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EFFECT OF SUBSTITUTION OF NATURAL GYPSUM WITH SYNTHETIC GYPSUM PRODUCED FROM CEMENT KILN DUST ON THE PHYSICO-CHEMICAL PROPERTIES OF ORDINARY PORTLAND CEMENT.

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ABSTRACT

This study was designed to investigate the effect of using synthetic gypsum on the properties of cement instead of he conventional natural gypsum being used by cement industries. Synthetic gypsum which was chemically roduced from precipitation reaction between cement kiln dust and sulfuric acid was ground together with clinker at % ($^w/_w$) using laboratory-scale ball mill to produce Ordinary Portland Cement. The chemical and physical roperties of the cement were compared with similar cement produced with natural gypsum. The results showed lightly higher figures for most of the parameters and increased mechanical strength development over a 28-day eriod for cement with synthetic gypsum compared with that of natural gypsum.

Key words: synthetic, natural, gypsum, cement and pollution.

Introduction

Gypsum is an essential raw material in Ordinary Portland Cement (OPC) production and is required up to 3-5% by weight during finish grinding in order to retard or control the setting time of OPC. It has however been reported that the addition of gypsum does not only control the setting time but also influence some other properties of OPC (1).

Synthetic Gypsum (SG) is a chemically produced gypsum and has identical chemical composition with Natural Gypsum (NG) i.e $CaSO_4.2H_2O$. The consumption of SG has since the late 1990s started to rise sharply especially in Europe and North America. The rise is expected to continue due to introduction of environmental legislation in the 1980s and the rising cost of disposal of combustion products(2). SG have been produced by various methods (3,4).However, Key and Jerry (5) described a method for treating raw or modified Cement Kiln Dust (CKD) using waste or by-product sulphuric acid solution to form gypsum product according to the equation: $H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4.2H_2O + CO_2$.

Cement kiln dust (CKD) is a waste residue generated as a by product of the manufacture of OPC. It is collected from cement kilns by dust control devices such as electrostatic precipitators or air pollution control devices. The main component of CKD is calcium carbonate ($CaCO_3$), which can be as high as 85% by weight but also contains sulphates, alkalioxides, silicondioxides, clinker compounds (principally as silicates) and heavy metals(5). CKD have been known to constitute environmental and health hazards. Fugitive dust from CKD contributes to particulate matter in the air which is a respiratory hazard. Prolonged or repeated inhalation of respirable crystalline silica from CKD can cause silicosis which is a fatal lung disease(6).Long term exposure to CKD may result in lung cancer, damage to liver, kidney and gastric systems(7).CKD also negatively impact on vegetation. The accumulation and toxicity of CKD on vegetation causes significant decrease in photosynthesis resulting in decreased growth rates, diversity and production(8,9).The washing off of CKD into surrounding water ways or the settling of air borne dust into water increases the level of sedimentation in river/waterways which may cause increase in levels of pH, hardness and silica in the water. It can also cause depletion of oxygen, increase in biological oxygen demand, eutrophication, and water temperature. All these makes aquatic life difficult and decreases species richness and diversity. The sedimentation also cause the water ways to become shallow thus reducing navigation. Therefore, the use of CKD in producing gypsum which can be utilized in OPC production would eliminate the health and environmental hazards posed by this substance if disposed into the environment and also save natural resources through recovery of a NG substitute.

MATERIALS AND METHODS

Samples and sampling: Cement kiln dust (CKD), clinker and NG samples were obtained from Shagamu Works of West Africa Portland Cement (WAPCO) plc. Samples of CKD were obtained from the discharge outlet of Electrostatic precipitator over a period of 72 hours at 6 hours interval. From these, representative sample was collected using standard sampling method. (10). Fresh clinker from the kiln was similarly sampled, while NG was sampled from the stock pile by standard sampling method (10).

Synthetic gypsum(SG) was produced from cement kiln dust (CKD) and sulphuric acid according to the method described by Key and Jerry(5).

Chemical Analysis:

Chemical analysis of CKD, Clinker, NG and SG to determine elemental oxides content was carried out by Wavelength Dispersive X–ray Fluorescence Spectrometry using the Oxford QX Spectrometer. Sample for X-ray analysis were prepared and pressed into pellets according to the procedure described by Robson (11). Price and Platt (12), Brady and Price (13). The spectrometer was first calibrated with standards having concentration range of interest. A mixture of helium and methane gas was used to flush the air between the sample and the detector to improve detection.

The residue and volatile component (loss on ignition) were determined by standard method. (10). Free CaO in Clinker was determined according to the method of NIS CBD/95 part 2 (10).

Production of cement:

Cement was produced by grinding clinker together with gypsum in a laboratory-scale ball mill. The mill driven by an electric motor powered by a 415V source was charged with 50mm, 30mm and 25mm grinding media balls to about one-third volume loading in the following weight proportion: 4.6kg, 2.9kg and 2.5kg respectively. Clinker sample from the kiln was charged into the mill together with 5% gypsum (S.G first and then N.G) and ground for a residence period of one hour. The mill was discharged and the ground cement packed into a clean, covered and labeled plastic container.

Chemical Analysis of Cement:

Elemental oxides content of the cement sample were determined using XRF spectrometry as done for chemical analysis of CKD, clinker, N.G and S.G. Free CaO, LOI, and Residue were similarly determined by standard method. (10).

Physical Tests:

Blaine's air permeability method was employed to determine the fineness of the cement while initial and final setting times were determined using the Vicat apparatus. Lechatelier method was employed to determine the soundness of the cement samples. All determinations including the compressive and the flexural strength were carried out according to standard test method described in the Nigerian Industrial Standard NIS CBD 3/95 (14).

RESULTS

Table 1: Result of chemical analysis of cement kiln dust (CKD) and clinker

Parameter	CKD (%)	Clinker (%)
CaO	43.96	64.58
S_1O_2	14.93	21.14
Al_2O_3	3.96	5.21
Fe_2O_3	2.11	3.51
M_gO	1.41	1.56
Na_2O	0.48	0.21
K_2O	0.42	0.31
SO_3	0.17	1.04
Free CaO	ND	0.67
Insoluble Residue	1.50	1.03
Volatile Component	30.18	0.71
Others	0.88	0.03

Comparison of the chemical properties of NG and SG are as contained in table 2.

Table 2: Result of analysis of natural gypsum and synthetic gypsum

Parameter (%)	Natural gypsum	Synthetic gypsum (%)
C_aO	28.54	27.87
S_iO_2	2.19	10.94
Al_2O_3	0.56	0.95
Fe_2O_3	0.33	0.54
M_gO	0.47	0.54
Na_2O	0.01	0.17
K_2O	0.01	0.08
SO_3	36.24	46.45
Insoluble Residue	1.20	3.68
Volatile Component (loss on ignition)	30.12	8.23
Others	0.33	0.55
Purity	77.91	99.87
Yield	–	76.88

The comparison of the chemical properties of cement produced with natural gypsum (NGC) and cement. produced with synthetic gypsum is as contained in table 3.

Table 3: Result of chemical analysis of cement produced with natural gypsum (NGC) and cement produced with synthetic gypsum (SGC).

Parameter	Cement with 5% natural gypsum	Cement with 5% synthetic gypsum
Total CaO	63.09	63.06
S_i0_2	21.52	21.69
Al_2O_3	4.78	4.63
Fe_2O_3	3.32	3.38
M_gO	1.48	1.54
Free CaO	0.53	0.30
SO_3	2.63	2.83
Na_2O	0.08	0.10
K_2O	0.14	0.15
Cl	0.02	0.02
Volatile component (Loss on Ignition)	1.24	0.90
Insoluble Residue	1.16	1.20
Others	0.25	0.20

The result of physical properties of cement produced with natural gypsum (NGC) and cement produced with synthetic gypsum (SGC) is contained in table 4

Table 4: Result of physical properties of NGC and SGC.

Parameter	NGC.	SGC.
Fineness (m^2/kg)	308	322
Initial Setting time (mins)	220	180
Final Setting time (mins)	316	270
Expansion (mm)	2.0	1.0
Compressive Strength (MN/m^2) :		
1 day (accelerated) strength	5.50	12.59
3 day strength	12.22	20.21
7 day strength	27.26	37.41
28 day strength	37.96	51.24

DISCUSSION.

From table 2, it could be seen that apart from S_1O_2 and SO_3 the two exhibit similar content in other components with SG having slightly higher figures. The high value of S_1O_2 in SG is due to the effect of silicious material such as shale, clay or red alluvium incorporated in the raw meal as kiln feed from which kiln dust was obtained. The purity of SG is almost absolute which could be ascribed to the fact that it was produced from stoichiometric equivalent of reactants unlike NG which has some natural and artificial impurities like calcite and shale embedded in it. This is reflected in the percentage SO_3 and volatile component content of each .The yield of SG could have been more but the strong effervescence due to evolution of CO_2 accompanying the highly exothermic reaction in which enormous heat was generated adversely affected the yield due to loss of product.

Table 3 shows the comparison of the chemical properties of cement produced with natural gypsum (NGC) and cement produced with synthetic gypsum (SGC). Almost all the parameters recorded higher values for SGC. This could be attributed to the presence of these components in the raw meal from which kiln dust was obtained before sintering in the kiln. NGC contains higher total CaO than SGC. This could be ascribed to the inherent CaO content in NG due to presence of impurities like calcite which makes the gypsum richer in CaO.. This also explains the higher figure of free CaO and volatile component in NGC.

From table 4, it would be observed that better communition of cement was achieved with SG than with NG as shown by the fineness i.e. specific surface area recorded in the table. This could be due to the softer nature of the SG. Since the residence time in the mill was the same in both cases, it thus implied that energy consumption in kw/h can be reduced using SG to grind to predetermined surface area. Similarly, residence time in the mill can be reduced thus leading to increase out put if SG is used. Also other properties of cement which are dependent or influenced by specific surface area/fineness are enhanced by SG in cement grinding. For instance, cement with SG will react more readily and faster with water in the hydration process thus accelerating setting. This can be seen in the figures for both initial and final setting time which are lower for SGC than NGC. Increase in shrinkage, and improvement of workability of cement is also enhanced.

Both the initial and final setting time for SGC are lower than that of NGC because the process of hydration in SGC is faster (owing to increase in specific surface area) than NGC.

Setting of cement is brought about by the hydration of tricalcium silicate (C_3A) according to the following reaction;

$$3CaO.\ Al_2O_3 + 6H_2O \longrightarrow 3CaO.\ Al_2O_3.6H_2O \quad (1)$$

Similarly, when $Ca(OH)_2$ is present in cement, C_3A hydrates according to the equation ;

$$3CaO.Al_2O_3 + Ca(OH)_2 + 12H_2O \longrightarrow 4CaO.\ Al_2O_3.13H_2O \quad (2)$$

However these two reactions would cause rapid setting of the cement paste. But in the presence of sulphate in the form of gypsum, the reaction proceeds as follows :

$$3CaO.Al_2O_3 + 3(CaSO_4.\ 2H_2O) + 26H_2O \longrightarrow 3CaO.Al_2O_3.\ 3CaSO_4.\ 32HO_2 \quad (3)$$

$$C_3A + 3(CS.2H) + 26H \longrightarrow C_3A.3Cs.32H$$

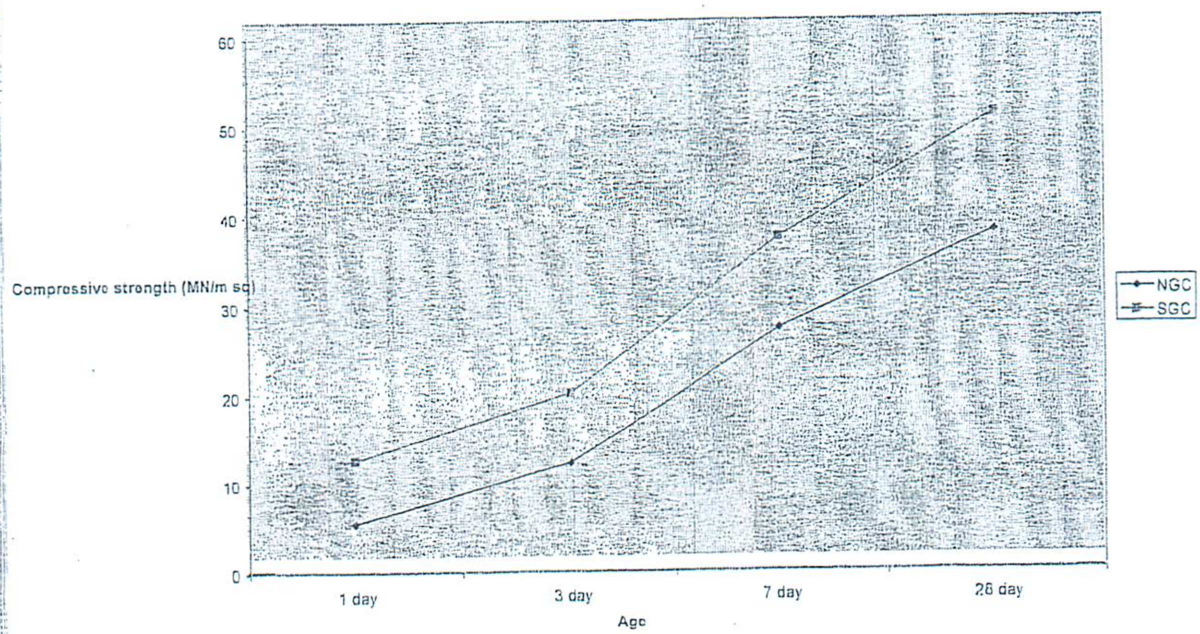
Aluminate gypsum water ⟶ ettringite

The ettringite ($C_3A.3Cs.32H$) formed in the reaction 3 is deposited as a thin film on the surface of the cement particles within the first few hours of hydration and thus prevent the setting of the cement paste until when it later forms long needle – shaped crystals which bridge the water – filled spaces between the cement particles and enmesh the particles. At this point, the process of setting begins. Initial set corresponds to a rapid rise in temperature and the final set occurs when the paste attains the peak temperature.

Hydration reactions are known to be exothermic in nature, and this have been found to be useful in promoting early strength of cement. Bareja indicated that an average of 120 Cal/g of heat is evolved during hydration of cement (15). SGC produces a higher heat of hydration which has been found to be useful in promoting early strength of cement. SGC also exhibits better soundness than NGC as indicated by the figures in table 4. This is further confirmed by free CaO concentration in the cement as shown in table 3. Unsoundness (expansion) in cement has been shown to be largely due to free CaO (16).

Mechanical strength of cement is the prime requirement for its structural use. The mechanical strength development of SGC and NGC is as shown in figure 1.

FIGURE 1: Mechanical strength development of NGC and SGC (Compressive strength (MN/m sq) vs Rate of hydration)



SGC exhibited higher early and later strength development than the NGC as shown by the figures for 1day (accelerated) and 28–day compressive strength. This finding is corroborated by the values of C_3S (figure 2) which has been widely reported to be responsible for early strength development of cement (17, 18, 19).

During hydration of cement, C_3S reacts with water to form calcium silicate hydrate (CSH phases) in which $Ca(OH)_2$ is split off according to the following reaction equation:

$6(3CaO.SiO_2)+18H_2O \rightarrow 5CaO.6SiO_2.5H_2O + 13Ca(OH)_2$ (4)

$6C_3S + 18H \longrightarrow C_5S_6H_5 + 13\ CH$.

The calcium silicate hydrate crystals formed are the principal strength – giving constituents of the hardened cement paste. This strength is attributable to the co-operation of powerful electrostatic forces of attraction between the small, hydrate phases. The $Ca(OH)_2$ formed according to equation 4 reaches its peak after 19 hours (20) and produces a strongly basic environment (pH>12) in the freshly hardened mortar and concrete. This high pH value inhibits the corrosion of embedded steel and is indeed what makes reinforced concrete such durable materials in which the reinforcing bars are normally and lastingly protected by the concrete.

The wide gap in the dicalcium silicate (C_2S) between the NGC and SGC (figure 2) can be adduced to the reason for the big difference in the latter strength of the two. C_2S which hydrates slowly evolve low heat of hydration and is known to be responsible for the latter strength of cement. Although both SGC and NGC showed progressive flexural strength, SGC was found to be higher in the early days (1-3day) than NGC while the trend was reversed in the latter days of the cement mortar. More investigations need to be carried out to explain the reasons for this.

FIGURE 2: Comparison of the Alite, Belite, Aluminate and Ferrite phases in NGC and SGC

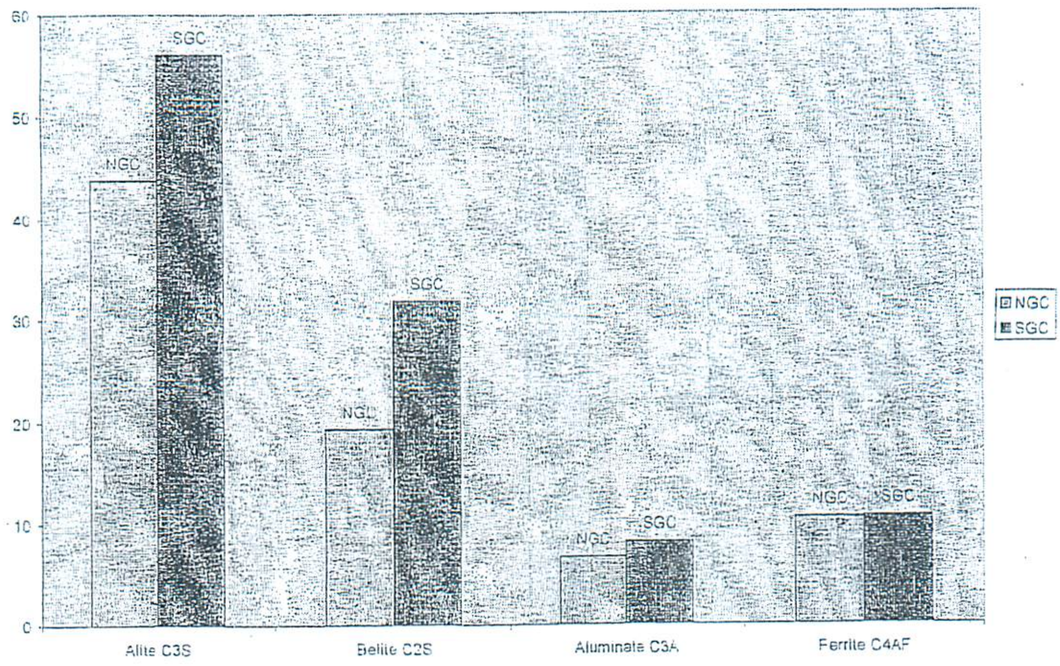
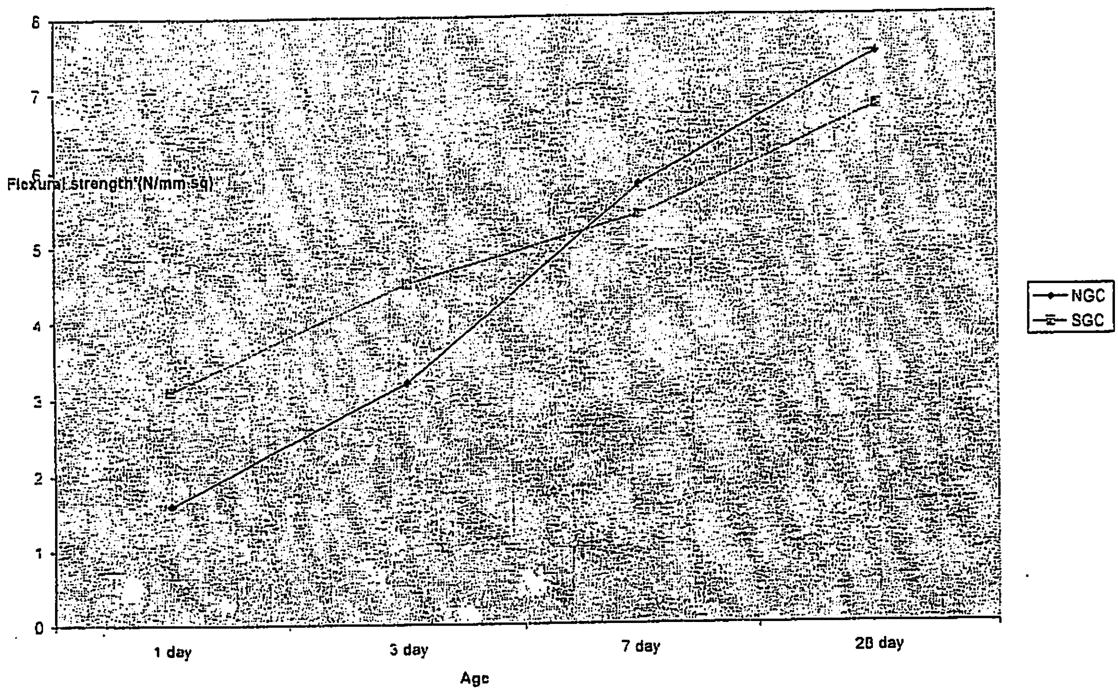


FIGURE 3: Flexural strength development of NGC and SGC



CONCLUSION

From the results above it can be seen that synthetic gypsum,(produced by precipitation reaction between cement kiln dust and sulphuric acid) can be suitably substituted for natural gypsum in cement production.

The use of synthetic gypsum from cement kiln dust enhances optimum use of raw materials and process optimization in cement production. Increase out put, lower cost of production can also be achieved with synthetic gypsum.More importantly using synthetic gypsum from cement kiln dust will reduce environmental pollution and hazards as heaps of hazardous kiln dust that would have been dumped into the environment is recycled back into production system.

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REFERENCES:

1. Sillo C.E. and Okumenogu, C.A. (1994), Adoka gypsum and its suitability for cement production, Journal of Mining and Geology, vol. 30 (2), 169-173
2. Anonymous, (2004), sharprise in synthetic gypsum consumption, http: //www. the – infoshop. com. accessed 4/14/2004.
3. Kikkawa, A. (1998), United State Patent, No 5,788, 944.
4. Krofchak, A. (2001) United State Patent, No 6, 231,767.
5. Key, Jr. and Jerry F. (2003), United State Patent No 6,613,141.
6. Lafarge-North America,(2008),Material safety data sheet-cement kiln dust, hazard identification, 2.
7. Kimbrough, D.E, Cohen y, Winer A.M., Creelman, L. and Mavuni, C., (1999), A critical assessment of chromium in the environment; critical reviews in environmental science and technology. 29(1), 1-46.
8. Hegazy, A.K, (1996), Effects of cement kiln dust pollution on the vegetation and seed bank species diversity in the eastern desert of Egypt, Environmental Conservation,23(3):249-258.
9. Iqbal, M.Z, Shafiq,M.(1998), Toxicity of cement dust on the growth of some tree seedlings, Ekologia-Bratislava, 17(4):434-439.
10. Standards Organization of Nigeria (1995), Nigerian Industrial Standard: Standard Test Methods for properties of cement (part 2), 1-2.
11. Neal S. Robson (1991), Future trend of XRF in the cement industry, world cement, 22(4), 2-3.
12. Price B. and Platt P. (1990), Decentralized analysis in cement making quality control; world cement, 21(7), 2-3.
13. Brady M.A and Price B.J. (1992), The rapid analysis of cement to ASTM: C -114; world cement 23(8), 2.
14. Standards Organization of Nigeria (1995), Nigerian Industrial Standard: Standard Test Methods for properties of cement (part 1 Tests for physical characteristics), 1-14.
15. Bareja, S.K. (1997), Quality control in cement manufacture and Physical Testing; Progress in cement and concrete-Testing and Quality control in cement Industry. Vol.3, 30.
16. Knofel D. (1983), Cement Chemistry – Cement Quality, Cement Engineers Hand book, 141.
17. Bentur, A. (1976), Effect of Gypsum on the Hydration and Strength of C_3S pastes, J. Am. Ceram. Soc. vol., 59, No5- 6 (may-June), 210-213.
18. Menetrier, D., Jawed, I. and Skalny, J. (1980), Effect of gypsum on C_3S Hydration, Cem. Concr. Res, 10(5), 697-701.
19. Odler, I. (1981), Interaction between gypsum and the C-S-H phase formed in C_3S Hydration, Proc. 7th Int. Cong. Chem. Cem., 4, 493-495.
20. Kim, N., UM, W. Lee, H., Lee, I. (2000), 'Interaction between Gypsum and C-S-H phase in C_3S hydration using ESCA, Cem. Concr. Res., 19, 8.