

Development of alum from kaolin deposit using response surface methodology

Abstract

A novel approach of for the formation of Hydrated Sodium Aluminium Sulphaite (Alum) from metakaolin was employed in this study. This process was used to form alum from metakaolin. It majorly involves captivating the self generated energy as a result of acid solvating in metakaolin-water solution to supply the mixing and activation energies requirement of the process without external heat source. The study gives a regression equation for the formation of Alum at a given volume of acid per gram metakaolin, temperature of reaction and desired conversion level.

Keywords: kaolin, metakaolin, dealumination, alum, yield

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Introduction

Kaolinite is a clay mineral which is part of the group of industrial minerals, with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen-atoms to one octahedral sheet of alumina octahedral. Rocks that are rich in kaolinite are known as kaolin or china clay.¹ The name is derived from Kao-ling, a village near Jingdezhen, Jiangxi province, China. The name entered English in 1727 from the French version of the word: "kaolin", following Francois Xavier d'Entrecolles's reports from Jingdezhen.² In Africa, kaolin is sometimes known as kalaba (in Gabon and Cameroon), calaba and calabachop (in Equatorial Guinea). Kaolinite has a low shrink-swell capacity and a low cation exchange capacity (1-5meq/100g). It is a soft, earthy, usually white mineral (dioctahedral phyllosilicate clay), produced by the chemical weathering of aluminumsilicate minerals like feldspar. In many parts of the world, it is colored pink-orange-red by iron oxide, giving it a distinct rust hue. Lighter concentrations yield white, yellow or light orange colors.

The primary source for the production of alum is bauxite, but with declining deposits alternative sources are been sought. One of the handy alternatives is kaolin and that it is next to bauxite in alumina content has made it more desirable for alum production. The word alum is derived from its Latin generic form "alumen", which was applied to several astringent substances, most of which contained aluminum sulfate which are single salt alums: $Al_2(SO_4)_3 \cdot xH_2O$ and double salt alums: Potassium alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$; Ammonium alum $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$; Soda alum $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$; Ferric alum. $FeSO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ etc.³ Alum is used in food and pharmaceutical related industries as well as in water purification. It is also extensively used in the manufacture of vegetable glues, porcelain cements, natural deodorants, tanning, dyeing, fireproofing textiles and paper, and in alumina production for catalytic and refractory applications.

Several sintering and acid-extraction processes have been investigated for kaolin and other clays. These processes include the lime sinter process,⁴⁻⁷ the lime-soda sinter process,⁸ nitric acid process,^{9,10} Hydrochloric acid process¹¹⁻¹⁴ and Sulfurous acid

processes.¹⁴⁻¹⁶ The acid processes are essentially suitable for clays and kaolin low in iron and titanium oxides and they have been used in extraction of other metals.¹⁷ In these processes, calcined aluminous ore is treated with a mineral acid, such as H_2SO_4 . The treatment produces soluble aluminum salt (e.g. aluminum sulfate) and the silica appears in the residue with the bulk of the impurities. Iron and titanium, also pass into solution together with aluminum salt which necessitate their removal by purification step before conversion to alumina. Early investigations of sulfuric acid processes for the production of alumina are described by Tilley GS.¹⁸ Some of the reported literature recommended calcinations temperature of 770-820°C.¹⁹ Concentration of about 70% H_2SO_4 has been patented to extract alumina from clays. Leaching with sulfuric acid was practiced at 90°C and 10-20% acid concentration.

Another patent reported 30% as the recommended concentration of the acid.¹² reported that a temperature of 105°C as a recommended extraction temperature, others recommended a temperature of 70-90°C for 10-2hours to extract 70-80% of alumina.¹² extracted alumina from Pakistani high-aluminous clays after calcinations at 700-800°C for one hour and leaching with sulfuric acid for 1-2hours at 110°C.

Acid activation has been widely studied as chemical treatment methods for improvement of the surface and catalytic properties of fibrous clays 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.^{20,21} Literature revealed the acid activation of metakaolins.²²⁻²⁴

Coagulation is a process in (drinking water or industrial effluent waste) water treatments. Alum, $Al_2(SO_4)_3 \cdot 14-27 H_2O$ or its equivalent double salts of either sodium or potassium is known to be the most common coagulant used in water treatment due to its effectiveness in treating a wide range of water types.²⁵ Alum's relatively low cost makes it to be the preferred coagulant despite its few short comings in terms of large sludge production and limited pH range of effectiveness when compared to the more recent coagulants such as polyaluminium chloride (PACl), polyaluminiumsulphate.²⁴⁻²⁸

Design of experiments (DOE) can be defined as the systematic method of determining the relationship between factors affecting a

process and the output of that process. DOE is an advanced statistical tool to study efficiently the effect of a large number of variables with a minimum effort in data collection.^{29,30} This investigates the effects of input variables (factors) on output variable (response) simultaneously. It is majorly used to find the cause-and-effect relationships, which is needed to manage process inputs in order to optimize the experimental outputs. In an experiment, one or more process factors or variables are deliberately changed in order to observe the effect the changes have on one or more response variables. The (statistical) design of experiments (DOE) is an efficient procedure for planning experiments so that the data obtained can be analyzed to yield valid and objective conclusions. An experimental design is the laying out of a detailed experimental plan in advance of doing the experiment. Simple experimental design and statistical tools for data analysis can provide much information about the system under investigation after only a few experiments. Such information can be key in decision making for further experiments and can enable the development of robust and reliable protocols for chemical synthesis, analytical methods or biological assays.³¹

Experimental procedures

Beneficiation

The raw kaolin clay used was procured from a kaolin field in Ogun State, Nigeria. The raw kaolin sample was crushed and grinded using mortar and pestle. The grinded kaolin was wet-beneficiated with deionized water in order to purify it from physically and chemically combined impurities such as metallic oxide, soluble salts and grits. The wet kaolin was stirred continuously using electric stirrer at 200rpm for 30minutes in order to separate all the agglomerates of clay particles. It was then sieved through a 106micron to get rid of intermediate coarse associated mineral particles. This process was done twice in order to remove all traces of grits. The fine kaolin suspension was thereafter allowed to settle overnight by gravity, decanted and further dewatered using filter paper, dried atmospherically for 2days and further dried at 60°C in an electric oven for 4hrs. The dried beneficiated kaolin lumps were milled to very fine particle size and the sample subsequently was analyzed. Table1 shows its major oxide constituents.

Table 1 Chemical composition of raw kaolin beneficiated kaolin and metakaolin

Chemical constituent	Arobieye kaolin	Beneficiated kaolin	Metakaolin
Oxides	Mol %	Mol %	Mol %
SiO ₂	48.79	45.94	49.24
Al ₂ O ₃	33.58	34.84	36.6
Fe ₂ O ₃	2.65	2.88	3.03
CaO	2.98	3.10	3.11
MgO	0.58	0.59	0.63
SO ₃	0.04	0.04	0.02
Na ₂ O	0.07	0.07	0.07
K ₂ O	0.01	0.01	0.01
TiO ₂	1.48	1.64	1.62
P ₂ O ₅	0.10	0.10	0.01
Mn ₂ O ₃	0.01	0.01	0.02
Si/Al molar ratio (Mol)	2.47	2.24	2.29

Calcination

The dry beneficiated kaolin was calcined at 850°C in an electric furnace (Nabertherm, 30 1400°C) for 6hours.³²⁻³⁴ The dried beneficiated kaolin was heated in a programmable furnace from room temperature to the desire temperature of 850°C at heating rate of 10°C/min. The metakaolin obtained was cooled in a desiccators and then package for analysis.

Dealumination of metakaolin

In a batch reaction, 46g of metakaolin was added to 156ml of deionized water in a three-neck round bottom flask placed on a magnetic stirrer. On the two necks were fitted with a reflux condenser and a thermometer while the neck was closed with a rubber cork. 98wt% H₂SO₄ was added to the metakaolin slowly in the flask.³³⁻³⁵ The volume of acid added was varied with constant residence time of 10minutes. The reaction was quenched with 200ml of deionized water, transferred to 500ml beaker and allowed to cool and settled down. The beaker content was filtered with filter paper (whatman 1-541). Dealuminated kaolin was dried atmospherically for 2days and further dried at 60°C in an electric oven for 4hrs. The dried sample lumps were milled to very fine particle size with ball and the sample subsequently was analyzed.

Optimization consideration of the process scale-up

In this research work, set of runs, 20ml, 25ml, 30ml, 35ml and 40ml of 98wt% H₂SO₄ per batch were added to 46g of metakaolin in order to form Alum. The modification scheme was done in order to assess the extent to which the operation will affect alum yield and conversion (Figure 1).



Figure 1 Picture of raw Kaolin.

Results and discussion

Material balance

Table1 shows the major oxide constituents of raw Kaolin, Beneficiated Kaolin and metakaolin. The reduction in the Si/Al Mol% from 2.47 (in the raw clay) to 2.29 (in the metakaolin) respectively, implies that the screened out particles are silica rich minerals. High Fe₂O₃ and CaO composition in the samples may be attributed to sources, location and mode of formation i.e. either potash or ferric kaolin. On the average, about 64wt% pure kaolin recovery was attained, the amount of Alumina in metakaolin is 36.6 wt%. The potential yield of Alum from kaolin is enhanced through the formation of metakaolin from 33.58 wt% to 36.6 wt%.

Optimization consideration and process scale-up

The effect of volume of acid/g metakaolin conversion and temperature of reaction are shown in Figures 2–4. The percentage alum yield increases as the volume of acid per batch increases. This

implies that Alum conversion increase as the volume of acid per gm metakaolin increase. Figure 2 shows the surface plot of the dependency of conversion and the volume of acid used on the mass of alum, while Figure 3 shows the surface plot of the dependency of temperature and volume of acid and Figure 4 shows the dependency of temperature and conversion on mass of alum produced respectively.

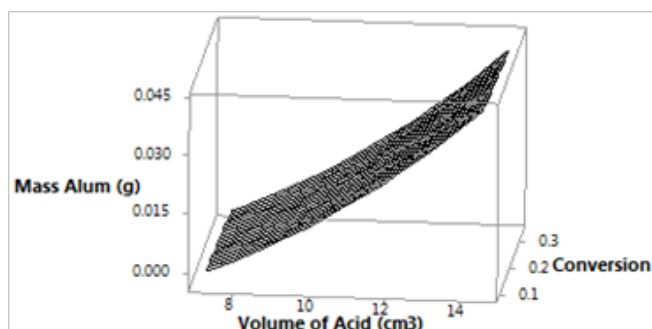


Figure 2 Surface plots of Mass Alum vs Conversion vs Volume of Acid.

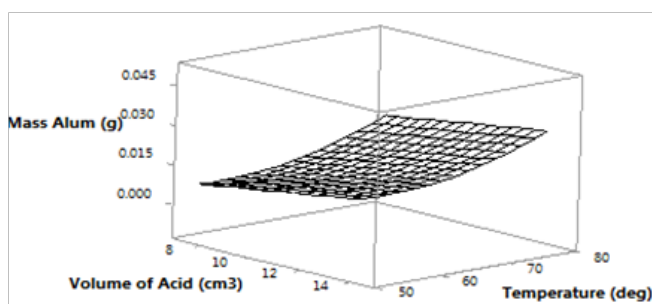


Figure 3 surface plots of Mass Alum vs Temperature vs Volume of Acid.

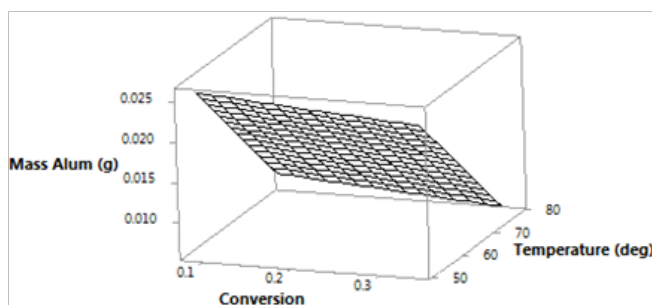


Figure 4 Surface plot of Mass Alum vs Temperature vs Conversion.

Regression Equation in Uncoded Units

$$\text{Mass Alum} = 0.03505 - 0.001016 \text{ Vol Acid} - 0.007983 \text{ Conv.} - 0.000680 \text{ Tempt.} + 0.000319 \text{ Vol Acid} * \text{Vol Acid}$$

The above regression equation helps to predict the quantity of Alum that can be produced per gram metakaolin at a given volume Acid/g metakaolin decreased conversion and at a given temperature. Second order differentiation of mass Alum per metakaolin with respect to volume of acid of metakaolin is positive. This indicates that there is a minimum volume of acid per g metakaolin that cannot be exceeded for the formation of Alum using this novel energy saving method.

Conclusion

It can be concluded from this work that Alum can be produced from metakaolin without any heat of reaction supply. The quantity of Alum produced per gram metakaolin can be predicted as a function of the volume of acid used, conversion level designed and temperature of reaction. The regression equation generated can be used to predict the amount of alum that can be produced with known volume of acid and controlled temperature.

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Conflict of interest

Author declares that there is no conflict of interest.

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