pH Models for Monitoring the Conversion of ‘Kankara’ Clay to Alum

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Abstract
All industrial chemical processes are designed to transform cheap raw materials to high value products (usually via chemical reactions). This work which excluded the beneficiation process involved the transformation of Kankara clay which was reacted with sulphuric acid into alum with the sole aim of using pH measurement for process control and to developing a specific quality monitoring parameter for the conversion of kaolinitic clay to alum. The alum was produced by reacting Kankara clay with sulphuric acid under controlled conditions. 10g of Kankara sample clay was dissolved in an equivalent amount of water required stoichiometrically to prepare 40wt% of H2SO4 and the pH of the stirred mixture was measured at different concentrations by using buffer and pH measurement techniques. Furthermore, 10g of the sample clay was digested with a stoichiometric amount of H2SO4 acid and reacted at different temperatures for which the pH was monitored. pH models for monitoring the conversion of ‘Kankara’ kaolinitic clay were generated; validated using regression methods. The system model data compared with the experimental model data showed a linear correlation of determination, R² = 0.999 at 5% level of significance. These models can be used as an effective tool for material balance, reactor design, process development and scale – up parameters for pilot plant design.

Keywords: alum, kankara clay, conversion, selectivity, alumina and yield

INTRODUCTION
Clay of kaolinitic minerals (kaolin) is found in large deposits in different parts of Nigeria (Macload, 1979 and Lori, et al, 2007). Kaolin occurs either as residual or sedimentary deposit and is often grouped with fireclays because of its good refractory nature (George, 1984). Nigeria has a deposit of 90,000 tons of clay in ‘Kankara’, Katina State. Analysis of this clay shows that it is essentially 48.02% silica; 37.50% alumina 0.10% ferric oxide and 14.47% combustibles (Macload, 1979). The main characteristic which determines the utility of the clay for various applications is its purity (Saikia, et al, 2003; Sei et al, 2004 and Lori, et al, 2007).

The economy of every nation keeps thriving on value addition of its mineral resources. To enhance this value addition, trial alum production from Kankara clay has been achieved. Alum is produced industrially by reacting sulphuric acid, H2SO4 with an alumina rich source. Alternative alumina – rich sources commonly used are:
- Hydrated alumina, being a synthetic product least in impurities among other raw materials
- Bauxite (50 – 60% alumina content), and
- Kaolinitic clays (38 – 41% alumina content).

Aluminium sulphate, Al2(SO4)3.18H2O due to its peculiar nature possesses a wide range of uses. It is mainly used in the industry for paper sizing, waste treatment, sewage treatment, food applications, pharmaceutical preparations, colour making (dyeing operations) and domestic cleaning (Alum, 2011). The first step in any reaction engineering analysis is formulating a mathematical framework to describe the rate (and mechanism) by which one chemical species is converted into another in the absence of any transport limitations (chemical kinetics). The rate is the mass, in moles of a species, transformed per unit time, while the mechanism is the sequence of individual chemical events, whose overall result produces the observed transformation. Knowledge of the rate of transformation, however, is essential for any reaction engineering activity. There are various ways and methods of monitoring the transformation of reacting species into product (s) (Ranade, 2002; Levenspiel, 2004). The choice of a monitoring process is a function of several factors such as nature of the reacting species, type of reaction, quality control, safety, cost, etc. The concept of hydrogen ion concentration, pH is of great importance in a large number of reactions and processes. Hydrogen ion concentration, pH is defined by equation 1.

\[ \text{pH} = -\log_{10}[H^+] \]

Where:

\[ [H^+] = 10^{-\text{pH}} \]

Here, H⁺ is the activity of the hydrogen ion. In dilute solution, the activity is essentially equal to the concentration (Mattock, 1961; Bates, 1973). pH is an
integral parameter for optimum quality in alum production. The primary detecting element in pH measurement is the glass electrode. When the glass surface is placed in contact with a solution, a potential will be set up at the pH sensitive glass membrane as a result of difference in hydrogen ion activity in the sample according to the familiar Nernst equation if a true pH response properly exist:

\[ E = E^o - \frac{2.303RT}{F} \cdot \text{pH} \]  

Most pH measurements are made to provide an index to some property of the solution related to a free acidity or basicity: the chief requirement is normally one of comparison rather than the actual significance in terms of H⁺ ion units (Mattock, 1961). The fractional conversion of a given reactant can be compared to hydrogen concentration. The fractional conversion, \( X_A \) of a given reactant \( A \) is defined as the fractional reactant converted into product, expressed as

\[ X_A = \frac{Na - Na}{Na} \]  

Fractional conversion is a convenient variable often used in place of concentration in engineering work (Levenspiel, 2004). It is assumed that all the reactants are in their purest form; that the reaction proceeds to completion and that the reacting system is a constant density, volume does not change.

Therefore,

\[ C_A = \frac{Na}{V} = \frac{Na(v \cdot (1 - Na))}{V} = C_0(1 - X_A) \]  

The fractional conversion can be expressed also in terms of H⁺ ion concentration as in equation 5

\[ X_A = \frac{Na - C_H^+}{C_H^+} \]  

Equation 5 can further be expressed mathematically as

\[ X_A = \frac{10^{-pH} - 10^{-pH}}{10^{-pH}} \]  

MATERIALS AND METHODS
Techniques for Buffer Standardization and pH Measurement
The electrode was washed with distilled water and carefully wiped dry with Wattman No. 24 filter paper. The pH meter (JENWAY 350) was standardized at 80°C with a buffer solution of pH = 4.16 to ensure a readout from the meter with temperatures above 29°C. After buffering, the dry and clean electrode system was introduced into the reacting system in a quick fit conical flask (250ml PYREX) on a magnetic stirrer hot plate (OHaus Explorer Pro) for pH measurement.

Effect of pH on Various Concentrations of Al^{3+} and Fe^{2+}.
10g of Kankara sample clay was dissolved in an equivalent amount of water required stoichiometrically to prepare 40wt% of H₂SO₄ according to the reaction (7)

\[ Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O \]  

The pH of the stirred mixture was measured at different concentrations.

Effect of pH on Temperature and Concentration of the Reacting Species
The pH of the reactants in equations 7 and 8 above were measured at different temperatures with respect to different concentrations. Furthermore, 10g of the sample clay was digested with a stoichiometric amount of H₂SO₄ acid and reacted at different temperatures for which the pH was monitored.

Model Validation
Experimental values of the corresponding conversion of the reactants in 2.3 were compared with system model fractional conversion data of Al₂O₃ using statistical regression and correlation analysis at 5% level of significance (95% confidence interval) Microsoft EXCEL (2007) software.

RESULTS AND DISCUSSION
Overview of the reactants chemistry
Kankara kaolinitic clay has been characterized to consist of the following oxides SiO₂, Al₂O₃ and Fe₂O₃ (Attah et al, 2007 and Lori et al, 2007). SiO₂ and Al₂O₃ are oxides of period III in the periodic table which appear as in the series:

Na₂O CO Al₂O₃ SiO₂ P₂O₅ SO₂ Cl₂O₇

Atomic size decreases from Na to Cl (ability to rupture O-H bond and release H⁺ ion in water increases). There is a pronounced change in acid – base character as one progress from left to right. Na₂O is a basic anhydride and Cl₂O₇ is an acidic anhydride. In this sequence we go from strong base producing element, Na to a very strong acid producing element, Cl. The situation in the middle is interesting, Al₂O₃ is amphoteric (neither a good acid producing nor a good base producing agent). Fe₂O₃ is a transition period oxide. It is known that metals form basic oxides; non – metals form acid oxides and semi – metals tend to form amphoteric oxides. In general: the electropositive the metal, the more basic is its oxide; and the more electronegative the non – metal, the more acidic is its oxide (Wilson and Newal, 1976). Thus, the oxides of Kankara Clay are classified as follows:

- SiO₂ – covalent, it is weakly acidic
- Al₂O₃ – Ionic, amphoteric in nature
- Fe₂O₃ – Ionic, weakly acidic

The resultant effect of the oxides reacting with H₂SO₄ can be described thus; SiO₂, though inert yet may increase the acidity, pH of the reacting mixture.
Al₂O₃, being amphoteric in nature will rather act as a base with H₂SO₄ acid to produce salt (Alum) and water as in equation 7 and the effect will be an increase in the pH value. Fe₂O₃, will react as in equation 8 to produce an acid salt, Fe₂(SO₄)₃.

Fig. 1: Effect of temperature on pH at different concentrations of ferric oxide

Fig. 2: Effect of temperature on pH at different concentrations of Alumina

Concentration and Temperature of the Reactants
Any increase in the concentration of the reacting species will follow the same trend as in 3.1.1 and thus increase the activity of the H⁺ ion, pH of the reacting system. It was generally observed that as the concentration of the reactants (Al₂O₃, Fe₂O₃ and H₂SO₄) increased, there was a corresponding increase in the pH (see Fig. 1 and Fig. 2). The temperature effect on the reacting mixture increased the mobility of the respective ions, hence the ability to rupture the O – H bond and thus increase the acidity, pH of the reacting mixture. In aqueous solutions, the activity of the H⁺ ion is very closely proportional to the concentration of a strong acid down to about pH, 0 and about pH, 14. However, beyond this limit, the H⁺ ion activity and the effective pH change much more rapidly than one could calculate simply from changes in the concentration of the reacting species of either strong acid or base (Williams, 1970).

Conversion of Kankara Clay to Alum
The conversion of Kankara kaolinitic clay to alum was observed to increase from 77.61% to 79.190% as the H₂SO₄ acid concentration increased from 30 – 40wt% at 0.9:1.0 acid to clay ratio over a reaction period of 18hours. The corresponding pH values are 2.42 and 2.37 respectively. An optimal conversion of 83.93% was achieved with 5g Al₂O₃ and 40wt% H₂SO₄ acid base on stoichiometry. This shows that as the surface area (contacting surface) of Al₂O₃ increased, there was a higher conversion yield.

The selectivity of H₂SO₄ acid on Al₂O₃ was 0.997 with a conversion of 83.68% and a product yield of 83.43% at a pH value of 2.54.

Fig. 3: Yield of Alum from Kankara Clay with reaction time

pH Models for Monitoring the Conversion of Kankara Clay
The following conversion models were developed and established using molar ratios based on stoichiometry and chemical analysis of the clay sample with respect to the experimental data.

\[ X_{H^+} = \frac{C_{H^+}}{C_{H_2O}}, \text{ basic conversion model} \]

\[ X_{Al^{3+}} = 0.997 \frac{C_{Al^{3+}}}{C_{H_2O}} \]
\[ X_{Fe^{3+}} = 3.0 \times 10^{-2} X_{H^+} \]

Fig. 4 shows the conversion distribution with reaction time when 5g clay reacted with 40wt% H₂SO₄ acid. The following conversions were achieved, 83.9% for H⁺; 83.6% for Al³⁺ and 0.26% Fe³⁺ during the 18hrs reaction time.

The model \( X_{Al^{3+}} \) was validated using statistical regression and correlation analysis at 5% level of significance; it was observed that both the
experimental model and system model (Fig.4) showed no significant difference ($t_0 = 1.193 < \text{tabular value}, \ t = 2.776$) with $(n - 4) = 2$ degrees of freedom.

CONCLUSIONS
From the experimental data, chemical analysis of the clay and stoichiometry, two system conversion models were developed for monitoring the conversion of Kankara Clay to Alum. There was no significant difference between the system model and the experimental data model at 5% level of significance.

The reacting species constituted an effective increase in the H$^+$ ion concentration, pH with rise in temperature. There was 83.68% conversion of Al$\text{}_2\text{O}_3$ to alum with a product yield of 83.43% during an 18hrs digestion time. There was a linear relationship between the system model and the experimental model as $Y = 1.003X - 0.129$ with a linear correlation of determination ($R^2 = 0.999$).

SYMBOLS

- $[\text{H}^+] =$ hydrogen ion concentration, mol/litre
- $C_{\text{H}^0} =$ initial concentration of H$^+$ ion
- $C_{\text{H}^+} =$ Concentration of H$^+$ ion at time, $t$
- $C_A =$ molar concentration of specie A at any time, $t$
- $N_A =$ Amount of specie A at time, $t$
- $N_{\text{Al}2\text{O3}} =$Amount of specie A at time, $t = 0$
- $X_A =$ fractional conversion of specie A at time, $t$
- $X_{\text{Al}2\text{O3}} =$ fractional conversion of specie A at time, $t = 0$
- $E_0 =$ standard potential
- $T = (^\circ\text{C} + 273.16)\ \text{K}$
- $F = 96493.1 \ \text{c/g equivalent}$

REFERENCES


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