



DEVELOPMENT OF PILOT SCALE DEALUMINATION UNIT OF 2.5 kg METAKAOLIN PER BATCH CAPACITY

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ABSTRACT

A pilot-size dealumination unit to handle 2.5kg of metakaolin per batch was designed and fabricated and test run. The metakaolin was prepared from Kankara kaolin. The metakaolin was completely split into silica and alumina. The silica component which was inert to the sulphuric acid used during the reaction and was obtained as a solid product. While the alumina which reacted with the sulphuric acid was obtained in liquid form as aluminum sulphate, known as alum. The dealumination unit comprises of the dealumination reactor, known as dealuminator, acid holding tank and metakaolin slurry mixing tank. The material of construction selected for the dealumination reactor was stainless steel type 304 lined internally with glass to withstand the corrosive environment of the concentrated sulphuric acid at the reaction temperature > 140°C. The capacity of the components are; acid holding tank 5 liters; metakaolin slurry mixing tank 20 liters, with 70 W capacity motor and the dealuminator 50 liters, which had pressure relief valve, pressure gauge (0-10 bars) and temperature gauge (0 - 300°C) on the cover. Woven glass fiber cloth was used as lagging material to minimize heat loss to the surrounding. The purity level of the silica obtained from the reaction was above 95%. The endothermic nature of the dealumination process was void of external heating.

Key words: Dealumination, metakaolin, reactor, dealuminator.

1. INTRODUCTION

Nigeria as a nation is faced with the challenges of harnessing her abundant solid mineral deposits for national development, and clay (kaolin) has been confirmed to have a prominent role to play in these developmental efforts [1]. A prominent kaolin process step that adds much value to this mineral is the dealumination step which splits the reactive phase of kaolin known as metakaolin to two major products, alum which contains the alumina component and silica. The cheap and abundant nature of kaolin and the fact that it is next to bauxite in alumina content had been given much attention [2]. In Nigeria particularly, there is no known commercial bauxite deposit. Nevertheless, kaolin clay is an alternative, containing 33 – 39wt% alumina content, which is abundantly available [3]. Kaolinite clay commonly known as kaolin is a naturally occurring mineral with the chemical make-up of: $Al_2Si_2O_5(OH)_4$. Clays are widely used as catalysts and catalyst supports for a quite broad range of processes. Clay catalysts have attracted much interest in catalytic application in petroleum refining industry [4]. Heat of sulphonation of acid-water had been reported to solely

sustain the dealumination reaction which ultimately enhance the energy economics of the process [5]. An earlier pilot size dealuminator to handle 1kg/batch was designed but had a lot of challenges with regard to the material selection for the reactor and components configuration of the dealumination unit [6], in this study, the challenges were adequately addressed. The alum produced from the dealumination pilot unit could be used for various industrial applications such as water treatment, aluminum hydroxide preparation and alumina production. While the silica could find applications as catalyst support as well as recipe for the preparation of other useful silica based chemicals such as sodium silicate and silica sol. The successes recorded for the production of zeolite Y and ZSM-5 from Kankara kaolin at the bench scale had given a morale boost for the production of these zeolites at a pilot scale, in which dealumination unit is a key fraction of zeolite production from kaolin. The products of dealumination unit are very useful for the zeolite recipe preparation. The pilot size became necessary in the quest to kick start zeolite Y and ZSM-5 production at industrial scale level from kaolin.

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2. EXPERIMENTAL PROCEDURE

2.1 Design

Basic and rational engineering principles, calculation and intuition which resulted to series of equations were used for the design. Basis of 2.5kg metakaolin per batch was used, the average percentage of the alumina content in the metakaolin was the determining factor for the reactor size from the equations generated. The dealumination unit comprises of;

- Dealumination reactor (dealuminator)
- Metakaolin slurry mixing tank, and
- Acid holding tank

2.1.1 Dealumination Reactor (Dealuminator):

Batch reactor model was chosen for the design of the dealuminator. Average alumina content from several X-ray Fluorescence (XRF) analysis = 40%. The basic dealumination equation and the material balance are shown in Equation (1) and Table 1 respectively. While

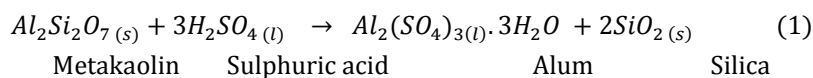


Table 1: Material balance around the dealumination reactor

	Stream 1 Metakaolin slurry (g)	Stream 2 Acid (g)	Stream 3 Quenching water (g)	Stream 4 Residue (g)	Stream 5 Alum (g)
Al ₂ O ₃	1000	0	0	20	0
SiO ₂	1300	0	0	1287	13
H ₂ O	4656	147.4	16645.86	4289.852	17159.408
H ₂ SO ₄	0	7150.374	0	357.5187	3932.7057
Al(SO ₄) ₃	0	0	0	0	3840.1496
Impurities	200	72.226	168.14	8.80732	431.55868
Sub-Total	7156	7370	16814	5963.17802	25376.82198
Total		31340			31340

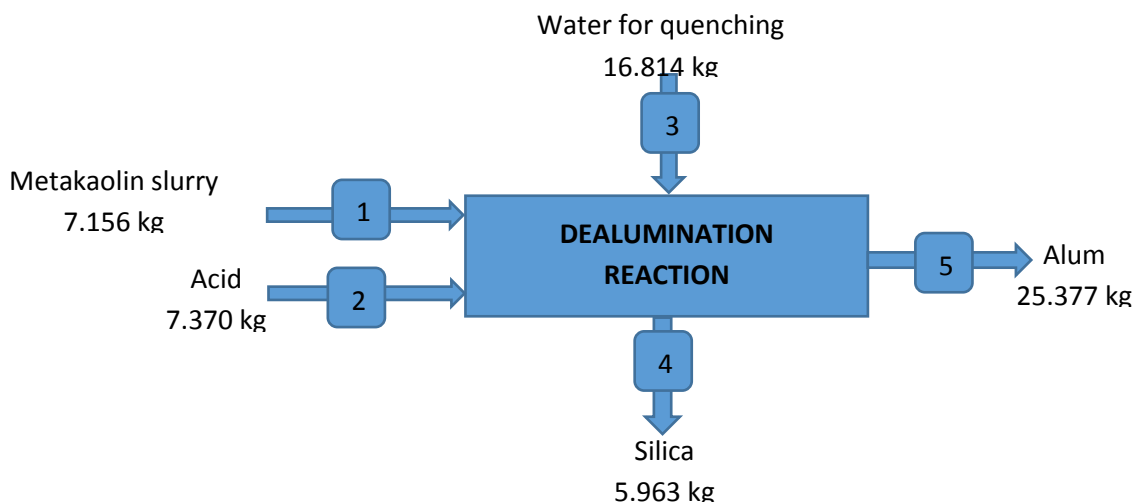


Figure 1: Material balance around the dealuminator

the flow of materials into and out of the dealuminator is shown in Figure 1.

Volume of Dealumination Reactor

Average density

$$\bar{\rho}_{\text{reactants}} = \frac{\sum_{i=1}^3 \rho_i X_i}{\sum_{i=1}^3 X_i} = \frac{1.315}{1} = 1.315 \quad (2)$$

Volume of dealuminator

$$V_{d*} = \frac{M_T}{\rho_{\text{reactants}}} = \frac{31340}{1.315} = 23832.70 \text{ cm}^3 \quad (3)$$

In order to avoid much pressure build up in the system, since the dealuminator is not being designed as a pressurized vessel and to also accommodate water vapour that will be generated at the initial stage of the reaction, which will occupy much space (basic properties of gases), a safety factor of 25% was chosen. The actual volume

$$V_d = 1.25 \times 23832.70 = 29791 \text{ cm}^3$$

The volume of the dealuminator (V_d) was approximately: 30000 cm³

The height (H_d) to diameter (D_d) ratio was taken as 2, which is in agreement with literature [7] H_d : 53.46 cm
 D_d : 26.73 cm

Time of dealumination reaction

Consideration of reaction kinetics developed for dealumination reaction [1],

$$-r_{Al} = 131.6e^{\frac{-3837.8}{T}} C_{Ac0} \quad (4)$$

The rate of dealumination was a first order reaction with respect to the leached alumina component, Evaluating the time of reaction for 95% conversion, the batch reactor performance equation was used:

$$t = N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_{Al})V} \quad (5)$$

$$t = \frac{N_{A0}}{V} \int_0^{X_A} \frac{dX_A}{(-r_{Al})} \quad (6)$$

$$t = C_{Al0} \int_0^{X_A} \frac{dX_A}{(-r_{Al})} \quad (7)$$

$-r_A$: Rate of dealumination (g alumina/g metakaolin) (min)⁻¹; C_{Al} : Concentration of alumina left in the raffinate (g alumina/g metakaolin); C_{Ac0} : Acid (mol/dm³) = 9.066; T : Reaction temperature (K) = 373; Assuming conversion of 95%; The pre-exponential factor is 131.6 dm³/(mol min);

In terms of conversion the rate of dealumination is expressed as:

$$-r_{Al} = 131.6e^{\frac{-3837.8}{T}} C_{Ac0} C_{Al0} (1 - X_{Al}) \quad (8)$$

$$t = C_{Al0} \int_0^{X_A} \frac{dX_A}{131.6e^{\frac{-3837.8}{T}} C_{Ac0} C_{Al0} (1 - X_{Al})} \quad (9)$$

$$t = \frac{C_{Al0}}{131.6e^{\frac{-3837.8}{T}} C_{Ac0} C_{Al0}} \int_0^{X_A} \frac{dX_A}{(1 - X_{Al})} \quad (10)$$

$$t = 14.573 \int_0^{0.95} \frac{dX_A}{(1 - X_{Al})}$$

$$t = 14.573 \times (-\ln(0.05))$$

$$t = 43.66 \text{ mins}$$

$$q' = \frac{2\pi(0.535)(90)}{\frac{\ln\left(\frac{0.137}{0.135}\right)}{16.0958} + \frac{\ln\left(\frac{0.137 + t_{gw}}{0.137}\right)}{0.0415} + \frac{\ln\left(\frac{0.139 + t_{gw}}{0.137 + t_{gw}}\right)}{273}}$$

$$46.58 = \frac{302.5746}{0.0000914 + \frac{\ln\left(\frac{0.137 + t_{gw}}{0.137}\right)}{0.0415} + \frac{\ln\left(\frac{0.139 + t_{gw}}{0.137 + t_{gw}}\right)}{273}}$$

$$24.096 \ln\left(\frac{0.137 + t_{gw}}{0.137}\right) + 0.003663 \ln\left(\frac{0.139 + t_{gw}}{0.137 + t_{gw}}\right) = 6.4957$$

$$t_{gw} = 0.042389 \text{ m} = 4.24 \text{ cm}$$

Determination of insulating material thickness

Glass-wool was chosen as the insulating material, its thickness round the reactor to minimize heat loss to the surrounding was evaluated as follow: Required design model:

$$q' = \frac{m_{total} C_{p_{av}} \Delta T}{t} \quad (11)$$

m_{total} : total mass of the reacting system; $C_{p_{av}}$: average specific heat capacity; ΔT : temperature difference; T_i is the initial temperature of the reacting system during dealumination; T_f is the final temperature of the reacting system just before quenching; t is the time for the dealumination reaction, $t = 43.33$ minutes:

$$q' = \frac{14.526 \times 4200 \times 2}{43.66 \times 60} = 46.58 \text{ W}$$

$$q' = \frac{2\pi L \Delta T_{overall}}{\frac{\ln\left(\frac{r_2}{r_1}\right)}{k_s} + \frac{\ln\left(\frac{r_3}{r_2}\right)}{k_w} + \frac{\ln\left(\frac{r_4}{r_3}\right)}{k_a}} \quad (12)$$

Where q' = energy flow per unit time; k_a = thermal conductivity of material a; L = height of the cylinder; r_1 is the inner radius of the stainless steel; r_2 is the inner radius of the glass wool; r_3 is the inner radius of the aluminum casing; r_4 is the outer radius of the aluminum casing, $K_s = 16.0958 \text{ W/mK}$; $K_w = 0.0415 \text{ W/mK}$; $K_a = 273 \text{ W/mK}$; $r_1 = 0.135 \text{ m}$; $r_2 = 0.137 \text{ m}$; $r_3 = (0.137 + d_{gw}) \text{ m}$;

d_{gw} = Thickness of the glass wool (lagging thickness);

$r_4 = (13.9 + d_{gw}) \text{ cm} = (0.139 + d_{gw}) \text{ m}$; $\Delta T \approx 393 - 303 = 90 \text{ K}$

$$L = 53.5 \text{ cm} \approx 0.535 \text{ m}$$

2.1.2 Metakaolin Slurry Tank

The metakaolin slurry tank was the chamber where the metakaolin was mixed with water before being channeled into the dealuminator. The quantity of materials in the mixing tank is presented in Table 2.

Table 2: Parameters for metakaolin slurry components

Reactants	Volume (cm ³) (V)	Density (g/cm ³) ρ_i	Mass (kg)	Fractional composition X_i	$\rho_i X_i$ g/cm ³
Water	4656	1.00	4.656	0.65	0.650
Metakaolin	1000	2.50	2.500	0.35	0.875
			7.156		1.525

$$\rho_{slurry} = \frac{\sum_{i=1}^n \rho_i X_i}{\sum_{i=1}^n X_i} = \frac{1.525}{1} = 1.525 \text{ g/cm}^3$$

Where ρ_i = density of component I; X_i = mass fraction of component i

$$V_{mT} = 4692.459 \text{ cm}^3$$

$$V_{Acmt} = 1.25 V_{mT}$$

Actual required volume (V_{Acmt}) was $V_{Acmt} = 5865.574 \text{ cm}^3$

The slurry tank was also used as the channel through which the water for quenching was introduced into the dealumination reactor (dealuminator) at the end of the reaction. Volume of water for reaction quenching was calculated as: 16814 cm³, the total volume required for the metakaolin slurry tank was taken as: $V_{Acmt}^* = 20,000 \text{ cm}^3$

Power requirement of the motor for metakaolin slurry mixing

$$N_p = f(Re, Fr) \quad (13)$$

Where: N_p = Power number

Re = Reynolds number Fr = Froude number

Equation 13 then becomes:

$$\frac{P}{\rho N^3 D_T^5} = f\left(\frac{\rho N D_T^2}{\mu}, \frac{N^2 D_T}{g}\right) \quad (14)$$

For un-baffled tanks, at higher Reynolds number, a vortex forms and the Froude number has a significant effect on the power number [8]. The general equation is then modified

$$P = N_p \rho N^3 D_i^5 \quad (15)$$

$$P = 1.446 \times 1525 \times (6.5)^3 \times (0.1542)^5 = 52.80 \text{ W}$$

To compensate for transmission losses, frictional losses in the gear box and reduced efficiency of the electric motor, a safety factor of 25% was selected.

$$P_{act} = 1.25 \times P_{min}$$

$$P_{act} = 1.25 \times 52.80$$

$$P_{act} = 66 \text{ W}$$

2.1.3 Acid holding tank

The tank is where the acid is kept before releasing it into the reactor for initiating the reaction when it comes in contact with the homogenous metakaolin slurry.

Amount of acid needed per batch = 4,027 cm³

Allowing 20% free board space, the actual volume of acid tank (V_{AT}) required is:

$$V_{AT} = 1.2 \times 4027 = 4,832.40 \text{ cm}^3$$

Considering cylindrical shape, with height diameter ratio of 2, considering 5,000 cm³ as the volume of acid tank: The diagrammatic representation and projection drawings of the dealumination unit are shown in Figure 2.

2.2 Material selection

The reactor for the dealumination was made of stainless steel type 304 which withstands mild acidic environment. Because of the elevated temperature of the dealumination reaction, the inner chamber of the reactor was lined with glass. The lining helped in avoiding direct contact of the reacting species and the stainless steel part of the reactor. Both the acid tank and the metakaolin slurry mixing tank were made of plastics, which were cheaper and would not be attacked by the reactants involved and were at room temperature.

But for the acid tank the appropriate type of plastic material to be used is polyethylene, rather than the material used in this work which was improvised. The piping and fittings were largely made of plastics where the temperature was not very high. A small fraction of the fittings were made of stainless steel material, especially parts that would experience high temperature.

2.3 Fabrication and assembling

The fabrication of the dealumination unit was done after the completion of the design and the selection of the appropriate materials for various components of the unit. It was assembled after fabrication. The instrumentation attached to the reactor includes pressure gauge, pressure relief valve and temperature read-out.

2.4 Test running

The materials used for the reaction in other to test run the dealumination unit include:

1. Concentrated sulphuric acid, 98wt%
2. Metakaolin, prepared from Kankara kaolin
3. Distilled water

The calculated amount of the sulphuric acid needed for the reaction of 2.5kg of metakaolin was poured into the acid holding tank. The required amount of distilled water was poured into the metakaolin slurry tank.

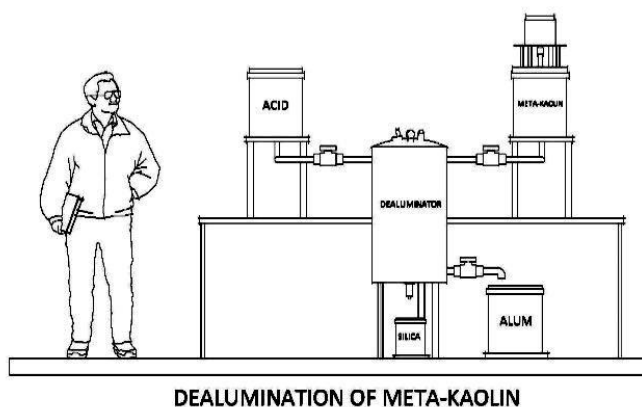


Figure 2: Diagrammatic representation of the dealumination unit of the pilot plant

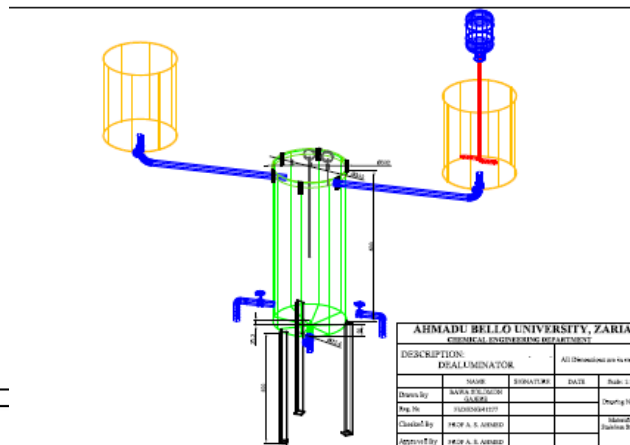
The motor was switched on after which the metakaolin slurry was emptied into the mixing tank. After homogeneity was attained in the slurry mixing tank, the metakaolin slurry (35% solid) was emptied into the dealumination reactor. The acid was then channeled into the dealumination reactor, in a controlled manner. The reaction began immediately and after 20 minutes the reaction was quenched by the addition of distilled water. The added water lowered the concentration of the acidic condition of the reaction from 60wt.% to 30wt.%. The alum, which contained the leached alumina from the metakaolin and silica, which was inert to the acid were collected at the side and bottom outlets of the reactor respectively. The silica was washed to get rid of the excess acid on it and dried before being characterized.

3. RESULTS AND DISCUSSION

The design specifications of the components of the dealumination unit which was comprised of the reactor, acid holding tank and metakaolin slurring mixing tank are presented in Table 3.

Table 3: Design specifications

S/No.	Design parameters	Specifications
1.	Volume of reactor, VR	50 liters
2.	Height of reactor, H	60 cm
3.	Internal diameter of reactor	30 cm
4.	Thickness	2 mm
5.	Volume of acid holding tank	5 liters
6.	Volume of metakaolin mixing tank	10 liters
7.	Speed of impeller, N	390 RPM
8.	Density of metakaolin slurry	1.51 g/cm ³
9.	Viscosity of metakaolin slurry	1.73 x 10 ⁻² Pa.S
10.	Reynolds number of impeller, N _{Re}	4983
11.	Power requirement	70 W
12.	Insulating material	Fiber glass
13.	Thickness of insulating material	14 mm
14.	Thickness of glass lining	4 mm
15.	Rate of heat loss	21.5 W



The assembled unit is as shown in Plate 1.



Plate 1: Dealumination unit

Table 4: Chemical composition of metakaolin and dealumination product

Oxides	SiO ₂	Al ₂ O ₃	Na ₂ O/K ₂ O	Fe ₂ O ₃	CaO	MgO
Metakaolin	59.52	36.55	1.06	0.94	0.53	0.18
Silica (Lab. Scale)	93.54	1.88	2.64	0.12	0.24	0.28
Silica (Run 1)	86.15	2.60	5.15	0.71	0.50	0.48
Silica (Run 2)	96.5	ND*	1.20	0.23	0.18	ND*

The metakaolin had two major components namely, alumina and silica, which accounted for 96.07% (Table 2) of the metakaolin. The molar ratio of silica to alumina was found to be 2.4, the value was above 2, which is reported in literature [9], owing to the fact that the 59.52% of silica was for both the structural and free silica in the metakaolin. The first run (before lining with glass) of dealumination reactor gave 86.15% of silica, at that initial stage leaching of the surface of the inner part of the reactor being stainless steel type 304 occurred. Part of the energy that supposed to be used for the dealumination process was used-up on leaching of the iron content of the stainless steel. At the second run, the percentage of silica obtained was 96.5% which was

better than the laboratory dealumination of 93.54% silica content as shown in Table 2. This observation could be attributed to the minimal heat loss to the environment, more so, no observable leaching occurred. The glass lining helped in preserving the heat for maximal unlocking of the alumina from the metakaolin and leaving the silica as the residue of the reaction. The external lagging reduced the heat loss to the environment, as such more heat was conserved in the reactor that boost the extent of dealumination. The weight percentage of silica in metakaolin of about 59% increased after the dealumination reaction for both the laboratory and pilot scale, as shown in Figure 2. When the dealumination reactor was completely lined at stage 2, in Figure 2, the extent of leaching of the alumina component was better than the laboratory scale. This observation could be attributed to the amount of energy of hydration generated when the acid was in contact with the metakaolin slurry in the dealumination reactor.

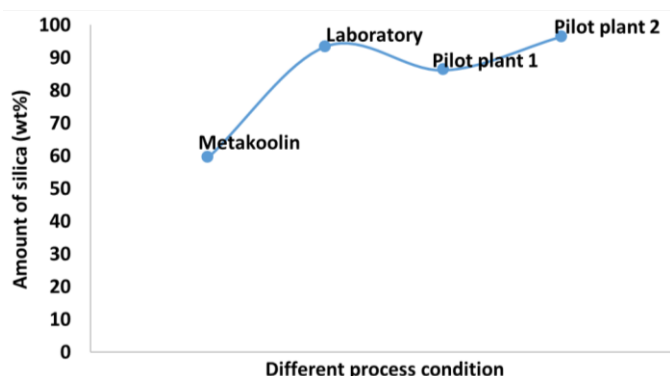


Figure 2: Amount of silica in the dealumination residue

4. CONCLUSIONS

Dealumination unit which comprised of dealumination reactor, acid holding tank and metakaolin slurry mixing tank was successful designed, fabricated and test-run. The materials selected for the fabrications were stainless steel Type 304, glass lining for reactor internal part, woven glass fiber and plastics which were suitable during usage. The alum and silica produced where good, the quality of the later was higher than the one obtained from the laboratory. It is anticipated that this work will promote large scale industrial production of metakaolin which is a chemical intermediate for zeolite production,

hence will engender socio- economic development of nations with abundant kaolin resource such as Nigeria.

5. ACKNOWLEDGEMENTS

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