NIGERIAN SOCIETY OF CHEMICAL ENGINEERS
(A Division of the NSE)

PROCEEDINGS

46th ANNUAL GENERAL MEETING, INTERNATIONAL CONFERENCE & EXHIBITION

Theme: DEVELOPMENT AND OPTIMISATION OF NIGERIA'S SOLID MINERAL SECTOR FOR NATIONAL ECONOMIC GROWTH:
The Role of Chemical Engineering

Date: Thursday, 17 – Saturday, 19, November 2016

Venue: Yar'adua Center, No. 1, Memorial Drive, Abuja, Nigeria.

In Partnership with

MINISTRY OF MINES AND STEEL DEVELOPMENT

Scanned with CamScanner

PREFACE

The theme of the conference which is **'Development & Optimization of Nigeria's Solid Minerals Sector for National Economic Growth- The Role of Chemical Engineering'** was chosen and it is in consonance with the current policy thrust of the Federal Government of Nigeria to diversify the economy.

With the dwindling oil revenue and the need to diversify the economy of the nation, one of the major sectors, that hitherto had been neglected and, which can contribute greatly to the nation's GDP is the Solid Mineral Sector.

Mining as a major economic activity that has a long history in Nigeria. Its importance can only be compared to agriculture as both sectors were once the only sources of revenue in the Nigerian economy. The mining of minerals in Nigeria accounts for only 0.3% of its GDP, due to the influence of its vast oil resources. The domestic mining industry is underdeveloped, leading to Nigeria having to import minerals that it could produce domestically, such as salt or iron ore..

Recently the government reiterated that the mining sector in Nigeria must aspire to contribute between 5-10 per cent to the GDP. The government also envisaged that bitumen processing will be developed into commercial quantities within one year. All this are tall order bearing in mind the state of our solid mineral development and infrastructure. Therefore this conference is to examine these issues and come out with ways to improve on the processing and optimisation of solid minerals in Nigeria, the technology and the infrastructure required.

Experts from the Industry, Academia, Research Institutes, Government organizations, Foreign Embassies & other relevant stakeholders, will be brought together to take a critical look at the challenges and opportunities that face the solid mineral industry, offering key insights into the solutions that will help the Nigerian Solid Mineral industry maximize national economic recovery. The overall objective is to increase the contributions of the solid mineral sector to the nation's GDP and to diversify the foreign revenue sources for a more stable and robust economy. This will also translate to significant wealth and job creation for our teaming unemployed Nigerians as well as engender a more inclusive economy. The conference will also explore solutions for commercial processing and utilization of key minerals found in the country. In particular it will seek to highlight and address potential low hanging fruits such as bitumen, barytes, bentonite and gypsum which are abundantly available locally and in high demand in the Petroleum and Cement Industries but which are imported up till now.

The engineers, scientists and members of the public showed a lot of interest in submission of more than 60 relevant papers including 10 lead papers. Due to time and space constraints we are only accommodating few of the papers. Solid Minerals being a unique sector, the initial decision of the LOC and the Council was to limit papers to invited organisations/individual assigned specific topic to present. However, this decision was relaxed later to allow for call for more

Scanned with CamScanner

papers. Therefore, we have many lead papers in this conference. While we express our gratitude to all who sent in papers, we particularly wish to use this opportunity to thank our colleagues in the academia and outside the Universities who helped to review the papers. You are great and dependable. Without your commitment, we would not have had this high quality book of proceedings. For those whose papers are not included here you will please bear with us. We are constrained by time and space.

On behalf of the Technical Sub-Committee of the Local Organising Committee, we wish to thank all the LOC members particularly the Chairman for all the support given to us to perform our onerous duty. We congratulate all participants of the conference and wish you all fruitful deliberations at the Technical Sessions.

Engr. Dr. Stephen Momoh, FNSE, MNSChE.
Chairman, Technical Sub-Committee.

Scanned with CamScanner

NSChE BOARD OF DIRECTORS 2016

National President	Prof. E. N. Wami, FNSChE
Deputy National President	Prof. S. S. Adefila, FNSChE
Immediate Past President	Engr. (Dr.) A. L. Yar'Adua, FNSChE
National Treasurer	Dr. M. A. Usman, MNSChE
Asst. National Treasurer	Engr. A. K. Oghenecovo, MNSChE
Publicity Secretary	Engr. D. O. Uweh, MNSChE
Asst. Publicity Secretary	Engr. B. Akaakar, FNSChE
Executive Secretary	Samuel. O. Bosoro, MNSChE

46th Annual General Meeting, Conference & Exhibition Local Organising Committee

Engr. Onochie A. Anyaoku (FNSChE)	-	LOC Chairman
Engr. Ben Akakaar (FNSChE)	-	Chairman, Exhibition Sub-Committee
Engr. Andrew Yakubu (FNSChE)	-	Chairman, Finance Sub-Committee
Engr. Dr. B. T. Wada (FNSChE)	-	Chairman, Golf Programme Sub-Comm
Engr. Dr. Steve Momoh (FNSE, MNSChE)	-	Chairman, Technical Sub-Committee
Engr. Abubakar Mamoud. Bello (FNSChE)	-	Chairman, Logistics/Publicity Sub-Comm
Engr. (Mrs.) Grace C. Akujobi-Emetuche (FNSChE, MNSE, MNIN, RES.)- Chairman, Welfare Sub-Committee		
Engr. Onyekachi Onugu (MNSChE)	-	LOC Secretary
Engr. Chinasa Edith Okengwu (MNSChE)	-	LOC Assistant Secretary
Engr. Abdulrahman Mohammed. (FNSChE)	-	Chapter Chairman
Engr. Professor Mobolaji Aluko (FNSChE)	-	Member
Engr. Dr. Elizabeth J. Eterigho (MNSChE)	-	Member
Engr. Tony Ogbuigwe (FNSChE)	-	Member
Engr. Ike Iwenofu (MNSChE)	-	Member
Engr. Salisu S. Ahmed(MNSChE)	-	Member
Engr. Adebisi Adefila	-	Member
Mr. Olanrewaju O. Francis	-	Member
Engr. Ahmed Dikko	-	Member
Engr. Olabisi Mojoyinola	-	Member
Engr. Olalekan Oyelade	-	Member
Engr. Cyril Ojeonu (MNSChE)	-	Member
Engr. Akinyemi O. Oyefeso	-	Member
Engr. Francisca Nwabugo Onyia, MNSChE	-	Member
Engr. Joseph Ejembi O.	-	Member
Engr. Dom Onoh	-	Member
Benjamin Ogede	-	Member
Engr. Robinson N.	-	Member
Frederick Bekibele	-	Member
Augustine Okeke	-	Member
Okpala Kenneth	-	Member
Millie Silas	-	Member
Ojukwu Chidiebele	-	Member
Ntiegot. Robinson	-	Member
Oladipo Agboola	-	Member
Offordile U.C	-	Member
Nwadike Perpetua	-	Member

Scanned with CamScanner

Technical/Editorial Sub-Committee

Engr. Dr. Steve Momoh (FNSE, MNSChE)	-	Chairman
Engr. Professor Mobolaji Aluko (FNSChE)	-	Member
Engr. Dr. B. T. Wada (FNSChE)	-	Member
Engr. Dr. Elizabeth J. Eterigho (MNSChE)	-	Member

Scanned with CamScanner

TABLE OF CONETNT

Scanned with CamScanner

Scanned with CamScanner

Scanned with CamScanner

EFFECTS OF DEALUMINATION ON THE PHYSIO-CHEMICAL PROPERTIES OF CLAY FOR INDUSTRIAL APPLICATIONS

[1*]Eterigho, E. J., Farrow T. S[2]., Uthman, Habib[3] and Faruq, Aisha[4]
[1,3 &4]Chemical Engineering Department,
Federal University of Technology, Minna, Niger State, Nigeria
[2]Chemical and Petroleum EngineeringDepartment,
Niger Delta University Wilberforce Island, Bayelsa State, Nigeria
e-mail: jummyeterighoj@gmail.com; *Corresponding author

Abstract

The physiochemical properties of natural clay and its modified form after acidic treatment were investigated for use as catalyst. The clay samples were collected from Ukpor, Enugu state, south eastern Nigeria. The samples were ground and sieved (2mm). To improve the activity of the clay, a known weight of the natural clay was mixed with a standard analytical-grade 36 N sulphuric acid (H_2SO_4) solution at a molar ratio of 1: 5. The aliquot was placed in open quartz crucible, which was heated in a furnace at 500°C, ramped at 5°C/min for one hour. The resulted clay was calcined in a furnace at a temperature of 600°C for a period of 6 hours. The natural clay and its treated samples were analysed using X-ray fluorescence equipment (XRF), X-ray diffraction (XRDP) powder patterns, Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Energy Dispersive X-ray (EDX). The XRD results showed the morphology of the clay was crystalline (42.06 nm) while the treated clay samples were amorphous. Based on the intensities of their photoelectrons, the XPS results of the treated sample revealed 67% increase of silicon and same percentage reduction of aluminium. The EDX of the treated clay samples revealed 36.5% Si, 2.4% Al, and that of the natural clay sample were 21.5% and 18.0% for Si and Al respectively. Interestingly, no significant change in the oxygen of both samples. Surface area was increased from 500 to 900 m^2/g for the treated sample. In addition, the Si/Al ratio was raised to 15.0 for the treated clay sample by the chemical reaction. The treatment method employed showed greater influenced on the morphology, surface area and percentages of the elemental composition of the treated clay samples compared to using aqueous HCl, $NaHSO_4$ and H_2SO_4. Which opens up higher possibility of controlling the degree of alumina, silica and aluminium sulphate by choice, for different industrial applications.

Keywords: Clay; Beneficiation; Dealuminated Clay; Dissolution; Sulphuric Acid

INTRODUCTION

Clays are solid minerals that can function as both Bronsted and Lewis acids in their natural and Ion exchanged form. Ion exchange is the property of clays to adsorb certain anions and cations as well as their capacity to retain them in exchangeable state. In other words, the adsorbed ions are exchanged for other anions and cations in an aqueous solution, however, such exchange reaction can also take place in non-aqueous medium. The exchangeable ions are held around the outside of the silica-alumina clay structural units, and the exchange reaction generally does not affect the structure of the silica-alumina packet (Carlson, 2004). A well-known example of the ion exchange reaction is the softening of water by the use of zeolites. Clay minerals are the most important chemical weathering products of aluminium rich rocks. Generally, clay is crystalline, the atoms are arranged in a regular order. The character of the clay mineral found in a given soil depends on the nature of the parent material, climate, topography, vegetation and time during which these factors have operated (Grim, 1992). Aluminosilicates is a three dimensional framework structure of silicate mineral in which the silicon atoms are replaced by aluminium atoms in a negatively charged framework with other cations uniformly distributed through it (Obaje *et al.*, 2013).

Treatments of clay involve subjecting clay to various treatments so as to modify the properties for the intended purpose. Such treatments include doping, desilication, dealumination, etc. Modifying the properties of clay can lead to variety of catalysts that are useful in effecting more different reactions and higher selectivity in product structure and yield. Their chemical composition and crystal structure are the basis on which clay is divided into groups, such as Kaolinite, Ulite, Smectite and Chlorite. Among these, the most useful as a catalyst is a sub-

Scanned with CamScanner

group of the Smectite clay called Montmorillonite which is the main constituent of bentonites and Fuller's earth. (Arata and Hino 2011). Clay is important in the construction industry both as a building material and as a foundation for structures. An important industrial application of clays can be found in petroleum and petrochemical processing. Others include ceramic, electrical, pharmaceutical, paint, paper, nuclear energy and textile industries, respectively, etc. Pillared clays which are more stable at higher temperatures (>200°C) are used in petroleum cracking, catalytic reforming and isomerisation of n-alkanes to branched chain alkanes. Many synthetic aluminosilicate can be made and several are manufactured industrially for use: as an ion exchanger and molecular 'sieves, examples are feldspars and zeolites (Fernando and Joan, 2007). The authors studied the dealumination of kaolin using sodium potassium hydroxide during gel formation for the synthesis of zeolite X. A variety of organic reaction that are catalysed by Bronsted acids or Lewis acids have been shown to take place in clays especially montmorillonite, more efficiently under milder conditions, with greater selectivity, better yield, and shorter reaction times.

EXPERIMENTAL PROCEDURE

The clay sample was pre-treated by grounding and it was sieved. Dealumination of kaolin was carried out according to Iyakwari *et al.* (2016). A known weight of the natural clay was mixed with a standard analytical-grade 36 N sulphuric acid (H_2SO_4) solution at a molar at a ratio of 1: 5. Aliquot of the mixture was placed in open quartz crucible. It was heated in a furnace at 500°C, ramped at 5°C/min for one hour. Once the reaction time and temperature was reached the crucible was left in the furnace for 6 h. The physio-chemical properties of the resulted material were analysed. The catalytic surface areas of the catalysts were obtained from N_2 adsorption isotherms determined at 77K using the Coulter™ (SA 3100™ series). The samples were outgassed under high vacuum for 2 h at 200°C prior to the analysis. The pore size was determined using ImageJ software with SEM images. The crystallite size of the modified sample was calculated using data from X-ray diffractogram and X'pert data viewer software in the Scherrer's formula.

RESULTS AND DISCUSSION

The textural properties and elemental analysis of the natural and the dealuminated clay are given in Table 1. For convenience clay is designated as 'C' and its modified form as 'DC'.

Table 1: Result of Physical Analysis

Parameter	Natural clay (C)	Dealuminated clay (DC)
Specific surface area, m^2/g	500	900
Particle size, μm	250	250
Particle density, kg/m^3	1120	850
Pore-volume, m^3/g	0.25	0.40
porosity	0.34	0.45

The XRPD pattern of the clay was crystalline with three mineral phases identified (kaolinite, quartz and mica) however, the quartz and mica were minor. In the X-ray diffraction pattern of dealuminated clay, there were no kaolinite crystalline peaks. The disappearance of these major peaks gave way to amorphous material with a very broad band within the low-range angle 15-35° 2θ as in shown in Figure 1**Figure**. Rosenberg and Anderson (2012) described the broad band as an amorphous phase of silica (SiO_2).

Scanned with CamScanner

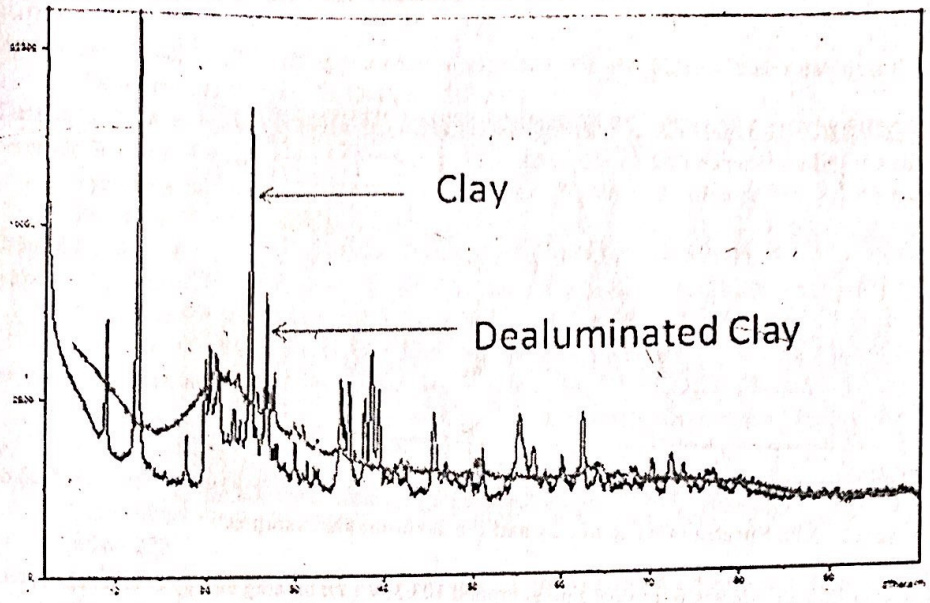

Figure 1: XRPD patterns of clay (blue) and dealuminated clay (green)
Figure 1Figure. Broad band as an amorphous phase of silica (SiO_2). Rosenberg and Anderson (2012)

The elemental analysis shows that the aluminium content was reduced by 86% and the silicon increased by 69% (Table 2). However, the level of oxygen remained relatively constant. The presence of 0.9 wt% sulphur in the dealuminated clay is due to the sulphuric acid that was used during the dealumination of the clay.

Table 2: Textural and Elemental Composition of clay and dealuminated samples

Catalyst	Crystallite size (nm)	Elemental analysis (EDX) (wt%)					
		O	Si	Al	P	Fe	S
C (clay)	42.06	57.8	21.5	18.0	1.9	0.9	-
DC (dealuminated clay)	-	57.3	36.5	2.4	2.9	-	0.9

The dealumination was clearly successful, as the SiO_2/Al_2O_3 ratio of the clay, which was initially 1:2 increased to 15.0 (EDX analysis in Table 3). The modified clay has more silica and less alumina than the natural clay.

Table: 3 Elemental Analysis and Textural Properties of Support

Sample	Si/Al (wt%)	XRD pattern
C (clay)	1.2	Crystalline
DC (dealuminated clay)	15.0	Amorphous

The effect of dealumination on percentage composition of the Si and Al was also shown by XPS analysis. The Al 2p spectra for clay and its dealuminated form at the same binding energy of 74.5eV (Figure2), correspond to aluminium (III) oxide (Moulder *et al.*, 1995; Wagner *et al.*, 2000)

Scanned with CamScanner

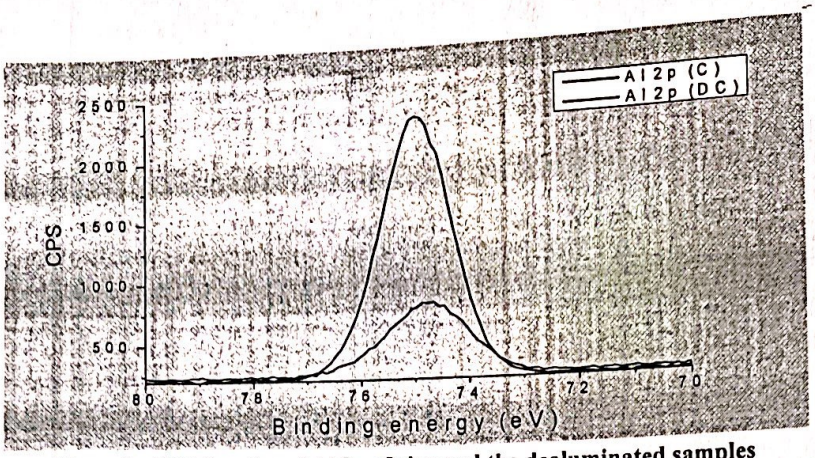

Figure2: XPS Spectra of Al 2p of clay and the dealuminated samples

The silicon (Si 2p) spectra of both samples were very similar around 103.3eV (the binding energy of silicon), as shown in Figure 3, which is a confirmation Si^{4+} in silicon oxide.

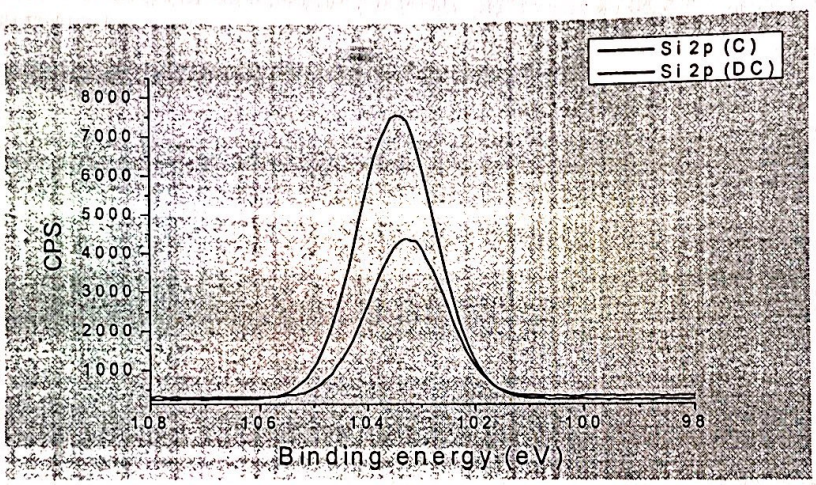

Figure 3: XPS Spectra of Si 2p of both clay and the dealuminated samples

CONCLUSION

The process of dealumination showed noticeable change in the properties of the clay. The result showed that the dealuminated clay had increased surface area; generally, it revealed improved physical properties of the treated clay sample. From the results obtained, it was deduced that the chemical composition of the dealuminated clay sample was different from the natural sample. However, the chemical composition was not relatively altered, but the percentages were altered. This research has successfully reduced the Al^{3+} and increase the Si^{4+} of clay via a very simple process. Thereby, increasing the clay's ability for Bronsted acid characteristics if used or doped with acid (e. g. H_2SO_4) for various industrial applications. The resulted aluminium sulphate is also an industrial chemical

Scanned with CamScanner

References

Arata, K. and Hino, M. (2011) 'Preparation of superacids by metal oxides and their catalytic action', *Materials Chemistry and Physics*, 26, (3-4), pp. 213-237.

Carlson, L., 2004. Bentonite Mineralogy, Finland Geological Survey Working Report 2004-02, pp 108.

Fernando G. C. and Joan Llorens (2007) 'Study of the dissolution of dealuminated kaolin in sodium–potassium hydroxide during the gel formation step in zeolite X synthesis', Microporous and Mesoporous Materials, 100, pp. 302–311

Grim, R.E., 1992. *Applied clay mineralogy*, McGraw-Hill Book Co., New York.

Iyakwari, J., Agbajelola, D. O., S. Farrow, T. S. and Eterigho, E. J. (2016) Assessment of Heavy Metal Contamination on Dumpsite in Kuyi Village, Niger State, Nigeria, Int'l Journal of Research in Chemical, Metallurgical and Civil Engineering. (IJRCMCE) Vol. 3, Issue 1 pp 42-44

Moulder, J. F., Chastain, J., Stickle, W. F., Sobol, P. E. and Bomben, K. D. (1995) *Handbook of x-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data.* Physical Electronics.

Obaje, S. O., Omada, J. I. and U. A. Dambatta (2013) Clays and their Industrial Applications: Synoptic Review, International Journal of Science and Technology, International Journal of Science and Technology pp264-270

Rosenberg, D. J. and Anderson, J. A. (2002) 'On determination of acid site densities on sulphated oxides', *Catalysis Letters*, 83, (1-2), pp. 59-63.

Wagner, C. D., Naumkin, A. V., Kraut-Vass, A., Allison, J. W., Powell, C. J. and Rumble, J. R. (2000) *NIST X-ray Photoelectron Spectroscopy Database* Available at: http://srdata.nist.gov/xps/Default.aspx (Accessed: 02/02/13).

Scanned with CamScanner