

The Effect of Beneficiation on Some Properties of Osun State Ceramic Raw Materials

Oluranti Adetunji Abiola^{a*} , Adekola Olayinka Oke^b , Babatunde Victor Omidiji^b ,
Dare Aderibigbe Adetan^b 

^aDepartment of Mechanical & Automotive Engineering, Faculty of Engineering, Elizade University, Wuraola Adejo Street, Ilara-Mokin, 340, Ondo State, Nigeria

^bDepartment of Mechanical Engineering, Faculty of Technology, Obafemi Awolowo University, Along Ife-Ibadan Expressway, Ile-Ife, 22005, Osun State, Nigeria

*e-mail: visitoluranti@gmail.com

Received: 3 August 2019/Accepted: 23 September 2019/Published online: 30 September 2019

This article is published with open access by AGH University of Science and Technology Press

Abstract

Clay, feldspar and silica sand are important industrial minerals which often need treatment commonly known as beneficiation to improve the quality of ceramic tiles produced from these materials. The different minerals, after sorting, were treated separately in distilled water, alcohol and hydrochloric acid before being crushed in a ball mill; they were then characterized using a pelletron accelerator. The results show an increased silicon content for clay, silica sand and feldspar; and reduced aluminum content for clay and silica sand but not for feldspar. Iron impurity and its oxide are also shown to reduce by over 50% in all the minerals while potassium was found to be the dominant element in feldspar among the defining elements. In conclusion, the increased quartz in the mineral will improve the hardness, density, porosity, and rigidity of ceramic tiles as well as providing support and controlling shrinkage. Furthermore, increasing the mineral quotient in feldspar will enhance its fluxing potential.

Keywords:

clay, feldspar, silica sand, beneficiation, ceramic

1. INTRODUCTION

Ceramic materials are clay minerals which include kaolin, smectite, illite, chlorite, sepiolite and attapulgite and have been part of human existence since time immemorial [1, 2]. Clay is the oldest known ceramic material and has a wide range of applications such as paper coating, paper filling, extender in paint, filling in rubber, filling in plastics, extender in ink, cracking catalysts, fiberglass, foundries, desiccant, cement, pencil leads, adhesives, tanning leather, pharmaceuticals, enamels, pastes and glues, insecticides, carriers, medicines, sizing, textiles, food additives, bleaching, fertilizers, plaster, filler aids, cosmetics, crayons, detergents, roofing granules, linoleum, tiles and polishing compound as well as cracking catalysts and adsorbent production [3–5]. It has been used as a natural nanomaterial throughout history for industrial and commercial uses. The development of the raw material is critical for the success of the ceramic subsector of a nation's economic and industrial growth [6]; beneficiation of the raw material improves the quality of the final products [7].

Beneficiation is an upgrading process that helps to remove impurities and achieves a required particle size and size distribution so as to make material fit for final applications [7–9]. The beneficiation methods of ceramic materials depend on the amount and nature of the mineral's associated impurities as well as the requirements of the user. Such requirements may include the degree of consolidation of the

crude material, the particle-size distributions in the different phases, the character of the contaminant phases, and the required brightness, grit content, plasticity and particle-size distribution [10, 11]. Most of these minerals (clay, feldspar and silica sand) are extracted from open-pit mines by motor-scrappers and then mixed with water and dispersants to form slurry. The coarse particles can be removed by centrifugation, decantation or filtration, depending on the particle size of the raw materials under processing. Coarse iron removal is performed by means of a magnetic separator, and a cake is then obtained by filter-presses which can be dried to remove the remaining water. Clay minerals can be beneficiated or used commercially in the form of balls (the form in which they are extracted) [10].

Established beneficiation approaches involve chemical, mechanical and physical methods and include: froth floatation, gravity and magnetic separation, reductive roasting, size reduction by hydro cyclone, selective flocculation and acid treatment/leaching. The processes for the beneficiation of clays also include grinding, and drying [10]. The preferred beneficiation methods of clay minerals depend on the amount and nature of the mineral impurities associated with it. Although these methods are quite useful in removing impurities, they are at the same time costly, complicated and environmentally hazardous. Bioleaching processes are usually more economical, ecofriendly, and uses less energy compared to other methods [3].

According to Manfredini & Hanuskova [12], the optimal utilization of raw materials is directly proportional to the level of knowledge about the raw materials and the properties of the end products. Beneficiation which removes impurities from ceramic raw materials contributes immensely to the better use of resources, enhances material applications and provides quality final products [3, 7]; hence it becomes imperative to study its effects on some properties of local ceramic raw materials: clay, feldspar and silica sand.

2. MATERIALS AND SOURCES

The clay mineral used in this study was kaolinite clay [13], collected from Ipetumodu, headquarters of the Ife North Local Government area of Osun State, Nigeria. Silica sand was collected from the Isasa River; the river serves as the boundary between the Ayedaade and Ife North Local Government areas of Osun State, Nigeria. Feldspar was collected from Osogbo, the capital of Osun State, Nigeria. Distilled water, alcohol and dilute hydrochloric acid (HCl) was employed for the purification (washing) of the ceramic raw materials. Equipment used for preparing the material samples were a ball mill, magnetic stir bar, dryer, and a Tandem Accelerator.

2.1. Beneficiation process

The beneficiation of the three ceramic raw materials followed the same process. The raw materials were dried separately in an open oven, with the temperature around the raw materials maintained at between 50 to 60°C. The open oven was preferred because it enhances the easy escape of moisture from the specimen. After drying, visible dirt was hand-picked from the different materials and they were ground separately to a powdered form in a Four Ball mill (Model: A5043). Hydrophilic molecules and other impurities that are soluble in water were removed by stirring the fine ground ceramic raw materials with distilled water for 1 hour. The water was decanted after it was allowed to settle for 72 hours. Impurities that are insoluble in water were removed using ethanol, under the same conditions as distilled water. Acid leaching, using dilute hydrochloric acid (HCl), was employed to remove metal contaminants such as iron oxide which is the impurity mostly associated with sand [14] and then distilled water was repeated to completely remove traces of the acid. The ratio of each ceramic material to each of distilled water, ethanol, and dilute HCl was at 0.74 kg/L as recorded by Jovanović & Mujkanović [7]. After decanting the acid, the materials were sun-dried for 72 hours and then dried in an open oven between 50–60°C for 36 hours. Magnetic impurities were then extracted from the dry ceramic raw materials powders using a magnet stir-bar in a 250 ml polyethylene centrifugal bottle.

2.2. Material characterization

Characterization of the raw materials was carried out on the NEC 5SDH 1.5 MV Pelletron Accelerator (Model: 5SDH with an accuracy of 0.0001%) to determine the elements

and oxide value contained in the different materials. The chemical composition of the raw materials (clay, feldspar and silica sand) was investigated with the aid of a Pelletron Accelerator before and after the beneficiation process. Fine grain (powder) size of each of the raw materials was molded into a pellet and exposed to an accelerated high energy charged particle (proton) to excite the sample. The chemical substances were then identified by the sorting of gaseous ions in the field according to their mass-to-charge ratios.

3. RESULTS AND DISCUSSION

3.1. Clay composition

The results presented in Table 1 shows the elemental as well as the chemical composition of the investigated clay before and after beneficiation. It shows that beneficiation increased the amount of silicon (Si) in the clay from 48.4457% to 64.9135% and its oxide (SiO_2) from 55.0463% to 71.3165%, whereas, it reduced the amount of aluminum (Al) from 24.9770% to 16.5986% and its oxide (Al_2O_3) from 25.0606% to 16.1062%. This is an indication of reduced minerals and increased quartz, although this is contrary to the claim by Jovanović & Mujkanović [7] and Kirabira *et al.* [9]. The inconsistency noticed in the result may be due to the type of acid and organic solvent used for the beneficiation process. Hydrochloric and oxalic acid behave differently due to the difference in their corrosive nature [15]. A closer look at the behavior of silicon and aluminum and their oxides in the result obtained in this study, reveals that the method of beneficiation employed will favor ceramic tile production in terms of shrinkage control, rigidity and support with the raw materials in the study area [16].

The results show that the iron (Fe) content was reduced by 64.56% from 14.5592 to 5.1591% by the beneficiation process. This indicates the scarcity of iron in the structure of the clay minerals, as well as the possibility of the attraction or removal of certain fine-grained iron minerals (limonite) by the magnet stir-bar. The iron oxide (Fe_2O_3) was also reduced by 65.7301% probably due to leaching by the acid which was used to remove associated contaminants or impurity such as iron [14].

The absence of elements such as sulfur (S) and cerium (Ce), and their oxides (SO_3 and Ce_2O_3 respectively) after beneficiation shows that the treatment was able to remove these elements and their oxide from the clay material even though, according to Dahle & Arai [17], cerium and its oxide are insoluble in water and dilute acid; Um & Hirato [18] claimed that concentrated acid and alcohol could dissolve cerium. The elimination of cerium, in this case, may be due to the soaking of the clay in alcohol followed by acid separately for 72 hours each as well as the washing with distilled water. For sulfur, its removal after beneficiation may be due to the ability of its mineral to dissolve over time as claimed by Skipton *et al.* [19]. Beneficiation reduced calcium (Ca) content from 1.6188% to 1.4020% and its oxide (CaO) from 1.2028% to 1.0075%, whereas, it increased the content of potassium from 5.2372 to 7.3946% and its oxide from 3.3500 to 4.5743%. The observation with calcium and its

oxide is in conformity with the claim of Salahudeen *et al.* [8] but negates her conclusions concerning potassium (K) and its oxide (K_2O). This could be as a result of the dilute hydrochloric acid used in this study compared to the oxalic acid used by Salahudeen *et al.* [8].

3.2. Silica sand composition

The results in Table 2 show the elemental as well as the chemical composition of the investigated silica sand before and after beneficiation.

Table 1
Elemental and chemical composition of clay

Periodic number	Element	Oxide	Element value [%]		Oxide value [%]	
			before beneficiation	after beneficiation	before beneficiation	after beneficiation
11	Na	Na_2O	0.6692	1.3722	0.4791	0.9499
12	Mg	MgO	1.9869	1.1410	1.7450	0.9715
13	Al	Al_2O_3	24.9770	16.5986	25.0606	16.1062
14	Si	SiO_2	48.4557	64.9135	55.0463	71.3165
16	S	SO_3	0.0516	-	0.0683	-
17	Cl	Cl	0.2782	1.1297	0.1477	0.5802
19	K	K_2O	5.2372	7.3946	3.3500	4.5743
20	Ca	CaO	1.6188	1.4020	1.2028	1.0075
22	Ti	TiO_2	1.7577	0.5978	1.5569	0.5119
23	V	V_2O_3	0.0268	0.0272	0.0210	0.0205
24	Cr	Cr_2O_3	0.0363	0.0305	0.0282	0.0229
25	Mn	MnO	0.1376	0.0370	0.0943	0.0245
26	Fe	Fe_2O_3	14.5592	5.1591	11.0540	3.7882
30	Zn	ZnO	0.0060	0.0018	0.0040	0.0011
37	Rb	Rb_2O	0.0001	0.0016	0.0005	0.0009
38	Sr	SrO	0.0749	0.0902	0.0470	0.0548
40	Zr	ZrO_2	0.1223	0.0832	0.0878	0.0577
56	Ba	BaO	0.0013	0.0202	0.0008	0.0116
58	Ce	Ce_2O_3	0.0024	-	0.0015	-

Table 2
Elemental and chemical composition of silica sand

Periodic number	Element	Oxide	Element value [%]		Oxide value [%]	
			before beneficiation	after beneficiation	before beneficiation	after beneficiation
11	Na	Na_2O	0.5762	0.6625	0.3729	0.4243
12	Mg	MgO	0.1670	0.1516	0.1329	0.1195
13	Al	Al_2O_3	2.5062	1.9904	2.2736	1.7865
14	Si	SiO_2	91.0578	93.7597	93.5340	95.2810
15	P	P_2O_5	0.0664	0.1026	0.0731	0.1117
17	Cl	Cl	-	0.0137	-	0.0065
19	K	K_2O	1.2527	0.7230	0.7245	0.4138
20	Ca	CaO	0.2220	0.3493	0.1492	0.2322
22	Ti	TiO_2	0.9368	0.9767	0.7496	0.7739
24	Cr	Cr_2O_3	0.0837	-	0.0588	-
25	Mn	MnO	0.0548	0.0337	0.0339	0.0207
26	Fe	Fe_2O_3	3.0419	1.1639	1.8790	0.7904
28	Ni	NiO	-	0.0036	-	0.0021
29	Cu	Cu_2O	0.0131	0.0414	0.0071	0.0221
30	Zn	ZnO	0.0042	0.0107	0.0025	0.00
35	Br	Br	-	0.0061	-	0.0029
37	Rb	Rb_2O	0.0173	0.0021	0.0090	0.0011
38	Sr	SrO	-	0.0090	-	0.0051

It shows that beneficiation increased the amount of silicon (Si) from 91.0578% to 93.7597% and its oxide (SiO_2) from 93.5340% to 95.2810%, whereas, it reduced the amount of aluminum (Al) from 2.5062% to 1.9904% and its oxide (Al_2O_3) from 2.2736% to 1.7865%. This shows that beneficiation enhances the quality of quartz contained in the silica sand content. This corroborates the report of Jovanović & Mujkanović [7].

The results of the beneficiation of silica sand directly opposed the trend for clay, as calcium increased from 0.2220% to 0.3493%, while its oxide decreased from 0.1492% to 0.2322%; potassium reduced from 1.2527% to 0.7230% and its oxide from 0.7245% to 0.4138%. Iron impurity in the silica sand is also shown to have reduced by 61.7377% and its oxide by 57.9351%.

The traces of chlorine noticed after beneficiation may be from HCl; while nickel, bromine, and strontium may have been formed from the reaction of the elements contained in the sand with alcohol and dilute HCl. Traces of chromium found in the raw silica sand may have been recognized as an impurity which the beneficiation method is capable of removing.

3.3. Feldspar composition

Table 3 shows the elemental as well as the chemical compositions of the investigated feldspar before and after beneficiation. It shows that beneficiation increased the amount of silicon (Si) from 60.7892% to 61.0271% and its oxide (SiO_2) from 68.1126% to 68.8503%. The aluminum (Al) content also increased from 16.8750% to 16.1590% while its oxide (Al_2O_3) slightly changed in quantity before and after beneficiation. This shows that beneficiation enhances the quality of quartz and minerals contained in the feldspar

sample. The increased quartz in beneficiated feldspar shows that the treated material will possess improved hardness, durability, resistance to chemical corrosion, control density, porosity, and shrinkage. The increased minerals will be expected to increase the fluxing potential of the material in ceramic tile production [16, 20]. Iron impurity in the feldspar reduced by 52.1241% and its oxide by 58.9265%. Calcium (Ca) and its oxide (CaO); as well as nickel (Ni) and its oxide (NiO), were completely eliminated from feldspar by the beneficiation process.

Feldspars, which is the earth's most abundant mineral group and estimated to constitute 60% of the earth's crust and forming a fundamental mineralogical component of many rocks, is either represented as orthoclase or potassium feldspar $\text{K}(\text{AlSi}_3\text{O}_8)$; Albite or sodium feldspar $\text{Na}(\text{AlSi}_3\text{O}_8)$; and anorthite or calcium feldspar $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$ [21–25]. The results in Table 3 show that the amount of potassium increased from 15.9849% before to 16.3283% after beneficiation. This is larger than the amount of sodium, which increased from 5.1554% to 5.7406%, while the traces of calcium found before beneficiation (0.4352%) were eliminated after treatment. This result suggests that the feldspar used in this study is likely to be orthoclase, since potassium is mostly represented in the minerals.

4. CONCLUSIONS

Beneficiation was found to be effective in improving the purity of the ceramic raw materials. About 66.3891% iron impurity and 65.7301% of its oxide were removed from clay while 61.7377% iron and 57.9351% of its oxide was removed from silica sand, and 52.1241% iron impurity and 58.9265% of its oxide were removed from feldspar through the beneficiation process.

Table 3
Elemental and chemical composition of feldspar

Periodic number	Element	Oxide	Element value [%]		Oxide value [%]	
			before beneficiation	after beneficiation	before beneficiation	after beneficiation
11	Na	Na_2O	5.1554	5.7406	4.2723	4.0807
12	Mg	MgO	0.1252	0.0700	0.1276	0.0612
13	Al	Al_2O_3	16.8750	16.1590	16.1175	16.1015
14	Si	SiO_2	60.7892	61.0271	68.1126	68.8503
15	P	P_2O_5	0.1642	0.1689	0.2313	0.2043
17	Cl	Cl	0.0328	0.2110	0.0202	0.1113
19	K	K_2O	15.9849	16.3283	10.3565	10.3726
20	Ca	CaO	0.4352	–	0.3743	–
22	Ti	TiO_2	0.0093	0.0495	0.0094	0.0436
24	Cr	Cr_2O_3	0.0020	–	0.0018	–
25	Mn	MnO	0.0028	0.0032	0.0022	0.0022
26	Fe	Fe_2O_3	0.3837	0.1837	0.3372	0.1385
28	Ni	NiO	0.0010	–	0.00008	–
35	Br	Br	0.0031	0.0013	0.0019	0.0007
37	Rb	Rb_2O	0.0512	0.0574	0.0345	0.0332

The increased silicon (95.2810%) in the silica sand minerals will improve ceramic tiles hardness, density, porosity, rigidity, provide support and control shrinkage in ceramic article as silica sand increases. Meanwhile, the potassium oxide dominance (10.3726%) in feldspar compared to sodium oxide (4.0807%) and calcium (0%) after beneficiation suggest that feldspar collected from Osogbo in Osun state of Nigeria is likely to be orthoclase.

REFERENCES

- [1] Murray H.H. (1997). *Clays for our future*. In: Kodama H., Mermet A.R. & Torrance J.K. (eds.), Proceedings of the 11th International Clay Conference, June 15–21, Ottawa, Canada, 3–11.
- [2] Yuan G. & Part A. (2004). Toxic / hazardous substances and environmental engineering. *Journal of Environmental Science and Health*, 39, 2661–2670.
- [3] Ajayi O.A. & Adefila S.S. (2012). Comparative study of chemical and biological methods of beneficiation of Kankara kaolin. *International Journal of Scientific & Technology Research*, 1(8), 13–18.
- [4] Adnan M., Sazzad H.M. & Fakhrul I.M. (2011). Potential of locally available clay as raw material for traditional-ceramic. *Journal of Chemical Engineering, The Institution of Engineers, Bangladesh*, 26(1), 34–37.
- [5] Murray H.H. (1999). Applied clay mineralogy today and tomorrow. *Clay Minerals*, 34, 39–49.
- [6] Irabor P.S.A., Jimoh S.O. & Omowumi O.J. (2014). Ceramic raw materials development in Nigeria. *International Journal of Scientific and Technological Research*, 3 (9), 275–287.
- [7] Jovanović M. & Mujkanović A. (2013). *Characterization, beneficiation and utilization of the clay from central Bosnia, B&H*. 17th International Research / Expert Conference. Trends in the Development of Machinery and Associated Technology (TMT 2013), 10–11 September, Istanbul, Turkey, 181–184.
- [8] Salahudeen N., Nasiru A., Ahmed A.S., Dauda M.M., Waziri S., Okonkwo P.C. & Isa M.T. (2015). Chemical and physical comparative study of the effect of wet and dry beneficiation of Kankara kaolin. *Nigerian Journal of Technology*, 34(2), 297–300.
- [9] Kirabira J.B., Jonsson S. & Byaruhanga J.K. (2011). Beneficiation and evaluation of Mutaka kaolin. Proceedings of Second International Conference on Advances in Engineering and Technology, December 20–21, Noida, India, 169–175.
- [10] González J.A. & Ruiz M. del C. (2006). Bleaching of kaolins and clays by chlorination of iron and titanium. *Applied Clay Science*, 33, 219–229.
- [11] Heckroodt R.O. (1991). Clay and clay materials in South Africa. *Journal of South African Institute of Mining and Metallurgy*, 91(10), 343–363.
- [12] Manfredini T. & Hanuskova M. (2012). Natural raw materials in “traditional” ceramic manufacturing. *Journal of the University of Chemical Technology and Metallurgy*, 47(4), 465–470.
- [13] Oke A.O. & Omidiji B.V. (2016). Investigation of some moulding properties of a Nigeria clay-bonded sand. *Archives of Foundry Engineering*, 16(3), 71–76.
- [14] Ayhan F.D., Temel H.A. & Bozkurt V. (2011). Removal of impurities from tailing (Quartz) obtained from Bitlis Kyanite Ore by flotation method. *International Journal of Applied Science and Technology*, 1(1), 74–81.
- [15] Zor S. & Yaka E. (2007). Corrosion behavior of PANI coated aluminum in oxalic acid containing different anions. *Bulletin of Electrochemistry*, 23, 149–153.
- [16] Iyasara A.C. Joseph M. & Azubuike T.C. (2014). The use of local ceramic materials for the production of dental porcelain. *American Journal of Engineering Research*, 3(9), 135–139.
- [17] Dahle J.T. & Arai Y. (2015). Environmental Geochemistry of Cerium: Applications and Toxicology of Cerium Oxide Nanoparticles. *International Journal Environmental Research and Public Health*, 12, 1253–1278.
- [18] Um N. & Hirato T. (2012). Precipitation of cerium sulfate converted from cerium oxide in sulfuric acid solutions and the conversion kinetics. *Materials Transactions*, 53(11), 1986–1991.
- [19] Skipton S.O., Dvorak B.I. & Woldt W. (2010). Drinking water: Sulfur (Sulfate and Hydrogen Sulfide). *NebGuide*, University of Nebraska-Lincoln Extension. Retrieved from: <http://extensionpublications.unl.edu/assets/pdf/g1275.pdf> (accessed 12.09.2017).
- [20] El Nouhy H.A. (2013). Assessment of some locally produced Egyptian ceramic wall tiles. *Housing and Building National Research Center Journal*, 9, 201–209.
- [21] Acchar W. & Dultra E.J.V. (2015). *Ceramic materials from coffee Bagasse ash waste*. 1st Ed., Springer International Publication.
- [22] Sokolář R. & Vodová L. (2014). Sintering behavior of feldspar rocks. *International Journal of Engineering and Science*, 4(10), 49–55.
- [23] Kyonka J.C. & Cook R.L. (2007). The properties of feldspars and their use in whitewares. *University of Illinois Engineering Experimental Station Bulletin*, 422, 5–34.
- [24] Potter M.J. (2003). *Feldspar and Nepheline Syenite*. U.S. Geological Survey Minerals Yearbook, 25.1–25.7.
- [25] Kauffman R.A. & Van Dyk D. (1994). *Feldspars*. In: Carr D.D. (ed.), *Industrial minerals and rocks*. 6th Ed., Littleton, CO, Society for Mining, Metallurgy, and Exploration, Inc., 473–481.