DOI: https://dx.doi.org/10.4314/gjpas.v23i1.4

GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 23, 2017: 27-34
COPYRIGHT© BACHUDO SCIENCE CO. LTD PRINTED IN NIGERIA ISSN 1118-0579
www.globaljournalseries.com, Email: info@globaljournalseries.com

PHYSICO-CHEMICAL CHARACTERIZATION OF OGUN AND SOKOTO PHOSPHATE ROCKS

A. O. FAYIGA AND G. O. OBIGBESAN

(Received 11 October 2016; Revision Accepted 3 January 2017)

ABSTRACT

There is a need to identify potential phosphate rock sources to supply phosphorus (P) for crop growth and sustain food production. Physico-chemical characteristics of phosphate rocks from two Nigerian deposits were evaluated to determine their suitability for processing or direct application as P fertilizer. Physical properties such as textural forms, hardness, specific gravity, shrinkage, water absorption capacity and firing color were determined. Ogun rock phosphate (ORP) and Sokoto rock phosphate (SRP) were also subjected to chemical and mineralogical analysis. Solubility tests were conducted at two different particle sizes in 2% citric acid. ORP had a higher water absorption capacity and shrinkage than SRP while specific gravity of ORP was lower. Total P_2O_5 of SRP and ORP were 36.1% and 31% respectively, which is greater than P_2O_5 content of Morocco rock phosphate. Both ORP and SRP contained carbonate fluorapatite and chlorapatite minerals. Gypsum, calcite and lime were associated with both rock phosphates indicating their liming potential in the soil. ORP was more soluble in water, probably because it has a lower pH (5.0) than SRP (7.8). Higher solubility of SRP in 2% citric acid may be caused by its high carbonate content. Solubility of both rocks in 2% citric acid increased with decreasing particle size. Solubility of both rocks in 2% citric acid was greater than 30% indicating that they are reactive rocks. The agronomic effectiveness of these rocks has been validated in several on farm trials. We recommend these phosphate rocks for production of P fertilizers and direct application in crop production.

KEYWORDS: Phosphorus, apatite, crop production, fertilizer, Ogun rock phosphate, Sokoto rock phosphate

INTRODUCTION

Phosphate Rock (PR) is used in agriculture to produce fertilizer and animal feeds, in the industry for production of detergent or food additives, in energy industry as a source of uranium and rare earth metals, and in environmental science for metal immobilization (Ibrahim *et al*., 2010). About 70% of the PR mined is used to prepare water soluble P fertilizers for crop production (Zhang, 2014). Global food production is dependent on PR because P is a limiting factor in crop production (Fayiga and Nwoke, 2016). Therefore, it is important to ensure steady supply and availability of PR for crop production by exploring available deposits worldwide. Extensive deposits of phosphates occur in 4 sedimentary basins in Nigeria; Dahomey basin in Ogun state; Lullemeden basin in Sokoto state; Anambra basin in Imo state; Niger Delta basin in Edo state (Adegoke *et al*., 1994). Two main types of phosphates were found in the Ogun state phosphate bearing beds; the granular and the nodular. Sokoto phosphates can be found in different forms; nodules and pellets in clays, shales and limestones; and primary phosphatic shales, limestones and siltstones (Adegoke *et al*., 1994).

Sedimentary PRs have been the major source of commercial phosphates and vary widely in chemical composition because of their widely different modes of occurrence in geological periods ranging in age from Precambrian to Miocene (FAO, 2004). Food and Agriculture Organization (FAO, 2004) has recommended that use of PR sources should be promoted in countries where they are indigenously available. However, PRs must first be characterized before they can be exploited and mined. The mineralogical, chemical and textural characteristics of phosphate rocks determine their suitability for use either directly applied to the soil or processed as water soluble P fertilizers. Direct applications of PRs are preferred because water soluble P fertilizers have been reported to contribute to P loading of surface waters (Bulut and Aksoy, 2008). Enrichment of surface waters with nutrients such as P may lead to eutrophication of surface waters. Even though, direct application of PRs has a lot of limitations such as low solubility and reactivity, they have been found to be as effective as water soluble sources in acid tropical soils deficient in P (Husnain *et al*., 2014).

The agronomic effectiveness of PRs depends on its solubility which is normally measured in 2% citric acid, 2% formic acid or neutral ammonium citrate (Leon *et al*., 1986). PRs have been shown to be a suitable direct P fertilizer source in situations that alter equilibrium reactions towards dissolution. The solubility of PRs determines the amount of P released for plant uptake. Solubility of PRs is affected by basic components such as calcium carbonate ($CaCO_3$) and complexing ions such as iron (Fe) and aluminum (Al)

A. O. Fayiga, Department of Agronomy, University of Ibadan, Ibadan, Nigeria.
G. O. Obigbesan, Department of Agronomy, University of Ibadan, Ibadan, Nigeria.

(Braithwaite *et al*., 1989). Particle size also influences the solubility of PRs. A past study showed that finer material was preferentially dissolved when ground PR was partially acidulated (Charleston *et al*., 1989). Anderson *et al*. (1985) also observed that PR solubility varied with particle size and time.

The goal of characterization is to find the appropriate match of raw material and processes which may result in the use of conventional or non conventional processes that can meet the technological, agronomic and economic requirements for the commercialization of a particular ore. Physical characteristics determine potential technical problems in processing while chemical characteristics will determine agronomic effectiveness of PR. Several studies have determined chemical composition but few have done a detailed analysis involving both physical and chemical characterization of PRs in Nigeria. Hence, this paper attempts to 1) provide information on physico-chemical properties of PRs from two deposits in Nigeria and 2) determine effect of particle size on the solubility of PR in different solvents to provide a better understanding of the potential processing and effectiveness of locally available PR for crop production.

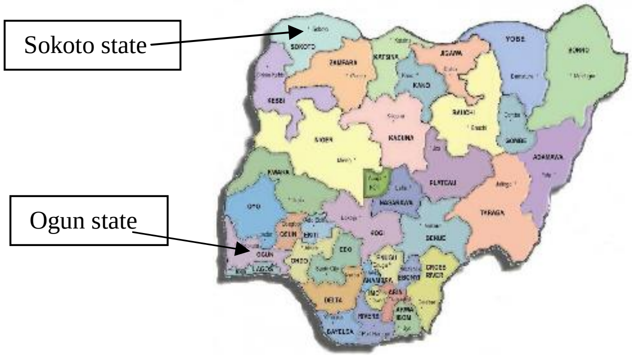

Figure 1: Map of Nigeria

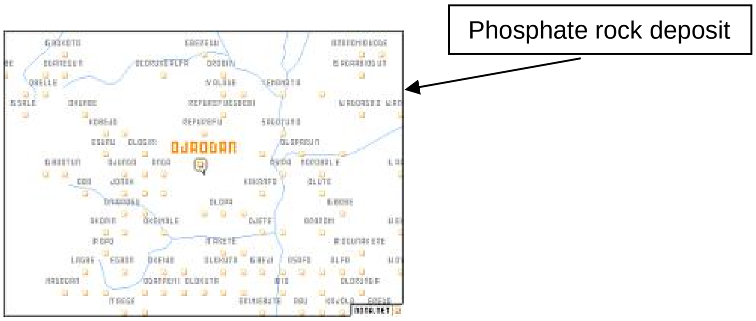

Figure 2: Map of Ogun State showing study site

2. MATERIALS AND METHOD

2.1 Collection of Phosphate Rocks

Ogun and Sokoto phosphate rock deposits were chosen out of four in Nigeria (Fig. 1) because they are found in commercial quantities (Obaje *et al*., 2014). Ogun State phosphate rock was collected from Oja-Odan, Ogun State, Nigeria with the assistance of a staff of the Geological Survey Department, Abeokuta, Ogun State, Nigeria (Fig. 2). Samples were collected from pits dug and excavated manually at 30 to 50 cm from the soil surface. Sokoto phosphate rock (Fig. 3) was collected from the Department of Agronomy, University of Ibadan, Oyo State, Nigeria. Ogun State is in the South Western region while Sokoto state is in the Northern region of Nigeria. Nigeria has two seasons; the dry season from November to March and rainy season from April to October. The North with its lower rainfall and shorter rainy season consists of savanna land while the humid, tropical forest zone of the south has longer rains.

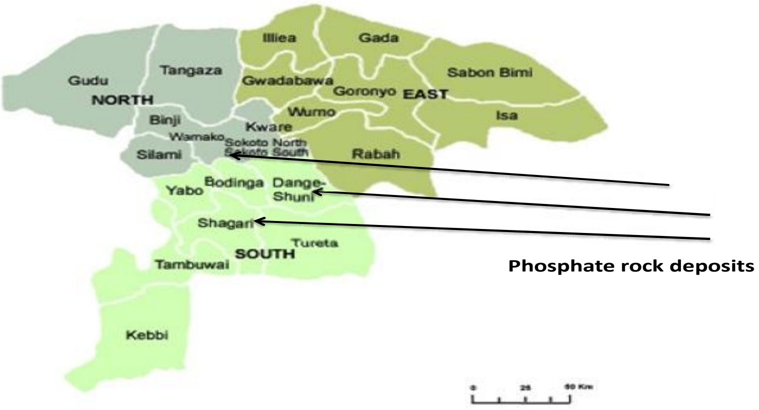

Figure 3: Map of Sokoto State showing location of phosphate rock deposits

2.2 Physical characterization

Physical properties determined were textural forms, color, particle size, porosity or water absorption capacity, hardness and specific gravity. Textural forms and color were determined by visual observation. Particle size was determined for the ground phosphate rock by using a set of sieves with mesh sizes ranging from 2mm to 45µ (McGlinchey, 2005). Water absorption capacity was determined using the method by Umunna and Azubuike (1995). This involved weighing rock samples collected from the field and drying in an oven at 100^{o}C for 30 mins to eliminate moisture. The oven dried rock samples were then weighed and soaked in water for hours. The capacity of water absorbed was calculated. The specific gravity of the rocks were determined using Archimedes principle which states that when a body is totally of partially immersed in a fluid, the upthrust on it is equal to the weight of fluid displaced. Hardness was read on MoH's scale. Color after ignition was determined by pelletizing and firing the pellets at 200 - 600^{o}C for 3 hrs. This firing test is significant since thermal treatment techniques are used for concentrating the run-of-mine phosphates (Abouzeid, 2008). After firing, the radii of the pellets were measured and shrinkage calculated in percentage. The pelletization machine used was a PYE UNICAM pelletizing model (SP 300).

2.3 Chemical characterization

Total P_2O_5, moisture content, solubility in water and citric acid were done using the Association of Official Analytical Chemist method (AOAC, 1975). Total P_2O_5 was read on Spectronic 20 at 480 nm. Na_2O and K_2O were read on an EEL photometer, model 230. Phosphate rock ground to 170-mesh (90 µ) was fused with 7.5 g of NaOH and dissolution was done with 5.5 N HCL. CaO was determined by titrating sample solution with mercaptoacetate solution and hydroxynaphtol blue indicator with EDTA solution (Gehrke *et al*., 1954). Silica was read on an SP6-300 spectrophotometer at 645 nm for 30 and 90 mins after adding ascorbic acid (Kiss, 1982). Alumina was also read on the SP-6 spectrophotometer at 600 nm while Fe_2O_3 was read at 365 nm (Giovanni and Luigi, 1961).

2.4 Mineralogical characterization

The basic principle underlying the identification of minerals is that each crystalline substance has its own characteristic structure which diffracts X-ray in a characteristic pattern. The characteristic patterns are recorded in 2Θ scale (glancing angle of reflection) against the peak intensities. Minute powdered samples were smeared into standard rectangular glass slides and these slides were in turn inserted into the aluminum sample holder of the diffractometer. These samples were analyzed using a Philips PM 9920/00 diffractometer with Cu-K alpha radiation. The following minerals were investigated; chlorapatite, fluorapatite, gypsum, calcite, lime, kaolinite, and vermiculite. X-Ray diffraction curves were interpreted by comparing peaks of notable intensities with those of standard minerals.

3. RESULTS

3.1 Physical Properties

Table 1: Physical Properties of Nigerian Phosphate Rocks

Property	Ogun Rock Phosphate (ORP)	Sokoto Rock Phosphate (SRP)
Textural form	Vesicular, nodular, granular, pellets	Nodular, pellets
Color (before firing)	Brownish grey	Silvery grey
Color (after firing)	Reddish brown	Silvery grey
Specific gravity	1.52	1.28
Water absorption capacity	24.4	11.1
Hardness	5.0	5.0
Shrinkage	5.0	2.5
Particle size analysis		
2 mm	5.0	8.0
1 mm	8.0	7.5
250 µ	9.0	8.0
125 µ	51.0	50.0
45 µ	27.0	26.5

Means of 3 replicates

The physical properties of Ogun Rock Phosphate (ORP) and Sokoto Rock Phosphate (SRP) are shown in Table 1.

ORP exists in forms such as nodules, granules, pellets and vesicles while SRP occurs as nodules and pellets (Plate 1). The specific gravity of SRP was 1.78 while ORP was 1.52 but they both have a hardness of 5. The water absorption capacity and shrinkage of SRP is lower than that of ORP. SRP maintained its color before and after firing while ORP turned reddish brown after firing (Plate 2). SRP was better preserved as pellets while ORP was easily broken or crushed (Plate 2). Particle size analysis showed that ORP had 13% between 1-2mm while SRP had 15.5%; ORP had 87% below 250µ while SRP had 84.5%.

Plate 1: Textural forms of Ogun rock phosphate (ORP) and Sokoto rock phosphate (SRP)

Plate 2: Pellets of Ogun rock phosphate (ORP) and Sokoto rock phosphate (SRP) before and after firing.

3.2. Chemical properties

Total P_2O_5 content of SRP was 36.1 % while that of ORP was 31 % (Table 2). The P_2O_5 concentration of SRP was 16.5 % higher than that of ORP. Similarly, CaO was 130.3 % higher in SRP than ORP. However, MgO content of ORP was 42% higher than SRP. Na_2O and K_2O content of both ORP and SRP were about the same. Fe_2O_3 and Al_2O_3 were higher in ORP than SRP. The silica content of ORP was 25.7% higher than SRP. The $CaCO_3$ content of SRP was 130% higher than ORP. The pH of SRP in water was 7.8 while ORP was 5. The moisture content of both phosphate rocks was the same.

Table 2: Chemical Properties of Phosphate Rocks

Property	**Ogun Rock Phosphate (ORP)**	**Sokoto Rock Phosphate (SRP)**	**Morocco Rock Phosphate [a]**
P_2O_5	31.0	36.1	24.4
CaO	19.2	44.2	71.0
MgO	1.35	0.95	0.30
Na_2O	0.60	0.11	1.05
K_2O	0.03	0.05	0.03
Fe_2O_3	7.28	2.19	0.35
Al_2O_3	6.91	1.79	0.28
SiO_2	26.9	21.4	0.89
$CaCO_3$	34.3	79.0	NA
pH (H_2O)	5.00	7.80	NA

Means of 3 replicates, a – Mar and Okazaki, 2012, NA-not available

Results of the solubility tests on both phosphate rocks are shown in Table 3. Solubility of both rocks was determined at two particle sizes; 125 µ and 45 µ to show the effect of particle size on dissolution of phosphate rock. Solubility of both rocks was tested in two solvents, water and citric acid. The percentage P that dissolved in water was higher in ORP than SRP at both particle sizes. There was a higher dissolution of both rocks in citric acid compared with water. The solubility of both phosphate rocks in citric acid was about 300 times than water at the two particle sizes. The dissolution of both rocks increased with decreasing particle size.

Table 3: Effect of particle size on solubility of phosphate rock in water and citric acid

Solvent /particle size	**Ogun Rock Phosphate (ORP)**	**Sokoto Rock Phosphate (SRP)**
Water		
125 µ	0.16	0.11
45 µ	0.23	0.14
Citric acid		
125 µ	31.8	31.9
45 µ	38.4	45.5

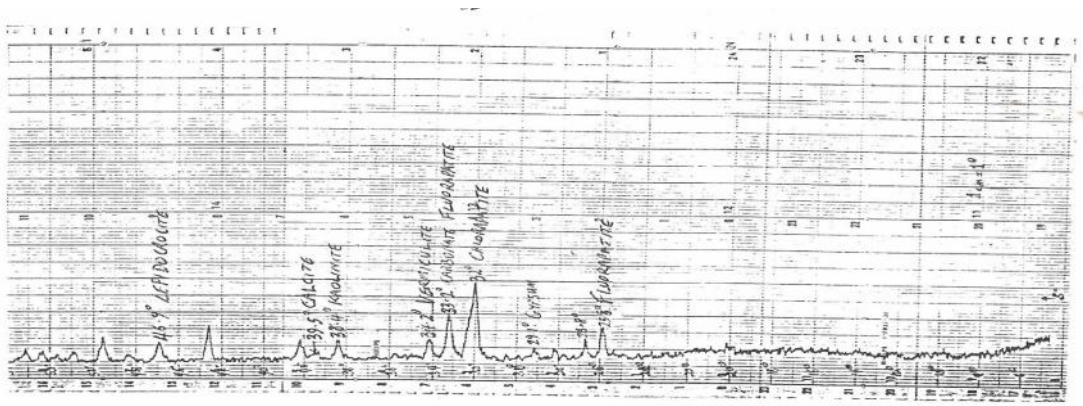

Fig. 4: X-Ray Diffraction of Ogun rock phosphate (ORP)

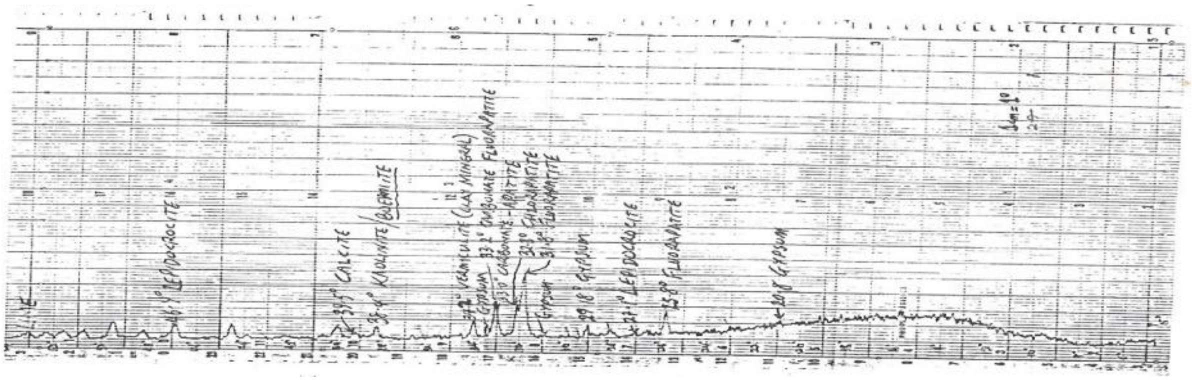

Fig. 5: X-Ray Diffraction of Sokoto rock phosphate (SRP)

X-Ray diffraction showed that ORP contains a mixture of carbonate fluorapatite, chlorapatite, and fluorapatite (Fig. 4) while SRP contains carbonate fluorapatite, carbonate apatite, and chlorapatite (Fig. 5). Gypsum, calcite and lime were associated with both rock sources indicating their potential for liming. The peak of the iron ore (lepidocrocite) is higher in ORP than SRP. Both phosphate rocks were associated with clay minerals such as kaolinite and vermiculite. However, some peaks were not easily identifiable.

4. DISCUSSION

The textural forms of ORP such as vesicles and granules showed lower rock strength than SRP. The water absorption capacity of SRP was 120% lower than ORP indicating higher rock strength of SRP. Similarly, the shrinkage value for SRP was 100% lower than ORP. This indicates higher rock strength of SRP since the lower the shrinkage, the higher the rock strength. The higher rock strength of SRP may contribute to technical problems in the processing of the rocks. Results have shown that SRP will require double the crushing strength of ORP. Pelletization of the rocks also showed the ease with which ORP was broken while SRP was better preserved as pellets. Pelletization of P fertilizers may help to reduce P leaching and run off losses after application which will reduce P loading of surface waters. Additives may be needed to reduce breakage of ORP during pelletization. SRP retained its color after firing while ORP turned reddish brown after firing. This suggests higher concentration of Fe_2O_3 in ORP than SRP which was confirmed by results of the chemical analysis of the rocks. ORP had a concentration of Fe_2O_3 that was 3 times that of SRP. This was confirmed by another study which reported heavy iron staining on nodular form of ORP (Adesanwo et al., 2010).

X-Ray diffraction gave a better insight into the chemical and mineralogical composition of the rocks. Similar apatite minerals such as carbonate fluorapatite and chlorapatite were present in both phosphate rocks. The peaks for apatites were more abundant in SRP than ORP confirming the higher concentration of P_2O_5 in SRP obtained during chemical analysis. Data on world PR production in 2012 shows that Morocco is now the largest producer, so we have compared our results with Morocco PR (Heckenmuller et al., 2014). The P_2O_5 content of ORP is 18.3% higher than Morocco PR while SRP is 32.5% higher than Morocco PR (Mar and Okazaki, 2012). Similarly, MgO content of ORP and SRP was 78% and 68.4% higher than Morocco PR respectively. However, CaO content of Morocco PR was 78% higher than ORP while it was 38% higher than SRP. The K_2O content of Morocco PR was also similar to that of ORP and SRP. X-Ray diffraction also showed that SRP contains more abundant peaks for carbonate apatite than ORP. This must have contributed in no small measure to the carbonate content of SRP which was about twice that of ORP. Both rocks were associated with minerals like calcite, lime and gypsum indicating their potential to be used as liming material apart from its use as P fertilizer. Monovalent ions such as Na^+ and K^+ are present in the same proportions in both rocks. Their very low content suggests that both rocks will not hinder the formation of a good soil structure when applied to the soil.

The pH of ORP shows the rock is strongly acidic and much lower than SRP which was found to be slightly alkaline. This may be due to their location which corresponds to different climatic regions of Nigeria. SRP is from the northern arid region while ORP is from the sub humid southwest region with bimodal rainfall and heavier rainfall patterns. The higher weathering of soils due to higher soil moisture in the sub humid region may be responsible for the lower pH of ORP. The higher carbonate content of SRP could also contribute to its slightly alkaline pH. Raw phosphate rock is very insoluble in water and this has been shown in this study. P concentrations of the rocks in water were 300 times lower than in citric acid. This is the major limitation for direct application of phosphate rocks because water soluble concentrations are readily available for plant uptake. Efforts to increase P availability for direct applications of PR involve increasing acidity to facilitate dissolution of the rocks. The lower pH of ORP may be responsible for higher water soluble concentrations than SRP. There was greater dissolution of SRP than ORP in citric acid probably due to higher carbonate content of SRP. Rajan *et al*. (1997) reported that increasing carbonate level decreases the unit cell A dimension and increases the solubility. The presence of complexing ions such as Fe and Al may reduce the solubility of P. ORP had higher concentrations of both Fe and Al oxides than SRP and this may be responsible for lower solubility than SRP. Dissolution of P in both rocks increased with decreasing particle size because of increasing surface area which increases its reactivity and solubility. Phosphate rocks are considered reactive if 30% or more are soluble in 2% citric acid (Braithwaite *et al*., 1989). Both rocks had more than 30% P soluble in 2% citric acid for both particle sizes and can therefore be classified as reactive rocks. High phosphorus content of both rocks indicates their potential to supply P for plant growth. These phosphate rock deposits need to be exploited to supply the increasing demand for P fertilizers globally.

CONCLUSION

This study has analyzed physical and chemical properties of PR from two deposits in Nigeria. SRP from the arid region of Nigeria had higher rock strength and was better preserved as pellets probably because it was not subjected to the high rainfall regime of the South Western part of the country where ORP is located. X-Ray diffraction showed that both rocks contain similar apatite minerals though they are present in more abundance in SRP. Chemical analysis, firing tests and X-Ray diffraction have all shown that ORP has a higher Fe-Oxide content than SRP which could be responsible for its low solubility. Solubility of both rocks increased with decreasing particle size and surface area. Even though ORP had lower P content and solubility than SRP, both rocks can be classified as reactive rocks and used to supply P for crop production.

REFERENCES

Abouzeid, A. M., 2008. Physical and Thermal Treatment of Phosphate Ores: An Overview. Int. J. Miner. Process. 85: 59–84. doi:10.1016/j.minpro.2007.09.001.

Adegoke, O., Ajayi, J., Nehikare, M and Rahama, M., 1994. Fertilizer raw material situation in Nigeria. Proceedings of a National Organic Fertilizer Seminar. Fertilizer Procurement and Distribution Department.

Adesanwo, O. O., Dunlevey, J. N., Adetunji, M. T., Adesanwo, J. K., Diatta, S and Osiname, O. A., 2010. Geochemistry and Mineralogy of Ogun Phosphate Rock. African J. Environ. Sci. Technol. 4(10): 698–708.

Anderson, D. L., Kusgow, W. R and Corey, R. B., 1985. Phosphate Rock Dissolution in Soil. Indications from plant growth studies. Soil Sci. Society America J. 49:819-925.

AOAC, 1975. Official Methods of Analysis. 12th Ed., Association of Official Analytical Chemists, Washington DC.

Braithwaite, A. C., Eaton, A. C and Groom, P. S., 1989. Some Factors Associated with the Use of the Extractants 2% citric acid and 2% formic acid as Estimators of available P in Fertilizer products. Fertilizer Research. 19:175-181

Bulut, E and Aksoy, A., 2008. Impact of fertilizer usage on phosphorus loads to Lake Uluabat. *Desalination*, 226(1–3): 289–297. doi:10.1016/j.desal.2007.02.112.

Charleston, A. G., Condron, L. M and Brown, I., 1989. The nature of the residual apatites remaining after partial acidulation of phosphate rocks with phosphate acid and sulphuric acids. Fertilizer Research 18:267-273

Fayiga, A. O and Nwoke, O. C., 2016. Phosphate Rock: Origin, Importance, Environmental Impacts and Future Roles. Environmental Reviews. DOI: 10.1139/er-2016-0003.

Food and Agriculture Organization (FAO)., 2004. Use of Phosphate Rock for Sustainable Agriculture. *In* FAO Fertilizer and Plant Nutrition Bulletin. Edited by F. Zapata and R.N. Roy. A Joint Publication of the FAO Land and Water Development Division and International Atomic Energy Agency (IAEA).

Gehrke, C. W., Affsprung, H. E and Lee, Y. C., 1954. Direct Ethylenediaminetetraacetate Titration Methods for Calcium and Magnesium. Anal. Chem. 26:1944.

Giovanni. C., Luigi, S. 1961. Spectrophotometric Determination of Ferric Iron. Anal. Chem., 1961, 33 (4): 579-580. DOI**:** 10.1021/ac 60172a029

Heckenmüller, M., Narita, D and Klepper, G., 2014. Global Availability of Phosphorus and Its Implications for Global Food Supply: An Economic Overview. Kiel Working Paper No. 1897. Kiel Institute for The World Economy, Germany.

Husnain, S. R., Sutriadi, T., Nassair, A and Sarwani, M., 2014. Improvement of Soil Fertility and Crop Production through Direct Application of Phosphate Rock on Maize in Indonesia. Procedia Eng. 83: 336–343.

Ibrahim, S. S., El-Midany, A. A and Boulos, T. R., 2010. Economic Preferences of Mechanical Activation Over Mineral Beneficiation for Phosphate Rock Direct Applications. Physicochem. Probl. Miner. Process. 44: 63–78.

Kiss, E., 1982. Determination of silica in geological materials by atomic absorption spectrometry, *Anal. Chimica Acta*, 140 (1):197-204, http://dx.doi.org/10.1016/S0003-2670(01)95465-0.

Leon, L. A., Fenster, W. E and Hammond, L. L., 1986. Agronomic Potential of Eleven Phosphate Rocks from Brazil, Columbia, Peru, and Venezuela. Soil Sci Am. J 50:798-802.

Mar, S. S and Okazaki, M., 2012. Investigation of Cd Contents in Several Phosphate Rocks Used For the Production of Fertilizer. Microchem. J. 104: 17–21. doi:10.1016/j.microc.2012.03.020.

McGlinchey, D., 2005. Characterisation of bulk solids. CRC Press, USA.

Obaje, S. O., Ojutalayo, A., Ogedengbe, O and Okosun, E. A., 2014. Nigeria's Phosphate and Uranium Mineral Occurrences: Implication for Mineral Investment. J Environ Earth Sci. 4(1): 83-89

Rajan, S., Watkinson, J and Sinclair, A. G., 1997. Phosphate rocks for direct application to soils. Advances in Agronomy 57:77-159

Umunna, A. C and Azubuike, A., 1995. Petrographic qualities, physical properties and polishing qualities of basement rocks in Ado-Ekiti Area, South Western Nigeria. BSc project. University of Ibadan, Nigeria.

Zhang, P., 2014. Comprehensive Recovery and Sustainable Development of Phosphate Resources. *Procedia Eng*. 83: 37–51. doi:10.1016/j.proeng.2014.09.010.