of known weight (W_d). This was subsequently fired at 1000°C for 1 hour in a

muffle furnace. At lapse of time, the crucible was brought out of the furnace and reweighed (W_f) after cooling down to room temperature. The LOI was calculated in percentage as $\left(W_d - W_f / W_d\right) \times 100$.

2.2. Calcination Procedures

Ground and sieved clay samples passing 300 μm sieve were subjected to thermal treatments in a muffle furnace at a heating rate of 15°C per minute up to the holding temperature (500°C, 600°C, 700°C, 800°C or 900°C) and held for 30, 60 or 90 minutes before furnace-cooling to room temperature. In addition, two sets of thermal treatment were used for the control experiment. A sample of the clay was reserved in the uncalcined condition (room temperature) and used as *control* 1; while another sample was heated up to 1000°C and held for 60 minutes and used as *control* 2.

2.3. Leaching of Clay Calcines

Analytical grade HCl acid and pure deionized water were used to prepare the leaching reagent. 1 molar standard solution of hydrochloric acid was prepared using deionized water. This was used as the leaching reagent for the leaching studies to determine the leaching response of the various clay calcines and the controls. The leaching was done under moderate leaching conditions, *i.e.* hydrochloric acid concentration of 1M, leaching temperature at ambient (~25°C), shaking speed of 100 rpm, and solid/liquid ratio or clay weight to acid volume ratio of 0.02 g/ml, using clay particles passing 300 μm (−50 mesh).

The leach contact time or duration ranged from 0 to 120 minutes at intervals of 30 minutes. The flask or reaction bottle was shaken at a constant rate of 100 rpm during the contact time (duration of leaching) to facilitate the reaction. This was achieved by means of a KOMA orbital shaker (model KED11). By the end of leaching, the resulting slurry was filtered to separate undissolved materials (residue) from the filtrate (leachate or pregnant solution). The leachate was analysed for aluminium ion concentration.

This procedure was repeated for all the clay calcines and the control samples, which were prepared at different temperatures and duration of calcination. The optimum condition for calcining the clay was determined using solubility data (concentration and fraction of aluminium ion solubilized).

After examination of the extent of aluminium extraction or solubilization from the clay calcines, the calcine with the best leaching response for each calcination temperature was subjected to activation energy studies to establish the thermodynamic basis for their better leaching kinetics. This was in accordance with the Arrhenius rate law, viz:

$$k = A e^{-\left(\frac{E_a}{RT}\right)} \ or \ \ln k = -\left(\frac{E_a}{R}\right) \cdot \frac{1}{T} + \ln A \tag{5}$$

where, k is the leaching rate constant, A is the Arrhenius frequency factor, E_a is the activation energy for the leaching reaction, R is the universal gas constant

(=8.314 J·mol^{-1}·K^{-1}), and T is the leaching temperature on the absolute scale.

Thus, samples held for 60 minutes at different temperatures of calcination were leached in 1M HCl at 25°C, 50°C, 75°C and 100°C for a reaction contact time of 60 minutes. All other variables such as clay particle size, shaking speed, and solid/liquid ratio were kept constant at less than 300 μm (−50 mesh), 100 rpm and 0.02 g/ml, respectively. The natural logarithm of rate constants ($\ln k$) as deduced from the solubility data (based on second-order reaction kinetics which appeared to fit the data) and the reciprocal of absolute temperature $\left(\dfrac{1}{T}\right)$ were used for Arrhenius plots to determine the activation energy (E_a) in the case of each clay calcine [34].
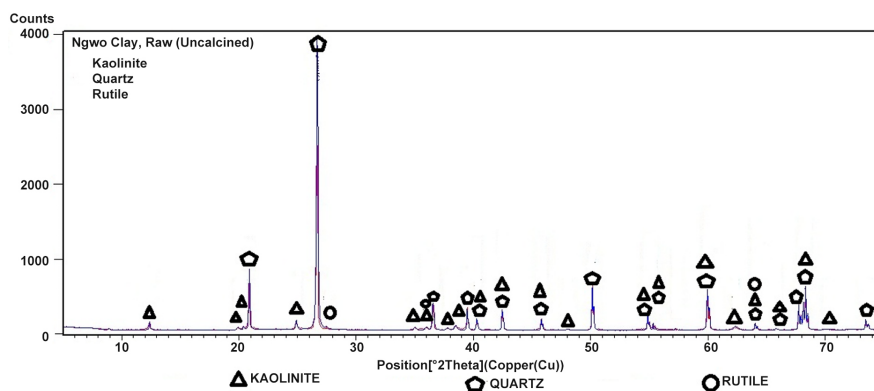
3. Results and Discussion

3.1. Type and Composition of Clay

Ngwo clay is dominated by kaolinite mineral with free silica or quartz, and rutile as associated impurities (Figure 2). The alumina content of 24.63% (Table 1) is considered good enough for hydrometallurgical treatment of the clay as a source of alumina, and hence aluminium [6] [35] [36]. The x-ray diffraction pattern of the raw clay (Figure 2) shows the peaks for the constituent mineral phases. Similarly, Figure 3 is the XRD pattern for the optimal clay calcine showing that the sharp kaolinite peaks in Figure 2 are no longer distinct. The disappearance of the kaolinite peaks is indicative of the appearance of an amorphous phase (metakaolinite) due to thermal transformation of the clay [28]. A study of the phase transformations of kaolinite from different deposits in Russia and Ukraine showed similar results [33]. It is this amorphous metakaolinite ($Al_2O_3 \cdot 2SiO_2$) that releases alumina (Al_2O_3) for dissolution making the clay respond to acid

Table 1. Chemical composition of Edda clay.

Chemical Composition (%)								
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI
52.15	24.63	1.53	1.58	0.44	1.52	0.52	0.54	13.8

Figure 2. XRD pattern of uncalcined Ngwo clay.
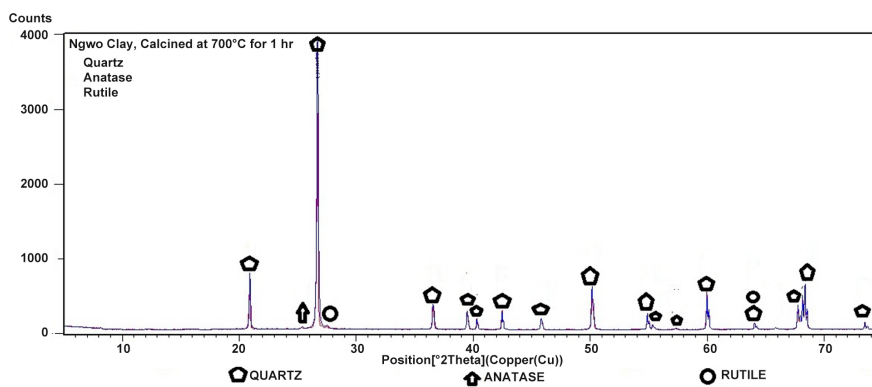
**Figure 3.** XRD pattern of Ngwo clay calcined at 700˚C for 1 hour.

leaching. Thus, proper thermal treatment and transformation of the clay activates it for acid leaching [28].

3.2. Dissolution of Alumina in Response to Acid Leaching

The presence of Al^{3+} ions in the leach solutions shows that a dissolution reaction occurred between the alumina in the clay calcine and the leaching reagent. It is proposed that hydrochloric acid ionized in water to produce protons or hydrogen ions (H^+) in the hydrated form known as hydronium (H_3O^+) in accordance with reaction (6) [37].

$$HCl + H_2O \rightleftharpoons H_3O^+_{aq} + Cl^-_{aq} \text{ or } HCl_{aq} \rightleftharpoons H^+_{aq} + Cl^-_{aq} \tag{6}$$

The dissolution of alumina (Al_2O_3) from the clay is therefore the result of interaction between hydrogen ions (H^+) and aluminium atoms of the alumina in accordance with reaction (7):

$$Al_2O_3 \cdot 2SiO_2 + 6\left(H^+Cl^-\right) \rightarrow \left(2Al^{3+}6Cl^-\right) + 3H_2O + 2SiO_2 \tag{7}$$
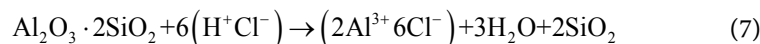
The extent of dissolution was expressed in percentage or as a fraction where the fraction of Al ions (X_{Al}) leached out of the clay into the solution was given as

$$X_{Al} = \frac{\text{concentration of Al ions in the solution}}{\text{concentration of Al ions in the original clay sample}}$$

while the percent Al ions (%Al) leached out of the clay into the solution was expressed as $\%Al = 100 \cdot X_{Al}$.

The effect of calcination temperatures at different durations of heating (30, 60 or 90 minutes) is illustrated in **Figures 4-6**. It was observed that response to leaching is lowest for the uncalcined clay sample (control 1, ~25˚C) followed by that calcined at 1000˚C (control 2). The ability of the acid (1M HCl) to extract alumina from the clay (and enrich the leach solution with aluminium ions) varied as calcination temperature increased from 500˚C to 900˚C. However, at 1000˚C (control 2), the ability of the acid to attack the clay and remove alumina dropped drastically. Under 30, 60 and 90 minutes holding times (**Figures 4-6**); the peak leaching response occurred in the case of samples calcined at 700˚C. As
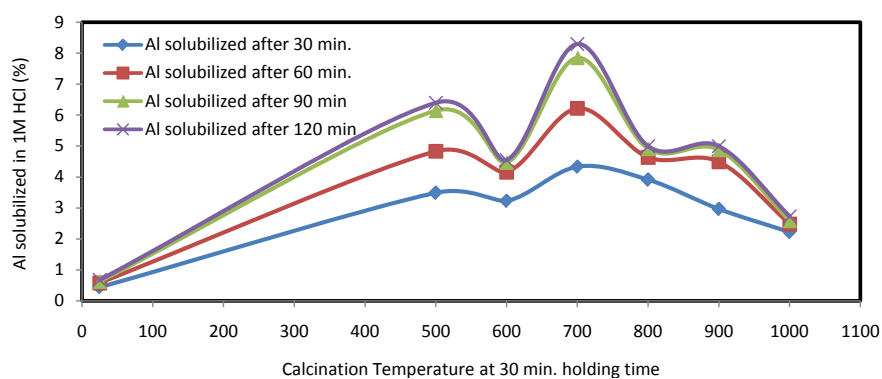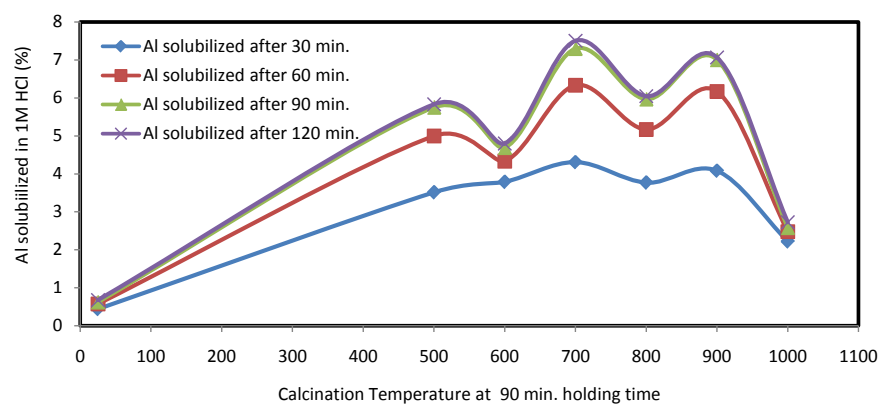
Figure 4. Effect of calcination temperature at 30 minutes holding time on the solubilization of Al from Ngwo clay leached at room temperature.
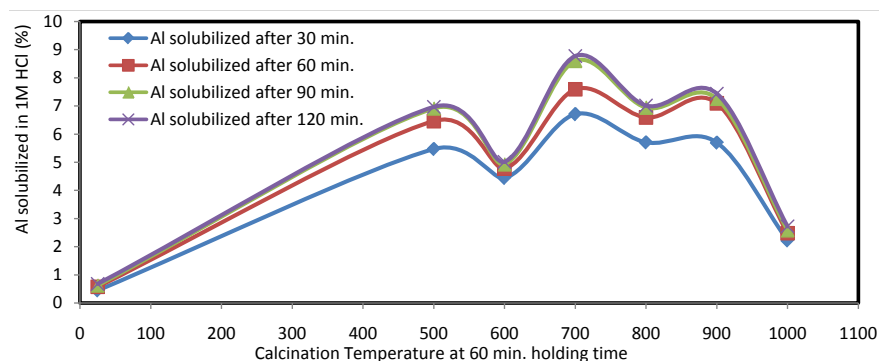
Figure 5. Effect of calcination temperature at 60 minutes holding time on the solubilization of Al from Ngwo clay leached at room temperature.

Figure 6. Effect of calcination temperature at 90 minutes holding time on the solubilization of Al from Ngwo clay leached at room temperature.

shown, between 500°C and 900°C; the response of Ngwo clay to leaching by acid attack increased and dropped, reaching its peak at 700°C. This behaviour is probably due to the transformation of the clay from its room temperature crystalline form (kaolinitic) to various degrees of amorphous state (metakaolinitic) and back to high temperature crystalline form at 1000°C and beyond, as the clay steadily lost physically combined water (through drying and dehydration) and chemically combined water (de-hydroxylation) as temperature increased. In

other words, the clay transformed completely to an amorphous phase (metakaolinite) when it was heated to 700˚C, while crystallinity or various degrees of crystallinity existed in the clay below and above 700˚C.

3.3. Effect of Holding Time

It was interesting to observe that samples held for 60 minutes in the furnace responded better on leaching than those held for 30 or 90 minutes at all calcination temperatures investigated (**Figure 7**). For example, after 120 minutes of leaching in 1 M HCl, the percent Al extracted in the case of samples calcined at 700˚C were 8.29, 8.77, and 7.51% respectively for holding times of 30, 60, and 90 minutes. This means that the ability of the acid to attack alumina in the clay and remove aluminium was low at 30 minutes holding time, reached peak value at 60 minutes holding time, and declined again when holding time was extended to 90 minutes at all temperatures studied (500˚C, 600˚C, 700˚C, 800˚C, and 900˚C). This observation could be because at 30 minutes, the transformation of the clay to amorphous (non-crystalline) state was just beginning, the transformation to amorphous metakaolinite reached advanced stage after 60 minutes but holding up to 90 minutes resulted to the reappearance of some crystallinity. Prolonged heating can therefore make the silica and alumina contents of clay to react, resulting in reduction of solubility. Furthermore, prolonged heating may also bring about the sintering of particles or phases leading to reduction in leaching response [38]. It can be concluded therefore that 60 minutes or 1 hour is the optimum calcination holding time for thermally activating Ngwo clay to respond maximally to leaching in acid.

These observations are in conformity with XRD patterns shown in **Figure 2** and **Figure 3** for the raw and optimally calcined clays. Thermal treatment therefore broke down the clay structure by removing the OH water (chemically combined) holding the network of silica tetrahedra and alumina octahedra, thus rendering the alumina acid-soluble. At sufficiently high temperatures or for prolonged heating durations, the silica and alumina recrystallized to form a crystalline and insoluble phase (e.g. mullite). It can be concluded therefore that
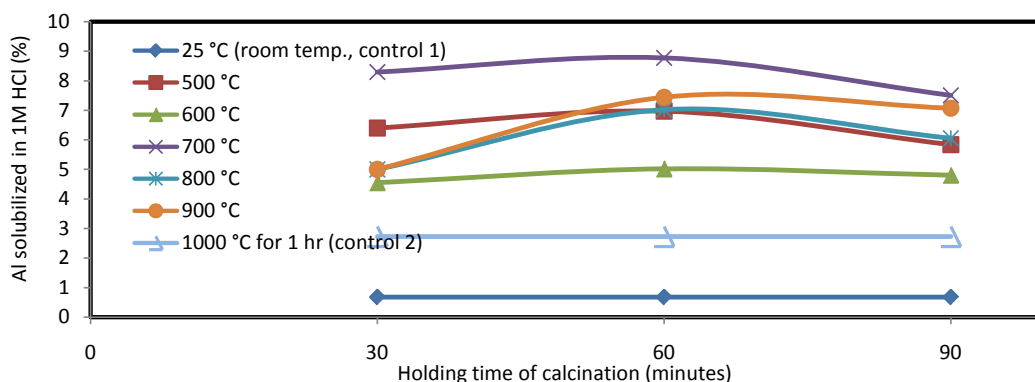

Figure 7. Effect of calcination duration (holding time) at different temperatures on solubilization of Al from Ngwo clay under 120 minutes leaching time.

heating to 700˚C and holding for 60 minutes is the optimum calcination temperature and duration for thermally activating Ngwo clay to respond optimally to acid leaching.

3.4. Effect of Leaching Temperature and Thermal Activation

As noted earlier, clay calcines produced by holding for 60 minutes in the furnace (at all calcination temperatures studied) responded to leaching better than those held for 30 or 90 minutes. The effect of leaching temperature on the leaching response of calcines produced under 60 minutes duration of calcination was studied further; the result is given in **Figure 8**. As shown, at all calcination temperatures investigated, leaching response increased as leaching temperature increased. In the case of the optimal calcine (700˚C held for 60 minutes), the amounts of aluminium solubilised after leach contact time of 1 hour in 1 M HCl were 12.46%, 24.23%, 38.76%, and 51.84% for leaching temperatures of 25˚C, 50˚C, 75˚C, and 100˚C, respectively. It can be concluded that leaching temperature has a significant effect on the rate of alumina dissolution from the clay. This is because high temperatures enhance diffusion or mobility and hence collision frequency of reacting species in addition to providing extra thermal energy for overcoming the energy barrier or activation energy for the process. Similar observations were made by other researchers [39] [40] [41].

The effect of thermal activation on leaching of clay calcines at different leaching temperatures is also shown in **Figure 8**. For example, the amount of Al extracted within 1 hour of leaching in 1 M HCl at 100˚C increased from 7.42% to 51.84% over the activation temperature range 25˚C (for uncalcined clay) to 700˚C (optimal calcine). Then there was a steady decline in Al extraction to 26.23% (for calcine produced at 1000˚C). Similar trends were also observed at leaching temperatures of 25˚C, 50˚C and 75˚C. This can be explained based on solid phase changes or transformations in the clay brought about by thermal treatment [38] [39] [40] [41].
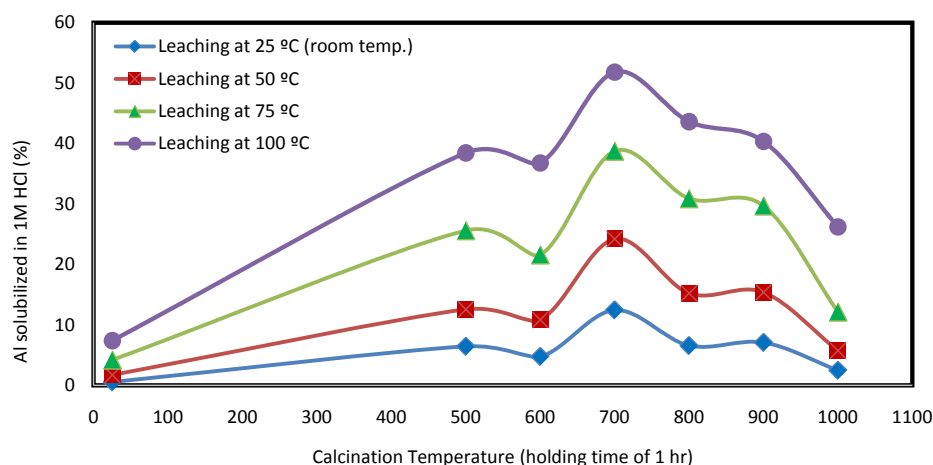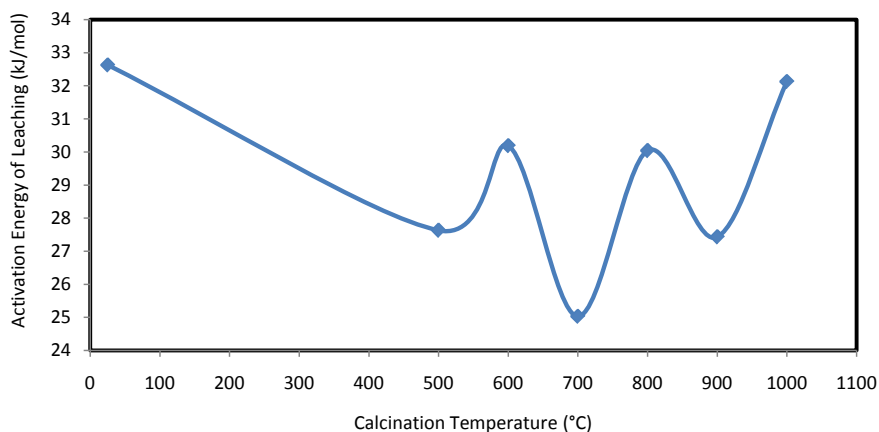

Figure 8. Effect of leaching temperature on the leaching response of selected Ngwo clay calcines within leach contact time of 60 minutes.

3.5. Effect Thermal Treatment on Activation Energy

The activation energy of leaching was found to depend on the thermal treatment given to the clay. Low activation energies were obtained in the case of the clay calcines that responded well to leaching *i.e.* those with high level of Al extraction. This shows that the optimal calcination temperature and duration corresponded with the lowest activation energy (**Figure 8** and **Figure 10**). **Figure 9** shows plots of ln*k* versus 1/T for samples calcined under 60 minutes holding time and leached at different temperatures, *i.e.* 25˚C (298 K), 50˚C (323 K), 75˚C (348 K) and 100˚C (373 K). The activation energies derived from **Figure 9** were used to plot **Figure 10**. The lowest activation energy for leaching (25.03 kJ/mol), as shown, correspond with the overall best calcine for the clay considering the aluminium solubility rate (51.84%). Given that activation energy is the energy
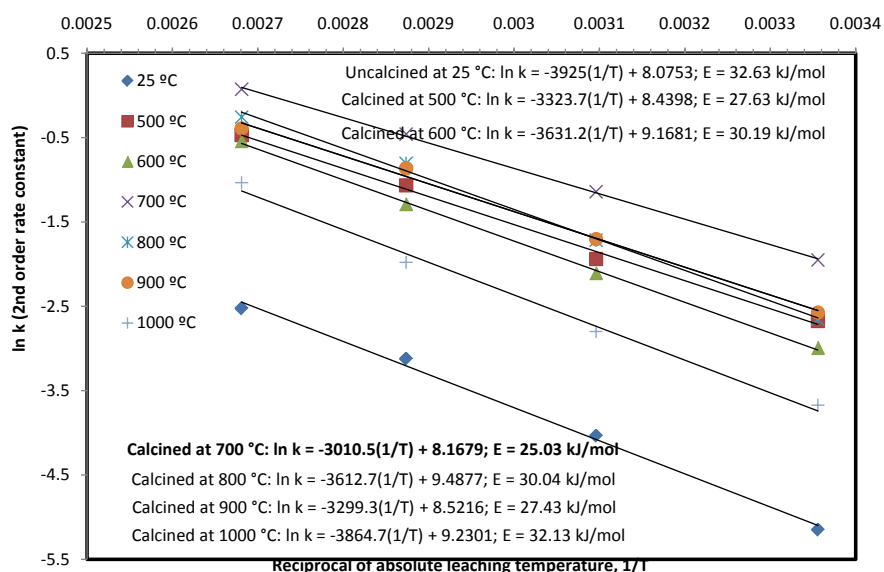
Figure 9. Arrhenius plots for the leaching of Ngwo clay calcined at various temperatures and leached in 1 M HCl at 198, 323, 348 and 373 Kelvin.

Figure 10. Effect of calcination temperature on activation energy of leaching for Ngwo clay leached in 1 M HCl for 60 minutes contact time.

barrier that must be surmounted for a reaction to occur; the lowering of this energy means that leaching reaction is made thermodynamically or energetically easier, thus enhancing reaction rates or kinetics. This explains why clay calcine produced at 700˚C (holding for 60 minutes) yielded the highest solubility of alumina from the clay as shown by the %Al in leach solution. It was also observed that the uncalcined sample of the clay required the highest activation energy of leaching (32.63 kJ/mol); explaining why it was very difficult to leach alumina from such sample, as seen in its very low solubility data (%Al taken into the leach solution). Thus, the alumina in uncalcined or unactivated clay is locked up in the clay chemistry, responding very sluggishly to acid attack. Similarly, clay sample calcined at 1000˚C for 60 minutes recorded the next highest activation energy (32.13 kJ/mol) after the uncalcined clay. Leaching of alumina was also difficult in this case because at 1000˚C, formation of crystalline phases had commenced. Thus, the alumina is again locked up in the mullite network, making it difficult for acid attack. Similar findings were reported in literature [38] [39] [40] [41]. As shown in Figure 10, activation energy varied between the extremes of the high values reported for the uncalcined clay at ~25˚C and those for samples calcined at 1000˚C; reaching the lowest value of 25.03 kJ/mol at 700˚C. This means that the clay was transformed completely to an amorphous form at 700˚C. In other words, the clay was thermally activated for maximum leaching response at 700˚C [28]. The alumina in the amorphous phase is therefore more soluble than that in the crystalline orsemi-crystalline phases that existed below and above 700˚C.

4. Conclusions

The thermal treatment conditions required for transforming Ngwo clay to metakaolinite and subsequent leaching of alumina were investigated. Different thermal treatments produced different degrees of leaching response from the clay based on the nature and degree of phase transformation. X-ray diffraction studies confirmed that the optimal leaching response corresponded with the thermal treatment that transformed the clay to an amorphous phase or metakaolinite. The clay was transformed from its low-temperature crystalline form to an amorphous form (at 700˚C) and then back to high-temperature crystalline phases. Prolonged heating (above 90 minutes) under isothermal conditions also caused the appearance of crystalline phases and loss of solubility. Best results were achieved under 60 minutes heating duration at 700˚C. Thermal treatment also affected the activation energy of leaching such that high solubility (high leaching response) corresponded with low activation energy. Thermally activated Ngwo clay can be used as alternative resource for alumina in Nigeria where bauxite is scarce or non-existent.

The present work has established the optimal calcination conditions for Ngwo clay. Further work is recommended to investigate the effects of the leaching variables such as clay particle size, acid concentration, leaching temperature, sol-

id/liquid ratio of clayweight to acid volume, and shaking rate. This will establish the optimal leaching conditions for solubilizing the alumina in the clay. Methods of recovering alumina from the leach solution should also be investigated.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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