

A New Approach to Metakaolin Dealumination

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Abstract: One of the millennium goals is development of energy saving processes and cleaner environment. In this study, a novel approach to metakaolin dealumination to produce alum from kaolin has been described. It majorly involves captivating the self generated energy as result of acid solvating in metakaolin-water solution to supply the mixing and activation energies requirement of the process without external heat source. This approach yielded above 80wt% alumina extraction from the kaolin structure. A mini scale-up attempt further substantiated the efficacy of this new approach as the alumina extraction percentage yield increased from about 81 to 85 as metakaolin quantity per batch increased from 50g to 500g.

Key words: Metakaolin, dealumination, energy-savings, solvating, alumina and yield

INTRODUCTION

Coagulation is a critical process in (drinking water or industrial effluent waste) water treatments. Alum, $Al_2(SO_4)_3 \cdot 14-27H_2O$ 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 (McCurdy, K., K. Carlson and D. Gregory, 2004). Its relatively low cost still makes it to be the choice 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), polyaluminium sulphate (PAS) (McCurdy, K., K. Carlson and D. Gregory 2004; Xu, G.R.; Z.C. Yan, Y.C Wang and N. Wang, 2009; Wu, X.; X. Ge; D. Wang and H. Tang, 2008) and chitosan (Renault, F.; B.Sancey; P.M. Badot and G. Crini, 2008).

In addition to the traditional role of alum as a coagulant, it is highly consumed in paper industry for various processes. It commonly serves as mordant in dyeing and is an essential precursor of many chemicals, among which alumina is a chief commodity (Ghasri-Khouzani, M.; M. Meratian, and M. Panjepour, 2008) .

Traditionally, alum is produced by acid (in particular sulfuric acid) leaching of bauxite. However, bauxite is globally diminishing in quantity and quality, which has become a serious concern (Aderemi, B.O.; A.S Ahmed., and B.D Abdul, 2006; Fan, M.; R.C. Brown; T.D Wheelock; A.T. Cooper; M. Nomura and Y. Zhuang, 2005). In addition, bauxite is often completely absent in known commercial quantity in most developing countries such as Nigeria, where their entire populace depend solely on alum for their water treatment. This has continued to muster many research and industrial efforts to ameliorate the situation by seeking alternative raw materials such as alunite (Cipriani, P., G. Marruzzo, L. Piga and F. Pochetti, 1997), fly ash (Fan, M.; R.C. Brown; T.D Wheelock; A.T. Cooper; M. Nomura and Y. Zhuang, 2005) and kaolin (Aderemi, B.O., 2002), and development of various alum recovery processes (Zhao, Y.Q; X.H Zhao and A.O. Babatunde, 2009; Xu, G.R.; Z.C. Yan, Y.C Wang and N. Wang, 2009)from its spent sludge depending on the prevailing endowment(s) of a given location. Consequently, Nigeria and Ethiopia (Nigussie, W., F. Zewge and B.S. Chandravanshi 2007) are among the countries of the world today with full fledged alum production factories from kaolin.

The initial setback to the commercialization of kaolin process was mainly economic in nature (i.e. production cost, especially higher energy input requirement) relative to that of bauxite (via the popular Bayer process), because alumina in form of gibbsite seldom require temperature above $150^{\circ}C$ in its processing (Whittington B.I., 1996). Howbeit, with gradual depletion of gibbsite-rich bauxite, this differential cost of production has continued to diminish in effect.

A quick review of kaolin process towards alum production showed that the two major energy consuming units differentiating it from bauxite as source raw material resulted foremost from the chemical inactivity of kaolin, requiring thermal activation to convert it to a reactive form at a reaction temperature $>600^{\circ}C$. And

secondly, the dealumination step to unlock the structural aluminum from the octahedral alumina sheet in the kaolin-metakaolin composite (Aderemi, B.O.; A.S Ahmed,. and B.D Abdul, 2006). While future focus may be to consider the role of microwave technology in kaolin activation, the present paper sought to address the latter of the aforesaid issues. Hence, this report is an innovative idea aimed at capturing the heat commonly liberated from acid dissolution and hydration in water and use it in-situ to dealuminate metakaolin without external heating source.

In this study, therefore, the potency of internally generated thermal energy by acid solvating in water has been demonstrated to be a sufficient agent to provide the required mechanical energy for stirring and activation energy for the dealumination reaction. This is more environmentally friendly; in the sense that it reduces the amount of heat energy dischargeable to the environment. Mini pilot batches were also attempted to evaluate extent of mixing limitation to expect when life scale is anticipated. Also addressed in this paper is the empirical effect of varying acid quantity on alum yield.

2. Experimental:

2.1 Beneficiation and Activation of Kaolin:

Kaolin sample used in this investigation was procured from Kankara village, Katsina State, Nigeria. Table 1 shows its major oxide constituents. The raw kaolin sample was crushed in a laboratory mortar and pestle before washing with water to remove some of its associated soluble salts. The washed clay was subsequently suspended in water and sieved through a 53 μ m sieve to get rid of intermediate to coarse associated mineral particles. The fine kaolin suspension was thereafter allowed to settle overnight by gravity, decanted and further dewatered to a thick mass under pressure before drying overnight at 120 $^{\circ}$ C. The dried kaolin lumps were crushed in a jaw crusher and ball milled into fine powder and subsequently classified using 212 μ m sieves. The <212 μ m particles were calcined to metakaolin at 750 $^{\circ}$ C for 2hrs to activate the kaolin.

2.2 Dealumination of Metakaolin:

In a typical batch reaction, 50g of metakaolin was added to 185ml of distilled water in a one liter flask and stirred. 169ml of 96wt% H₂SO₄ (equivalent to 5 fo(so ad (fo(so ad (fo(so ad0.0000 0.0000 cm0.00 0.0Tc1.2600 Tw(In a)T

RESULTS AND DISCUSSION

3.1 Significance of Beneficiation:

3.1.1 Material Balance:

Following the beneficiation process, on the average, about 91wt% kaolin recovery was attained, the balance possibly being the associated montmorillonite, mica, quartz and soluble components. Loss on ignition of about 14.147 wt% was recorded when calcined at 750°C for 2hrs. This is in good agreement with the theoretical expectation of 13.95wt% as kaolin hydroxyl composition. Table 1 presents the major oxides in the raw, beneficiated and calcined kaolin samples respectively. It is easily deduced from Table 1 that beneficiation generally resulted in concentration of the clay's common oxides from 81.71wt% (in the raw clay) to 93.38wt% in the metakaolin. The remainder 6.62wt% is most probably un-decomposed carbonates of the listed metals. Also of significance is the reduction in the silica/alumina mole ratio from 2.292 to 2.02 respectively, implying that the screened out particles are silica rich minerals such as quartz and montmorillite. The high K₂O in the samples may be indicative of mica and feldspar rich environment of the kaolin formation (Onaji P.B., 1992).

Table 1: Oxides/Elemental composition of raw and beneficiated kaolin and metakaolin

Sample	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	TiO ₂	Sum	**SiO ₂ Al ₂ O ₃
Raw Kankara kaolin (wt %)	45.10	33.41	0.343	0.555	1.49	0.693	0.016	0.100	81.71	2.295
Beneficiated kaolin (wt %)	47.48	36.80	0.325	0.562	1.27	0.544	0.050	0.066	87.10	2.179
Metakaolin* (wt %)	49.40	41.56	0.289	0.483	1.12	0.427	0.038	0.067	93.38	2.0203*

Sample calcined at 750°C for 2hrs; ** mole ratio

3.1.2 Effect of Beneficiation on Alum Quality:

From Table 2, the effect of clay beneficiation on alum quality is mostly significant in terms of magnesium oxide reduction, which also accounted for the higher value of sulphate concentration in the alum sample produced from unbeneficiated metakaolin. This is significant when alum is targeted for water treatment because MgSO₄ is known to contribute to water hardness and sludge formation.

Table 2: Effect of beneficiation on alum quality

Sample	Oxides in WT %									
	SiO ₂	SO ₃	K ₂ O	CaO	Fe ₂ O ₃	MgO	CuO	Na ₂ O	Cr ₂ O ₃	NiO
Unbeneficiated kaolin	ND	74.57	ND	0.17	0.13	1.96	0.049	0.095	0.008	0.01
Beneficiated kaolin	ND	69.61	ND	0.19	0.125	0.275	0.06	0.13	0.01	0.02

ND= Not detectable

3.2. Comparative Yield Between the Newly Developed Dealumination Scheme and the Conventional Scheme:

Alum yield in this work is based on the total alumina content of the metakaolin. From Table 1, this translated to 20.78g of alumina in every 50g of the metakaolin. Therefore, based on the dry weight of each alum sample at 250°C and the resulting XRF analysis, the percentage alumina yields were estimated and were taken to be equivalent to alum yield. This was to avoid possible errors that occluded water, acid and other materials could introduce, were the yield to be based directly on the wet alum weights directly.

The comparative alum yields from the proposed energy saving scheme and the conventional heating system are shown as Figure 1. Apparently, the new scheme gave a yield of 81.29wt% of alum in comparison to the conventional method (heating externally at 98°C for 3hrs), which gave a corresponding yield of 87.36wt%. It should be noted however, that the marginal difference of about 6wt% yield, following the conventional method may not justify the quantity of external heating input and prolonged reaction time involved, especially in such a process where the raw material cost (kaolin) is not the critical factor controlling the production cost. It is our belief that a process scheme offering reduction in energy consumption, in view of kaolin's relative cheapness, availability and wide spread in comparison to bauxite will bring it at par with that of bauxite process and may even become superior with further integrated efforts.

3.2.2 Mini Scale-up and Optimization Consideration:

The results of the mini scale-up exercise are presented in Figure 2. Contrary to popular expectation, the percentage alum yield increases as the mass of metakaolin per batch increases. This may not be unconnected with the use of clay pot (of about 10 liters capacity with a cover lid) for the higher metakaolin batches. The clay pot, having better insulating property undoubtedly conserved the internally generated energy better, thereby providing higher quality and quantity of heat to overcome the increase in drag resulting from increase in mass of the metakaolin. Equally tenable is the increase in the absolute energy available from the hydrations of the acid and the metakaolin, which increases as the mass of both substances increases.

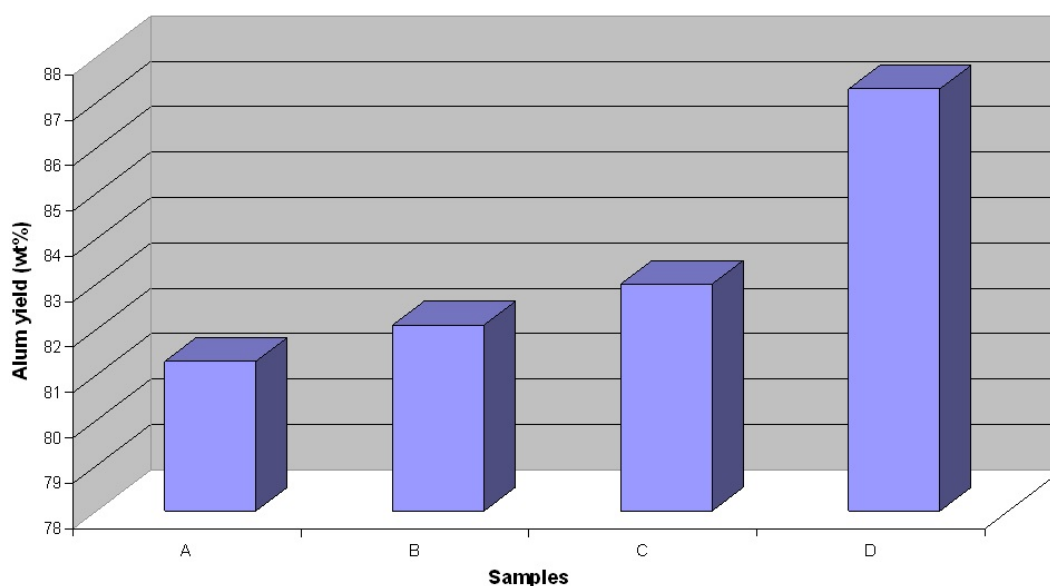


Fig. 1: Comparative alum yields from the new approach versus the conventional procedure. A-New approach (No external heating source) B-heating externally for 1hr, C-heating externally for 2hr and D-heating externally for 3hr at 98°C

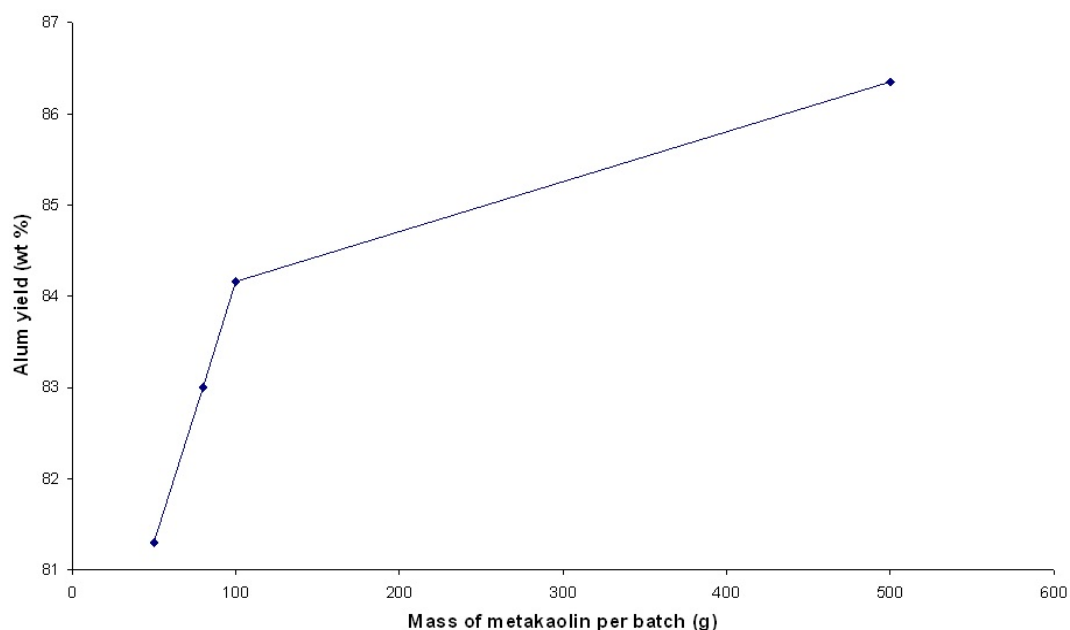


Fig. 2: Effect of scale up on alum percentage yield.

Among the factors considered in our previous investigations on metakaolin dealumination using the conventional method of extraction are solid –liquid ratio, acid strength, temperature and time. There we reported that to have a reasonable kinetic equation and at the same time achieve a good product separation from the gangue, a 5-fold stoichiometric quantity of acid at 60wt% acid strength and reaction time, 1-3hrs was recommended (Aderemi, B.O. and J.O Oludipe, 2000; Aderemi, B. O.; E.F Oloro; D. Joseph and J.O Oludipe, 2001). However, in view of the significant contribution of the excess acid involved and its reclamation for reuse to overall production cost, necessitated our re-evaluation of this factor as it relates to the new approach. Figure 3 presents our findings. Expectedly, alum yield increases with increase in acid to metakaolin ratio within the range investigated. Again, going by our previous argument, a difference of only 2.4 wt% offered by 5-fold acid (81.30 wt% yield) in comparison to that 2-fold (78.90 wt%) may favour the use of 2-fold acid, economically.

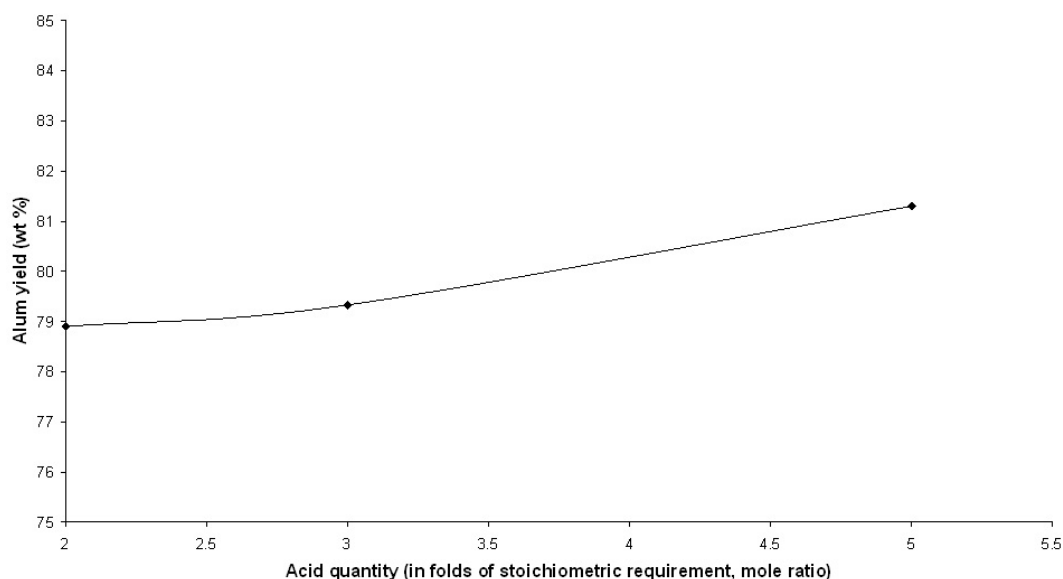


Fig. 3: Effect of acid to metakaolin mole ratio on percentage alum yield.

4.0 Conclusions:

The following summaries can be drawn from the results of this work:

1. Beneficiation reduced the magnesium and silicon carrying minerals significantly in the produced alum from kaolin
2. The innovative energy saving scheme developed proved adequate in providing the mechanical (stirring/mixing) and activation energies requirement of the dealumination process
3. Contrary to the orthodox expectation that heterogeneous system should suffer from lower yield as capacity increases due to mixing challenges, this new approach investigated showed increase in relative product yield with increase in capacity, without external energy input to the dealumination process.

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