Petroleum Technology Development Journal

Ferric Alum Production from Brown Kankara Kaolin Clay*

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Abstract

In seeking a substitute for bauxite, as an alumina precursor, kaolinites clays such as white Kankara and Bauchi kaolinites have attracted so much attention in comparison to the brown Kankara kaolin (a ferric-rich variant). However, it is interesting to note the current appreciation on the uses of ferric alum in dyeing, tanning, etching operation and so on, thus opening up opportunities for the brown kaolin utilization. The effort made in this work is aimed at studying the feasibility of producing ammonium ferric alum from brown (Kankara) kaolin clay and to ascertain its reproducibility by applying statistical instruments: range, mean, standard deviation and normal distributions to the yields of the alum. Ten batches of alum were produced using 50g metakaolin each. An XRF analysis of two random samples of the alum shows alumina content of 15.20% and ferric oxide content of 5.75% and 6.00%. The mean yield of the alum was found to be 74.93% and standard deviation of 2.94%. 70% of the batches produced fall within the standard deviation on either side of the mean ($\bar{x} \pm \sigma$).

INTRODUCTION

Alum refers to several astringent substances most of which contain aluminum sulfate with the formula $Al_2(SO_4)_3$[1]. It is originally produced by the reaction of bauxite with sulfuric acid. The main ingredient in the production of alum is the alumina content of the bauxite. Due to the decline in bauxite reserve (both qualitatively and quantitatively) and the need to explore the use of locally sourced raw materials, various research works had been carried out and it has been shown that kaolin clay (which is next to bauxite in alumina content), can be used for alum production[2]. Although, clays such as white Kankara and Bauchi kaolins have been extensively studied for this purpose, brown Kankara clay has received less attention.

Brown Kankara kaolin clay, characteristically, has high ferric oxide content which is responsible for its pink-orange-red coloration and is equally reactive with sulfuric acid when calcined to give ferric alum. Although the presence of iron (Fe) in alum/alumina discourages it use in metallurgical and ceramic applications[3], interestingly, there is a current increasing need for ferric alum in various other applications some of which includes dyestuffs production, organic synthesis, and tanning in Nigeria and beyond. Ferric alum is also known to be paramagnetic, acidic and toxic towards microorganisms.[4] Present production of ferric alum is insufficient to satisfy the demand and supply schedules[5], thus opening up opportunities for the utilization of the

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[1] Kirk Othmer. (1997). Encyclopedia of Chemical Tech**.** Wiley Interscience New York. Vol 2 p 219-230, 234- 268 Microsoft Encarta 2009/alum; www.wikipedia.com/alum/Retrieved on 20/2/2010

[2]Aderemi, B.O. (2002). Kinetics Study on Aluminum Sulphate Crystal Growth out of Kankara Kaolin Dealumination Spent Acid – A Spent Acid Recovery Process. NJE 10(1) 27– 34.

[3] Kirk Othmer, Op. Cit

[4] Aderemi, Op. Cit

[5] http://www.niir.org/projects/projects/chemicals.php Accessed on 20/10/2010.; www.alibaba.com/2009/ferric alum

brown kaolin type so as to minimize the extent of dependence on foreign supply. This work was therefore aimed at studying the feasibility of producing ferric ammonium alum from Brown Kankara kaolin clay and to see the effect of the ferric oxide on the alum produced.

Moreover, alum production from kaolin clay, like any other budding scientific inventions needs to be subjected to some process and measurement analysis in order to establish the reproducibility and repeatability of the process. The manufacturing environment, by its very nature, relies on two types of measurements to verify quality and to quantify performance:

1. measurement of its products, and
2. measurement of its processes.

Therefore, product evaluation and process improvement require accurate and precise measurement techniques.[6] These also can be established by carrying out reproducibility and repeatability studies. Reproducibility is the variability resulting from external sources such as operators and their unique techniques, setups, and environmental fluctuations over time while repeatability is the variation of measurements due to instrument error[7]. The degree of variation can be determined by finding the standard deviation of the test results.

In this work, a reproducibility study of alum production from brown Kankara kaolin clay was carried out and the variation of the test results was analyzed statistically.

EXPERIMENTAL PROCEDURE

The established procedure of producing alum from kaolin clay at optimum conditions as put forward by Aderemi et al[8] and Edomwonyi-Otu et al[9] was followed for this work.

Beneficiation of Clay

1kg of Kankara brown kaolinite clay was weighed in a weighing machine (Avise, England) and soaked in 15 liters of water in a plastic bucket. The mixture was stirred rigorously intermittently for 3 days. The suspended impurities were discarded on the first, second and third day respectively after which micro sieve (53μm) was used to filter the clay suspension. The clay was then centrifuged so as to obtain a thick mass which was then dried at 30^{o}C in an oven (TM OV-420; Gallenkamp). The dried clay was then grounded in a mortar and pestle to finer particle size.

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[6]Smith R. R., McCrary S. W. and Callahan, R. N. (2007). Gauge repeatability and reproducibility studies and measurement system analysis: A multi-method exploration of the state of practice. JIT 23, 1, p2.; David W. H. and L. Chad. (2007). Gauge R&R: An effective methodology for determining the adequacy of a new measurement system for micron-level metrology. JIT 23, 4, p3

[7] David W. H. and L. Chad. (2007). Gauge R&R: An effective methodology for determining the adequacy of a new measurement system for micron-level metrology. JIT 23, 4, p3

[8]Aderemi, B.O; Edomwonyi-Otu, L; Adefila, S.S. (2009). A new approach to metakaolin dealumination. Australian Journal of Basic and Applied Sciences (AJBAS). INSInet Publication. 3(3), 2243-2248.; Aderemi, B.O; Ahmed, A.S; Abdul B.D. (2006). Production of alum from Kankara clay. In JNSChE 21(1,2) 120-124. Also Aderemi, B.O. (2002). Kinetics Study on Aluminum Sulphate Crystal Growth out of Kankara Kaolin Dealumination Spent Acid – A Spent Acid Recovery Process. NJE 10(1) 27– 34.

[9]Aderemi, B.O, Oloro, E.F, Joseph, D, Oludipe, J. (2001). Kinetics of the Dealumination of Kankara Kaolin Clay, NJE 9 (1), p 40-44.; Edomwonyi-Otu, L; Aderemi, B.O; Ahmed, K.S. (2010). Effect of beneficiation on the yield and quality of alum from Kankara kaolin. NJE 16(2) PP36-43; Edomwonyi-Otu, L; Aderemi, B.O. (2009). Alums from Kankara kaolin. JRE. 6 (1) p105-111.

Calcination and dealumination of metakaolin

The beneficiated clay was poured into a crucible and calcined in a furnace (Gallenkamp, TM OV-420) with temperature range 0-1400^{0}C, at 750°C for two and half hours to obtain the more reactive metakaolin.

In a typical batch, 50g of metakaolin was weighed using Mettler Toledo analytical balance, model AB204, and poured into a conical pyrex flask and then mixed with 164cm^3 of de-ionized water. 156.80cm^3 of 96wt% sulfuric acid was then added to the clay suspension in the conical flask (Pyrex) and allowed to react for about 20 minutes after which a calculated quantity of de-ionized water was added to quench the reaction. The dealumination mixture was then filtered through a pyrex Sinta glass filter attached to a SPEEDIVAC high vacuum pump (Edwards ES50). The silica rich cake residue obtained was then discarded and the equipment washed with de-ionized water.

The same procedure was repeated for other 19 runs to make a total of twenty samples.
The possible reaction for the conversion of the brown kaolinite to its metakaolin is shown in Equation (1) below;

Calcination Reaction

$$2(OH)_8Si_4Al_3O_9.Fe_3O_{4(S)} \xrightarrow{\Delta} 3Al_2Si_20_7.Fe_2O_{3(S)} + 8H_2O_{(g)} + 2SiO_{2(s)} \quad \ldots\ldots\ldots\ldots\ldots(1)$$

Kankara Brown kaolin ferrous metakaolin silica

Crystallization Process

33g of ammonium sulphate (Johnson and Johnson Chemicals, London), which was used as received without further purification, was added to the filtrate from each of the 20 batches as a salting agent. After then it was kept in the refrigerator (Thermocool C1202, England) for about 6 hours at 0^{0}C so as to hasten the crystallization process and to enhance the crystallization yield. The cooled samples were then filtered through the Sinta glass filter to separate the wet alum from the mother liquor. The alum from the 20 separate dealumination batches was then weighed in a balance to determine the mass/yield of ammonium alum from the respective batches and dried at 250^{0}C for 5 hours before been analyzed by the X-Ray Flourescence machine (ED-XRF, PANalytical XRA 1160) to determine their elemental composition. The possible dealumination reaction that would yield the ferrous alum is as shown in Equation (2).

$$Al_2Si_2O_7.Fe_2O_{3(s)} + 5H_2SO_{4(aq)} + 30H_2O_{(l)} \longrightarrow FeSO_4.Al_2(SO_4)_3.26H_2O_{(aq)} + 2SiO_{2(s)} + FeSO_4.4H_2O(aq) \quad \ldots\ldots\ldots\ldots\ldots(2)$$

RESULTS AND DISCUSSION

The results of the test are as presented in Table 1 below

BENEFICIATION/CALCINATION

Table 1 Elemental composition of raw Kankara brown clay and its metakaolin derivative

Oxides	Raw Kaolin (wt %)	Metakaolin (wt %)
Al_2O_3	31.600	37.600
SiO_2	41.900	45.000
K_2O	0.280	0.430
Fe_2O_3	14.940	15.640
CaO	0.250	0.310
TiO_2	1.580	1.270
V_2O_5	0.120	0.053
Cr_2O_3	0.130	0.052
MnO	0.060	0.087
Ag_2O	1.590	1.340
Eu_2O_3	2.400	0.130
CuO	0.051	0.044

The aluminum oxide content of the raw brown (Kankara) clay was 31.60% and its metakaolin content of 37.60% was found to be less when compared to the metakaolin from other local clay sources such as white Kankara[10] – 41.56% and Bauchi[11] - 41.80%. However, the ferric oxide content of raw brown Kankara of 14.94% and its metakaolin of 15.64 is much higher than that of white Kankara[12] – 0.56% and Bauchi[13] - 1.31%. It can also be observed from Table 1 that the beneficiation and calcinations process improved the alumina content from 31.60% to 37.60% and the silica-alumina ratio as also reported elsewhere by Edomwonyi-Otu et al[14].

The metakaolin has a brighter brown-red appearance than the raw kaolin clay. This bright coloration confirms the high concentration of ferric oxide in them[15] as observed in Table 1. This difference in coloration is obviously due to the temperature treatment on the raw kaolin (750^0C/2.5 hrs) that resulted in the change in oxidation state of the ferric oxide content (equation 1 referred).

ALUM PRODUCTION

The quality and quantity of alums produced from ten batches were analyzed for consistency or variations 50g of metakaolin was used as starting material.

[10] www.alibaba.com/2009/ferric alum
[11] [10]David W. H. and L. Chad. (2007). Gauge R&R: An effective methodology for determining the adequacy of a new measurement system for micron-level metrology. JIT 23, 4, p3
[12] www.alibaba.com/2009/ferric alum
[13] [10]David W. H. and L. Chad. (2007) Op. Cit
[14] www.alibaba.com/2009/ferric alum
[15] Kirk Othmer. (1997), Op. Cit.; Microsoft Encarta 2009, Op. Cit.; See also Columbia Encyclopedia. (2006). 6th edition, Columbia University Press.

X-Ray Fluorescence Analysis - Quality Verification

The X-ray fluorescence analysis of two random alum samples produced gives the elemental composition shown in Table 2. The two random alum samples analyzed had same alumina content of 15.20%, and ferric oxide content of about 6.00% which are marks of consistency in the quality of the alum produced.[16]

Table 2 Elemental composition of Alum Sample A and B (wt %)

Channel Compound	Al Al_2O_3	Si SiO_2	S SO_3	K K_2O	Ca CaO	Cr Cr_2O_3	Mn MnO	Fe Fe_2O_3	Ge GeO_2	Ag Ag_2O	Eu Eu_2O_3	**LOI**
SAMPLE A	15.200	0.460	62.600	0.087	0.190	0.071	0.020	5.710	13.000	1.260	0.600	0.802
SAMPLE B	15.200	0.430	62.900	0.054	0.190	0.074	0.022	6.000	12.000	1.350	0.069	1.711

It was observed that some of the alum produced had large crystals while the others had fine crystals. Those with large crystals were obtained when ammonium sulfate was added to the filtrate when warm while the fine grain crystals were obtained when the filtrate cools down before the ammonium sulfate was added. This shows that the morphology of the alum crystals may be affected by the preparation methods employed (though there is need to further investigate this). The color of the alum was light-greenish; a characteristic color that reveals the presence of Iron (II) compounds.

<u>*Calculation of yield*</u>

The XRF analysis of the metakaolin derived from brown Kankara kaolin as shown in Table 2, contains 37.60wt% alumina which implies 18.8g of alumina in 50g metakaolin.

$$Al_2Si_20_7 \longrightarrow Al_2O_3 + 2SiO_2 \quad \ldots\ldots\ldots\ldots \quad (3)$$

Metakaolin alumina silica

The theoretical yield was based on alum (aluminum sulfate) obtainable where the kaolin to exist in pure phase while the experimental yield was based on alum from the analyzed metakaolin (Table 1).

Statistical Analysis – Quantity Verification

The masses of the ammonium alum produced and the statistical calculation for the ten batches are shown in Table 3.

[16]Smith R. R., McCrary S. W. and Callahan, R. N. (2007). Gauge repeatability and reproducibility studies and measurement system analysis: A multi-method exploration of the state of practice. JIT 23, 1, p. 2; Also Reproducibility - Madagascar.mht, Retrieved 20/2/2010.

Table 3 Mass of ammonium alum produced from brown (Kankara) kaolin clay

Batch	Mass (g)	Theoretical Yield (%)	Exp'tal yield x_i (%)	$x_i - \bar{x}$ (%)	$(x_i - \bar{x})^2$
A	176.37	86.45	72.23	2.70	7.26
B	183.59	89.99	75.19	-0.27	0.07
C	172.61	84.60	70.69	4.24	17.94
D	177.47	86.99	72.68	2.25	5.04
E	182.62	89.51	74.79	0.14	0.02
F	186.68	91.50	76.45	-1.53	2.33
G	179.21	87.84	73.40	1.53	2.33
H	196.49	96.31	80.47	5.55	30.75
I	181.29	88.86	74.25	0.68	0.46
J	193.88	95.03	79.40	-4.48	20.03
$\sum_{i=A}^{T} x_i$			749.25		86.21

Range

The range of the yield of the alum produced was found to be 9.78% (23.88g), which is fairly low and signifies the closeness of the masses of alum produced and it agrees with acceptable levels.[17] The differences are obviously due to the inability to maintain constant operating conditions during drying and the variation in crystallization condition due to inconsistent power/voltage supply.

Mean and Standard Deviation

$$\textit{Mean, } \bar{x} = \frac{\sum_{i=A}^{T} x_i}{N} = \frac{749.25}{\mathbf{10}} = \mathbf{74.93\%}$$

$$\textit{Standard Deviation, } \sigma = \sqrt{\frac{\sum_{i=A}^{T}(x_i - \bar{x})2}{N}} = \sqrt{\frac{\mathbf{86.2062}}{\mathbf{10}}} = \mathbf{2.94\%}$$

The mean experimental yield of 74.925% of the alum was quite reasonable implying that, ferric ammonium alum can be produced and reproduced from brown (Kankara) kaolin clay. The difference observed between the experimental and theoretical yields is due to the presence of impurities in the metakaolin which also translates to impurities in the alum. The standard deviation of 2.94% from experimental yield of 100% (244.18g) was fair and indicates that the

[17]Smith R. R., McCrary S. W. and Callahan, R. N. (2007) Op. Cit; David W. H. and L. Chad. (2007), Op.Cit

masses of the alum produced were close/clustered around the mean mass,[18] and it also indicates that the mean yield of 74.93% (182.95g) obtained was close enough to the expected theoretical and experimental yield of 100% (204.02g and 244.1781g respectively). This is reasonable since the yields reported were the result of a single crystallization step and considering the solubility index of alum in the mother liquor.[19]

Normal Distribution

For normal distributions, it turns out that 68.27% of the cases (yields) should be included between $\bar{x} - \sigma$ and $\bar{x} + \sigma$ (i.e. one standard deviation on either side of the mean) while 95.45% and 99.73% of the cases should be included between $\bar{x} \pm 2\sigma$ and $\bar{x} \pm 3\sigma$ respectively.[20] The normal distribution of the yields of the alum shows that 70% of the cases were between $\bar{x} - \sigma$ and $\bar{x} + \sigma$, and 100% between $\bar{x} \pm 2\sigma$ and $\bar{x} \pm 3\sigma$. This was above 68.27% given in the literature, and hence it can therefore be safely said that ferric ammonium alum is reproducible from brown Kankara kaolin clay. Consistency in operating conditions such as power/voltage supply will definitely enhance the reduction in the standard deviation to give a perfect/near perfect distribution.

CONCLUSION

The quality of brown Kankara kaolin was improved by beneficiation. Ferric ammonium alum was produced from brown Kankara kaolin and the results of the yields were found to be reproducible both qualitatively and quantitatively. The alum samples produced were found to have an alumina content of 15.20% and a mean yield of 74.93% with a standard deviation of 2.94%, while 70% of the samples fell within $\bar{x} \pm \sigma$ for the normal distribution. The crystal size/morphology may be affected by the operating conditions. These results show that brown Kankara kaolin can be considered for utilization in dyestuffs production, organic synthesis, tanning and such other industrial uses.

[18] Murrey, R.S and Stephens, L.J. (2008). Shaum's outlines of theory and problems of statistics. 4th edition, New York: McGraw Hill Companies, p 98.

[19] Kirk Othmer. (1997), Op Cit.

[20] Smith R. R., McCrary S. W. and Callahan, R. N. (2007), Op. Cit; [10]David W. H. and L. Chad. (2007), Op. Cit and also Ibid