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THERMAL TREATMENT OF PHOSPHOGYPSUM AS A SET RETARDER FOR PORTLAND CEMENT PRODUCTION

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Abstract

Phosphogypsum (PG), the by-product of phosphoric acid industry, comprises of calcium sulfate dihydrate, and other contaminants which restricts the industrial use of phosphogypsum in cement industry as a set retarder. Remedial thermal treatment of phosphogypsum as a set retarder for Portland cement production is investigated in this research work. The SEM-EDS analysis of the raw phosphogypsum sample showed the presence of agglomerates in needle, rhombic and hexagonal shape. The treated PG samples fill and intertwine with each other to form a more compact structure. The XRD pattern of the treated phosphogypsum shows new silica and alumina rich products such as amorphous calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H), including crystalline phases of phosphogypsum dihydrate crystals. The sulphite content of the heated phosphogypsum was 43.64%, which translates to a purity of 93.83 %. The phosphorous content reduced appreciably from 1.05 mg/L to 0.38 mg/L and also the fluoride content reduced from 2.22 mg/L to 1.25 mg/L respectively for the raw and treated PG as shown in table 3.2. The compressive strength of the Portland cement produced was also observed to be higher in the treated condition than the untreated condition, due to the removal of the binding obstruction admixtures by thermal treatment of the PG. The heat of hydration value of 294 kJ/kg obtained is in accordance with ASTM C-150 (2015) and meets the requirement for ordinary Portland cement. In conclusion, the laboratory

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Portland Cement,
Retarder,
Production.

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tests performed in this study indicated that phosphogypsum could serve as a replacement of natural gypsum as a set retarder because thermal treatment of phosphogypsum significantly removed the impurities present successfully.

Introduction

Cement is a hydraulic binder owing to the fact that it is water loving and reacts with water to give its binding property. It solidifies through hydration reactions and sticks to different materials to bind them together like sand and gravel (aggregates) to form concrete, which retains its stability and mechanical strength even under water (Oyenuga, 2014). According to Edwards (2011), cement is one of the key construction materials in use today; it is just behind water as the second most generally utilized material on the planet. Cement isn't typically utilized alone, but instead blended in with sand and rock (aggregate) to bind them together. Little amount of gypsum is added to the crushed clinker during the final milling of the cement manufacturing process to control the setting time for easy workability of the cement produced (Oyenuga, 2014).

Gypsum is a material that is broadly utilized in the cement industry, phosphogypsum (PG) on the other hand is typically not utilized, but is stored indefinitely in the light of the fact that through the wet procedure, some contaminants found in the phosphates rock which incorporates fluoride, sulphate, residual acidity, natural matter, heavy metals, sodium silicofluorides and phosphates becomes amassed in phosphogypsum which limit the compressive strength utilization of phosphogypsum in cement industry as a set retarder (Al-Hwaiti *et al.*, 2013).

Thermal reaction of phosphogypsum containing calcium oxide with bentonite clay can give di-calcium silicates and tri-calcium silicates with perceived binding properties due to the materials binding possibility and properties gotten (Hammas-Nasri, 2016).

Currently, complete use of phosphogypsum resource is the most ideal approach to take care of the issue of phosphogypsum contamination, and the utilization of phosphogypsum binder preparation is the principle bearing of resource reutilization.

MATERIALS AND METHODS

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MATERIALS

The materials and equipment used in the course of carrying out this research work are as follows:

The clinker samples were collected from one of the foremost indigenous cement companies, Obajana Cement Plant Kogi State Nigeria. The bentonite clay was obtained from Iwa/Oyo in Kogi State and the Phosphogypsum was obtained from Dakar, Senegal.



(a) (b)

Plate 2.1 Sample of (a) Raw Phosphogypsum (b) Clinker.



(a) (b)

Plate 2.2 Sample of (a) Heated Phosphogypsum and clay (b) Bentonite Clay

Equipment/Apparatus

XRF/XRD analyzer, oxygen bomb calorimeter, muffle furnace, weighing balance, laboratory test sieves, air-jet sieve shaker machine, electrothermal blast drying oven, jaw crusher, ball mill, thermostatic digital hot plate, conical flask, pH meter, platinum crucible, compacting machine, vicat apparatus, automatic cement compressive/flextural machine, prism moulds, vials, humidity cabinet, curing tank, expansion moulds, expansion moulds.

Sample Preparation

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The clinker samples were collected from one of the foremost indigenous cement companies, Obajana Cement Plant Kogi State. The sample collected was sieved through a 10 mm mesh size and retained on a 5 mm mesh size in order to determine the litre weight. A representative sample was also collected in order to determine the sample composition and the clinker free lime. The high-grade limestone sample also collected from Iwa-Oyo was grounded using a jaw crusher to reduce the size and then milled into fine powder. One gram of the milled sample was taken for loss on ignition (LOI), while 10 g was milled with ethylene glycol pellets and then pressed on a ring for analysis. The Bentonite clay also collected from Iwa-Oyo Kogi State, was dried in an oven at 105 ^{o}C for four hours, after which it was grounded with a jaw crusher and then later milled in a milling machine before being sieved to pass through 850-mesh sieve. The Phosphogypsum sample was obtained from Dakar, Senegal and then packed in plastic bags. The samples were then dried in an electric furnace at 105 °C for at least four hours to constant weight. The PG waste samples were pulverized, homogenized and sieved into particle size ranging between 0.25-0.01 mm, using an automatic vibratory screen. The laboratory cements were made by milling varying quantities of clinker, limestone and phosphogypsum with the aid of a laboratory cement ball mill, till the desired particle size and blain were attained. The cement blend was sieved through 1mm mesh. The samples were then stored in polyethylene bags to prevent hydration.

Methodology

A high temperature furnace (Naberthern 3000) was used to heat the phosphogypsum and bentonite mixture at varying temperatures (up to 1000 ^{o}C), at a heating rate of 10 °C/min for one hour. X-ray fluorescence (XRF) and X-ray diffractometer (XRD) analyses were performed on the samples using ARL 9900 XRF spectrometer (USA), operating mode: U=50 kV, I=50 mA). Scanning Electron Microscope SEM/EDS analysis was also carried out to determine the microstructural composition of the samples. Measurements of flexural and compressive strength were conducted by using conventional resistance measurement instruments according to the NIS 444-1:2003. The thermodynamic heat of hydration (HOH) was then determined by mixing 60 g of cement sample and 24 ml of distilled water by hand for 4 minutes and then filled into 3 glass specimen tubes/vials and sealed with wax and corked, prior to the determination of the thermodynamic heat of hydration.

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RESULTS AND DISCUSSION OF RESULTS

Sulphite Content of the Gypsum Sample

The mean sulphite content of the treated phosphogypsum was 43.64 %, which translates to a purity of 93.83 %. The sulphite content of gypsum is related directly to its purity; high sulphite content shows high purity. The percentage purity of the phosphogypsum was calculated to be 93.83 % indicating high gypsum purity, since gypsum having more than 80% sulphite content in $CaSO_4.2H_2O$ is considered suitable for maintaining SO_3 in cement manufacture (Singh, 2003).

XRF Analysis of Samples

XRF analysis of the clinker sample

Table 3.1 shows the bentonite clay compositions as well as the parent clinker sample compositions, which was characterized in terms of chemical and mineralogical properties.

Table 3.1: XRF Analysis of the Clinker Composition.

Chemical composition		Mineral composition	
Chemical content	**% Content**	**Mineral content**	**% Content**
SiO_2	21.09 ±0.06	C_3S	65.75
Al_2O_3	5.50 ±0.02	C_2S	13.81
Fe_2O_3	3.65 ±0.02	C_3A	8.81
CaO	65.17 ±0.04	C_4AF	11.63
SO_3 **MgO** **K_2O**	0.63 ±0.01 1.10 0.30	Litre Weight (g/L)	1260±0.58
Na_2O **Free lime**	0.02 1.35 ±0.01	-	-
LOI	1.19 ±0.02	-	-

Table 3.1 indicated that the clinker is good for high quality Portland cement. The free lime content of 1.35 % indicates that there was proper reaction of lime with the oxides to form the mineral compounds.

XRF analysis of the clay sample

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The bentonite clay used in the course of carrying out this experiment is analyzed using XRF equipment and the composition of the bentonite clay is presented in Table 3.2.

Table 3.2: XRF analysis of the Bentonite clay

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	MnO	K_2O	LOI
Weight (%)	67.82	12.88	10.64	0.36	1.50	0.15	0.14	0.15	6.36

The silica content of the clay was 67.82%, The clay composition was more of a bentonite material as it had higher silica to alumina ratio of 2:1 as shown in table 3.2 (Rodriguez *et al*., 2015).
The results of the PG samples are compared with extreme amounts of different elements in a general phosphogypsum sample as shown in figure 3.3 (Singh, 2002).

Table 3.3: Main Chemical Components of the raw and treated PG

Constituents (wt. %)	Raw PG	Treated PG	Phosphogypsum Min - Max
CaO	44.90	46.28	28 - 45
SO_3	43.64	44.63	39 - 47
SiO_2	5.65	5.82	0.5 – 6.0
P_2o_5	1.05	0.38	0.05 – 1.4
K_2o	1.52	0.68	0.01 – 0.80
Al_2O_3	0.65	0.80	0.02 – 0.85
MgO	0.37	0.36	0.05 – 0.40
F	2.22	1.05	$\leq$ 1.5

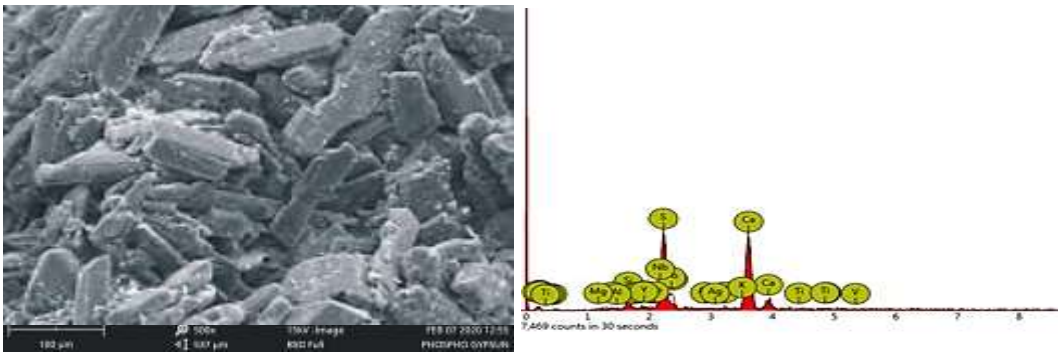
IS: 12679-1989

The chemical composition of the raw and treated PG is shown in table 3.3, it can be seen that the treated PG complies with the requirements given in IS: 12679-1989, specification for gypsum use in plaster, concrete, blocks and boards. The analytical results showed a better removal of P_2O_5 and fluorine than that obtained by raw PG (Van-Der-Merwe and Strydom, 2004).

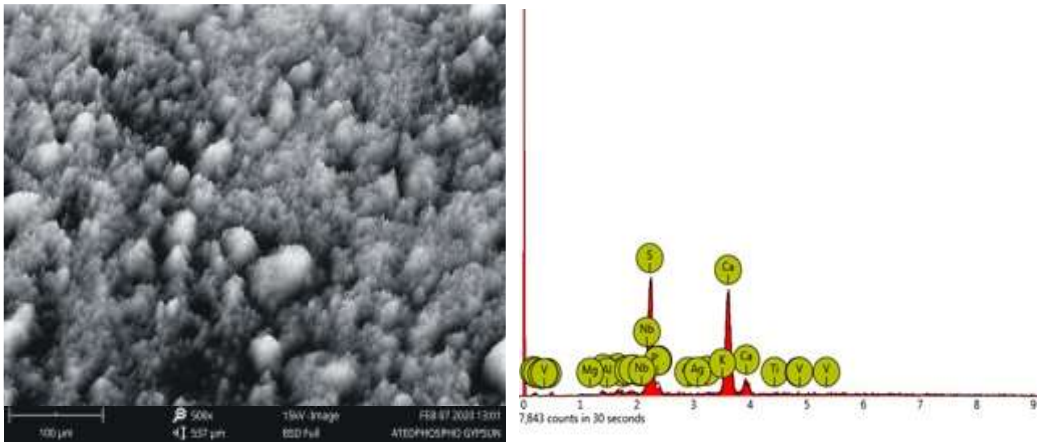
Microstructural and Chemical Analysis (SEM/EDS)

The morphology using SEM/EDS image analysis coupled with EDS atomic composition of the raw phosphogypsum particles is presented in figure 3.1.

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(a)



(b)

Figure 3.1: SEM micrograph of (a) Raw Phosphogypsum (b) Treated Phosphogypsum

The SEM-EDS analysis of the raw phosphogypsum sample showed the presence of agglomerates in tabular form and other in hexagonal form as shown in figure 3.1. Its semi quantitative composition analyzed by SEM-EDS showed high contents of Ca, S, O and impurities such as P, Si, Na and F (Bennis *et al*., 2010). The treated PG samples fill and intertwine with each other to form a more compact structure a more compact structure with a mean particle size of 2,980.3 µm.

X-Ray Diffraction Pattern of the Samples

X-Ray Diffraction Pattern of the Clinker Sample

The clinker sample was analyzed through X-ray diffraction (XRD) to determine their crystalline composition (Waseda et al., 2011).

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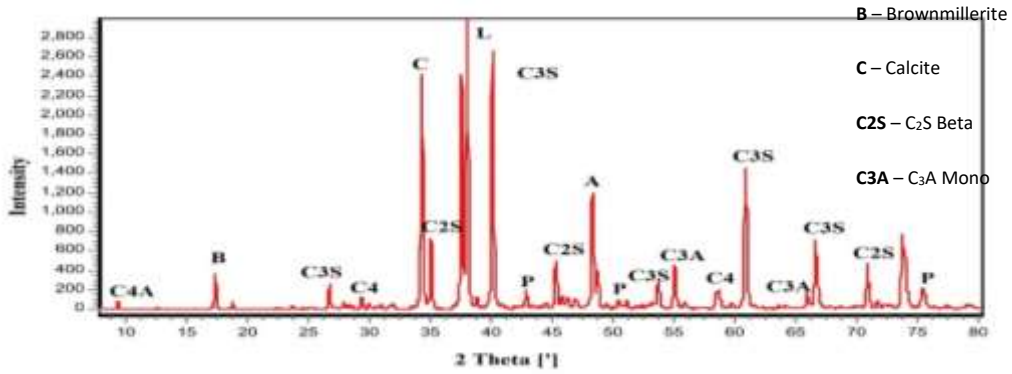


Figure 3.2: XRD analysis of clinker sample

In figure 3.2 the peaks of the clinker sample can be clearly observed and this shows the liquid phases of the X-ray diffraction pattern analysis; alite (tricalcium silicate) C_3S, belite (dicalcium silicate) C_2S, tricalciumaluminate C_3A, and tetracalcium aluminoferrite C_4AF. This result indicates that the liquid phases C_3S, C_2S, C_3A, and C_4AF contents lies within the range recommended by the European standards specifications for ordinary Portland cement purposes (Waseda *et al*., 2011).

X-Ray Diffraction Pattern of the Phosphogypsum Sample

The peaks of the raw phosphogypsum in Figure 3.3 were identified to be mainly gypsum ($CaSO_4.2H_2O$), which crystallizes in the monoclinic system as space group with the coexistence of other impurity phases.

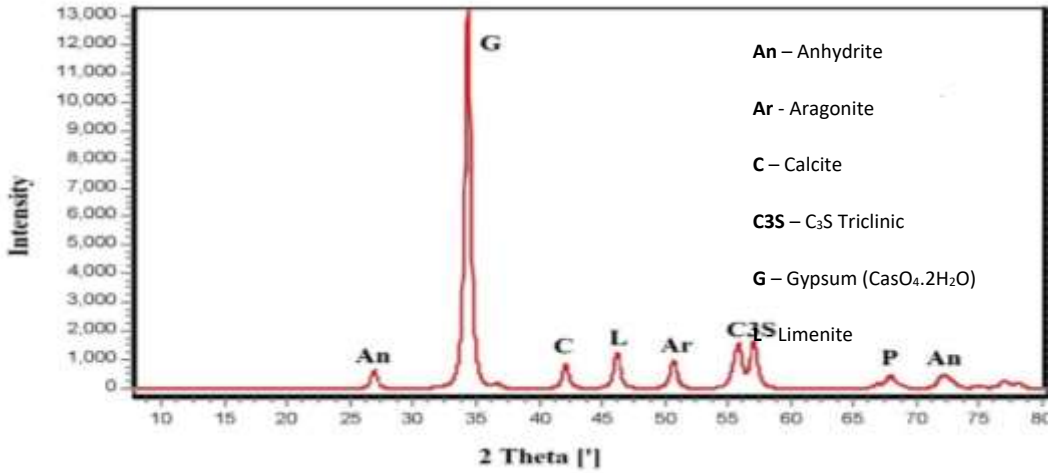


Figure 3.3: XRD Analysis of the heated Phosphogypsum

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The XRD pattern of the treated phosphogypsum shows new silica and alumina rich products such as amorphous calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H), including crystalline phases of phosphogypsum dihydrate gypsum crystals. All the diffraction peaks displayed in the XRD pattern were easily indexed to pure hexagonal and rhomboid structure according to Joint Committee on Powdered Diffraction Standard (JCPDS) card for gypsum (JCPDS:09-0432). The flat line of 2θ ranging from 10-30^0 signifies crystalline phases (Leon-Rena *et al*., 2009).

The compressive strength of the cement produced using thermally treated PG as compared with National Industrial Standards (NIS) is presented in Table 3.5. The Compressive strengths of treated PG at 2 days, 7days and 28 days have adequate strength for ordinary Portland cement (OPC) applications. Thermal treatment of phosphogypsum and integration of bentonite clay conforms and meets the requirements obtained in Nigeria Industrial standard (NIS 446:2003).

Table 3.5: Compressive Strength of the Standard Cement using Ordinary Gypsum and PG Portland Cement Produced.

COMPRESIVE STRENGTH (MPa)						
	NIS Standard Requirement for Ordinary Gypsum Portland Cement			**Experimental Values obtained for Heated Phosphogypsum Portland Cement**		
Product	**2D**	**7D**	**28D**	**2D**	**7D**	**28D**
CEM I (52.5)	≥ 20	≥ 44	≥ 52.5	27.5	48.5	63.5
CEM II (42.5)	≥ 20	≥ 33	≥ 42.5	25.8	35.8	46.0

These results were confirmed and fulfilled the requirement with the specification of OPC obtained in Nigeria Industrial standard (NIS 446:2003).

CONCLUSION

The heat treatment of phosphogypsum allows for the inertisation of impurities and also the production of anhydrite which has a wide application in the manufacturing of cement. Several treatments methods have been considered by several authors and thermal treatment of phosphogypsum has been found to have fewer impurities than the other treatment methods. Thermal treatment of

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phosphogypsum to temperatures over six hundred degrees centigrade results to the deterioration and expulsion of the admixtures that may obstruct the compressive strength development or create delayed setback for the setting time of the Portland cement produced (Hammas-Nasri, 2016).

In this study, the laboratory results obtained shows that the pH analysis of the value of phosphogypsum saturated solution samples increased, as a result of decomposition of the heated product.

As shown in Figure 3.1, SEM-EDS examination of the raw phosphogypsum sample revealed the existence of aggregates in tabular and hexagonal shapes. The treated PG samples fill and intertwine with each other to form a more compact structure. The XRD pattern of the treated phosphogypsum in Figure 3.3 shows new silica and alumina rich products such as amorphous calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H), including crystalline phases of phosphogypsum dihydrate crystals.

The sulphite content of the heated phosphogypsum was 43.64%, which translates to a purity of 93.83 % also, the free lime content of 1.35 % indicated that there was proper reaction of lime with the oxides to form the mineral compounds as shown in Table 3.1. The phosphorous and fluoride content reduced appreciably from 1.05 mg/L to 0.38 mg/L and 2.22 mg/L to 1.05 mg/L respectively for the raw and treated PG respectively as shown in Table 3.3. The compressive strength of the Portland cement produced was also found to be higher than in the treated state, due to the removal of the binding obstruction admixtures by thermal treatment of the PGC.

In conclusion, the laboratory tests performed in this study indicated that thermal treatment of phosphogypsum significantly removed the impurities present effectively, allowing it to be used as a replacement of natural gypsum in the manufacturing of Portland cement.

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