UJEAS

UNIZIK JOURNAL OF ENGINEERING AND APPLIED SCIENCES

UNIZIK Journal of Engineering and Applied Sciences 2(3), December (2023), 368-375
Journal homepage: https://journals.unizik.edu.ng/index.php/ujeas
PRINT ISSN: 2992-4383 || ONLINE ISSN: 2992-4391

Effects of Percentage Composition of Essential Chemicals in Portland Limestone Cement on the Strength and Workability of Concrete.

Aginam, C. H[1*], Onodagu, P. D[2] and Obi, O. K[3]
[1]Department of Civil Engineering, Nnamdi Azikiwe University Awka, Anambra Nigeria.
[2]Department of Civil Engineering, Nnamdi Azikiwe University Awka, Anambra Nigeria.
[3]Department of Civil Engineering, Nnamdi Azikiwe University Awka, Anambra Nigeria.
[*]Corresponding Author's E-mail: Kin.obi@stu.unizik.edu.ng

Abstract
This paper investigates the effects of percentage composition of essential chemicals in Portland limestone cements on the strength and workability of concrete. Three samples of Portland limestone cements, produced by different manufacturers that sourced their raw materials from different locations were used in this study. The samples were labeled Sample A, Sample B and Samples C. They were classified as CEM II, grade 42.5N in conformity with BS EN 197-1 (2011) and ASTM C150 (2019). Properties of concrete materials like chemical composition, sieve analysis, specific gravity and fineness tests were investigated. An X-ray fluorescence test was conducted on the three samples of Portland limestone cements. Workability and compressive strength tests were also carried out on concrete samples. The results revealed a variation in the chemical composition of the three samples. For the key chemical components, SiO_2, (A=8.694, B=12.418, C=9.516), for Al_2O_3, (A=5.042, B=5.945, C=9.516), for Fe_2O_3, (A=3.676, B=3.735, C=2.836), for CaO, (A=77.171, B=70.326, C=74.178) and SO_3, (A=3.385, B=2.396, C=3.124). This variation in the chemical composition was found to be from different limestone sources, other raw materials and manufacturing process. These variations impacted the performance of the concrete as samples with higher SiO_3, Al_2O_3, and Fe_2O_3 gave higher strength. Moderate CaO and low MgO exhibited high slump values and compressive strength. However, all the samples gave desirable consistency and strength. The average of three cubes cured for 7, 14, 21 and 28days was tested for compressive strength. Sample B, due to its higher Silica Oxide, Alumina Oxide, and Iron oxide content gave higher values of $15.17N/mm^2$, $24.40N/mm^2$, $29.43N/mm^2$ and $34.07N/mm^2$ for strength at 7, 14, 21 and 28days. Sample A gave $13.40N/mm^2$, $23.03N/mm^2$, $28.33N/mm^2$ and $32.33N/mm^2$ for 7, 14, 21 and 28days. Sample C gave $14.67N/mm^2$, $22.57N/mm^2$, $26.93N/mm^2$ and $31.3N/mm^2$ for 7, 14, 21 and 28days.

Keywords: Portland limestone cement, chemical composition, X-ray fluorescence test, workability, Strength.

1.0 Introduction

Portland limestone cement is a type of cement that has higher percentage of limestone as a partial replacement for clinker in its composition. It is a very important construction material that can be used alongside aggregates and water in producing concrete (Obi and Adinna, 2023). The use of Portland Limestone cement in the construction industry has helped in addressing the issue of poor durability of infrastructures such as homes, offices, highways and bridges. Also, the reduced amount of clinker in the production of Portland limestone cement is of great benefit to the environment as it mitigates the emission of carbon dioxide (CO_2) into the environment (Ikumapayi and Alamu, 2022). There is a problem of inconsistency of Portland limestone cement quality from numerous manufacturers resulting to different properties and performance of cement in concrete. Poor understanding on how different brands of Portland limestone cements with varying chemical compositions impact the workability and strength of concrete have resulted to structural failures, loss of lives and investments. This is due to the fact that some Portland limestone cements do not meet the standard requirement for some projects (Bamigboye et al., 2015). There is need to identify the properties and chemical compositions of cements to know their suitability in various construction works.

Many manufacturers of Portland limestone cements source their raw materials from different locations (Dinh and Truong, 2022). Limestone is readily available near cement factories and all geological formation containing calcium carbonate can be used to make Portland limestone cement (Tyopine, 2014). The compositions and concentration of raw materials particularly limestone in different locations vary and may have some impurities which may eventually find their way into the production process Araromi et al., (2015), there by impacting the properties of concrete. There is need to maintain and regulate the percentage composition of essential chemicals in Portland limestone cements through frequent monitoring by regulatory authorities. This paper therefore seek to solve the problem of inadequate knowledge and research information in this area of research as comprehensive studies that systematically analyse the relationship between percentage composition of essential chemicals in Portland limestone cement and properties of concrete will be provided creating a base for further research in this area to guide engineers in making decisions of which cement qualities to use for specific purpose.

2.0 Literature Review

After carrying out a comprehensive literature review on Portland limestone cement and Portland cement, Marvillet and Benboudjema, (2019) concluded that Portland limestone cement exhibits similar and sometimes superior early-age strength, durable and improved resistance to chloride-induced corrosion compared to Portland cement. This is due to the chemical composition of limestone used to replace clinker in Portland limestone cement. In a review on some common Portland limestone cements of grade 42.5, Araromi et al., (2015) concluded that the samples in their review had similar compositions even though some variations were observed. They pointed out some limitations in the investigation. The main limitation was the use of traditional techniques instead of spectrometry methods like X-ray fluorescence method which has high level of precision and accuracy. BS EN 197-1 (2011) specifies the chemical composition of Portland limestone cement to primarily consist of CaO, SiO_2, Al_2O_3 and Fe_2O_3 with minor amount of Na_2O, K_2O and MgO coming from clay fraction of raw materials and SO_3 from gypsum. A data science analysis was conducted from the literature results of physicochemical characterization of Portland limestone cements by Chaves et al., (2023). Their analysis included various physicochemical variables such as the percentage by mass of different oxides like CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, SO_3, Na_2O, K_2O and TiO_2. The main objectives of their study was to evaluate the information provided on cement characterization results from different publications. In their results, they discovered that the main oxides CaO and SiO_2, which made up approximately 85% of the cements mass, showed low variability among the literature data of different brands, indicating a certain standardization of these compounds in cement production. However, other oxides such as Na_2O, MgO, CaO, K_2O and Na_2O exhibited higher dispersion and variability.

Some brands of Portland limestone cements are more susceptible to cracks as a result of their chemical compositions. These brands are often neglected in preference to others. Abdulhakeem (2023) carried out an investigation on the physicochemical and strength assessment of six Portland limestone cements in Nigeria which includes; Dangote, BUA, Lafarge Supaset, Sokoto, Ashaka and UniCem. He carried out different tests on concrete materials including chemical oxide composition and mineralogical properties among others to determine their suitability for construction purposes in line with standard specifications. In his results for XRF analysis, CaO, the main compound that gives strength was low in UniCem 62.02% hence its lower compressive strength of 28.35N/mm^2, 43.17N/mm^2 at 7 and 28days. Dangote cement has the highest percentage composition of CaO 64.96%, SiO_2 21.98% hence the reason it gave the highest compressive strength of 31.53N/mm^2, 48.02N/mm^2 for 7 and 28days curing. BUA and Supaset followed in that other. In general, the six Portland limestone cement samples contain similar oxides compositions and are in close proportions across the samples. He concluded that the choice of cement strength class for any construction type interdepends on the physical, chemical and mineralogical compositions of the cement to be used.

In a research by Chaves et al., (2023) they established that the main chemical component of limestone is calcium carbonate, which undergoes thermal decomposition during cement manufacturing process to form calcium oxide (lime). Awadh and Al-Owaidi (2021) in line with the findings of Tyopine, (2014) pointed out that marl or clay and limestone are the two main ingredients of Portland limestone cement because they have major oxides that make them suitable.

3.0 Materials and Methods

Cement: The type of cement used in this research is Portland limestone cement produced by different manufacturers who sourced their raw materials for production from different locations. In line with the findings of Tyopine, (2014), limestone is readily available near cement factories, hence manufacturing companies source their raw materials basically limestone around their factory locations. Three different Portland limestone cements were used in this research, they include; Dangote cement Sample A, Bua cement Sample B and Elephant Superset cement Sample C. These Portland limestone cements from different manufacturers were bought from Building Materials Market Umuokpu in Awka, Anambra State. The Portland limestone cement Samples were classified as CEM II, grade 42.5N and are in conformity with BS EN 197-1 (2011) and ASTM C150 (2019). The samples were tested and analysed in line with standard specifications.

Fine Aggregates: Fine aggregate passing 4.75mm sieve was used for this research, it was sourced from River Niger in Onitsha, Anambra State Nigeria and labelled Sample 1. The fine aggregate met the specifications of BS EN 12620 (2018) and is in conformity with ASTM C33/C33M (2018). It was kept clean and dry to prevent bulking of aggregates.

Coarse Aggregates: Coarse aggregate passing 25mm sieve size was used for this research with an average size of 19mm. It was sourced from Ezza in Abakaliki, Ebonyi State, Nigeria. Sieve analysis test and specific gravity test were carried out in accordance with BS EN 12620 (2002) to determine the suitability of the material in concrete.

Water: The water used for mixing concrete in this research was clean, drinkable and free from impurities. It was sourced within the Concrete Laboratory at Nnamdi Azikiwe University, Awka. It was tested in conformity with BS EN 17075 (2018). The pH value of the water was 7.6.

Characterization of Cement Samples Using X-ray Fluorescence Test Method: An X-ray fluorescent (XRF) test, a non-destructive analytical technique used to determine the elemental composition of cement samples was carried out on the three samples of Portland limestone cement. In preparing the samples, each sample was crushed with an electric crusher and then pulverized for 60 seconds using Herzog Gyro-mill (Simatic C7-621). Pellets were prepared from the pulverized samples, first by grinding 20g of each sample for 60 seconds. After each grinding, the Gyro-mill was cleansed to avoid contamination. 1g of stearic acid was weighed into an aluminium cup to act as binding agent and the cup was subsequently filled with the sample to the level point. The cup was then taken to Herzog pelletizing equipment where it was passed at a pressure of 200KN for 60 seconds.

The X-ray fluorescent (XRF) Nitron 3000 was then powered on and allowed to stabilize for 5 minutes after initialization. The CU-Zn method was chosen which normally detect large number of elements and sesquioxides due to its intensity. Each 2mm pellet sample was placed on the sample holder of the X-ray equipment (Phillips PW-1800) for analysis. The ray point was placed over it and the ray button was pressed to start taking the data. The data were collected in triplicates and the average was automatically taken. This procedure was followed for all the X-ray fluorescent (XRF) test on samples to get the percentage chemical composition in oxide and elemental form.

The method that was used to determine the percentage of chemical composition in the three Portland Limestone Cement samples operates on the principles of atomic physics and quantum chemistry. During the process the samples were exposed to the entire spectrum of photons consisting of primary radiations emitted from a standard X-ray tube. The irradiated specimen caused the element in it to emit secondary fluorescence with their characteristics X-ray line spectra.

The energy and intensities of the emitted lines were determined by the detection system. This was made up of two units; the primary channel simultaneous wavelength dispersive spectrometer and the personal computer for control and data processing. The rapid detection system employs prepositioned (analyzing) crystal around the specimen. These caused the dispersion of the wavelength of the secondary radiation. The intensity of the individual wavelength is measured in a mass gas flow detector. The system allows simultaneous measurements of up to ten elements at peak and background positions. The output signals from the detector were fed into the analyzer, where the photon counts were stored in the computer memories. The count rate was calibrated for each element by comparing it to the count rate from a standard of accurately pre-determined composition. The spectra line energies of wavelengths of the emitted lines were used in the quantitative analysis of the element in the specimen. The intensities of the emitted lines were related to their concentration for quantitative analysis.

The samples were tested with X-ray fluorescence test machine at Allschoolabs scientific, a research laboratory company, which is located at Suite C1, God’s promise complex, Bells Drive Ota, Ogun State, Nigeria.

***Analysis on Concrete Materials*:** All the concrete materials used in this research were tested and analysed in accordance with the required standard specifications. The Portland limestone cement samples were tested for fineness using a BS sieve 90µm, a weighing balance of 0.01g sensitivity and a mechanical sieve shaker in accordance with BS EN 196-6, (2018). Sieve analysis and specific gravity tests were carried out on the fine and coarse aggregates to determine their suitability in concrete and right proportion to be used in mixing concrete and they proved adequate to be used in concrete.

***Concrete Mix*:** Concrete mix design was calculated in accordance with BS 8110: Part 1- (1985). The ratio of 1:1.83:3.39:0.522 was obtained for a concrete characteristic strength of 25N/mm^2. Concrete was batched, mixed, tested for slump and compacted in iron moulds using the following equipment; weighing balance, shovel, trowel, moulds, iron rod, clean containers and a measuring cylinder. The cubes were labelled A1, B1 and C1. A total of 36 cubes were produced, 12 cubes for each Portland limestone cement sample to be tested for compressive strength at 7, 14, 21 and 28days of curing. The average of three cubes were considered as the compressive strength for each curing age.

4.0 Results and Discussions

X-Ray Fluorescence Test Result for Samples

The key findings from the XRF test results for Samples A, B and C are presented in Table 1.

Table 1: Presents the Chemical Oxide Composition of samples A, B and C

No.	**Chemical Component**	**Chemical Formula**	**Weight Percentage Concentration**		
			Sample A	**Sample B**	**Sample C**
1.	Silicon Dioxide	SiO_2	8.694	12.418	9.516
2.	Aluminum Oxide	Al_2O_3	5.042	5.945	4.561
3.	Iron (III) Oxide	Fe_2O_3	3.676	3.735	2.836
4.	Calcium Oxide	CaO	77.171	70.326	74.178
5.	Sulfur Trioxide	SO_3	3.385	2.396	2.971
6.	Magnesium Oxide	MgO	0.00	2.229	3.124
7.	Potassium Oxide	K_2O	0.510	1.333	1.112
8.	Others	V_2O_5, MnO, Co_3O_4, NiO, CuO, Nb_2O_3, MoO_3, WO_3, Ta_2O_5, TiO_2, ZnO, Cl, ZrO_2 and SnO_2	1.522	1.618	1.702

Table 1 presents the chemical oxide composition of the Portland limestone cement samples A, B and C from the X-ray fluorescence test. Silicon Dioxide (SiO_2), Aluminum Oxide (Al_2O_3), Iron (III) Oxide (Fe_2O), Calcium Oxide (CaO), Sulfur Trioxide (SO_3), Magnesium Oxide (MgO) and Potassium Oxide (K_2O) are the main and essential chemical oxide composition of Portland limestone cement. They made up about 98.298% to 98.478% of the chemical oxide composition. It was observed that Sample A exhibits higher concentration of Calcium Oxide (CaO = 77.171%) and Sulfur Trioxide (SO_3 = 3.385%). Sample B exhibits higher concentration of Silicon Dioxide (SiO_2 = 12.418%) and Aluminum Oxide (Al_2O_3 = 5.945%). Sample C exhibits higher concentration of Magnesium Oxide (MgO = 3.124%). All these differences in chemical composition can affect the reactivity of the Portland limestone cements in concrete in slightly different ways. Translating the variations in chemical composition into real-world performances, higher concentration of SiO_2 and Al_2O_3 can impact the workability, setting time and contribute to overall durability and sulphate resistance of concrete. Higher CaO contribute effectively to the hydration process and early strength development of concrete while Fe_2O_3 influence color, setting time and early strength development of concrete. The results shows that different sources of raw materials for producing Portland limestone cements and the manufacturing processes of different Portland limestone cement factories may have contributed to the variations in oxide compositions of the different samples. It can also affect its performance in the workability, strength and durability of concrete. However, a careful investigation shows that some of the components are in close proportion and may likely give the same properties in concrete.

***Sieve Analysis Results*:** The sieve analysis results show that the fine aggregate and coarse aggregate used in this study are suitable for making concrete. For the fine aggregate, the coefficient of uniformity Cu is 2.5, and coefficient of curvature Cc is 1.15. Physical observations showed that the fine aggregate is densely graded and has wide range of sizes, low void content, low permeability and grain to grain contact. Air gaps are filled with finer particles. For the coarse aggregates the Coefficient of uniformity Cu is 1.88 and coefficient of curvature Cc is 1.44 suggesting a uniformly graded aggregate with narrow range of sizes and predominantly 19mm. The aggregates were tested in accordance with BS 12620 (2013) and met the specifications of ASTM C117 (2017). Figure 1 and Figure 2 presents the cumulative percent finer against sieve sizes. For the Portland limestone cement, Sample A has an average fineness index of 98.36%, Sample B 97.61% and Sample C 97.99%. Since the rate of hydration of concrete is increased with an increase in the fineness of the cement used, Sample B will give a faster hydration in concrete compared to samples A and C.

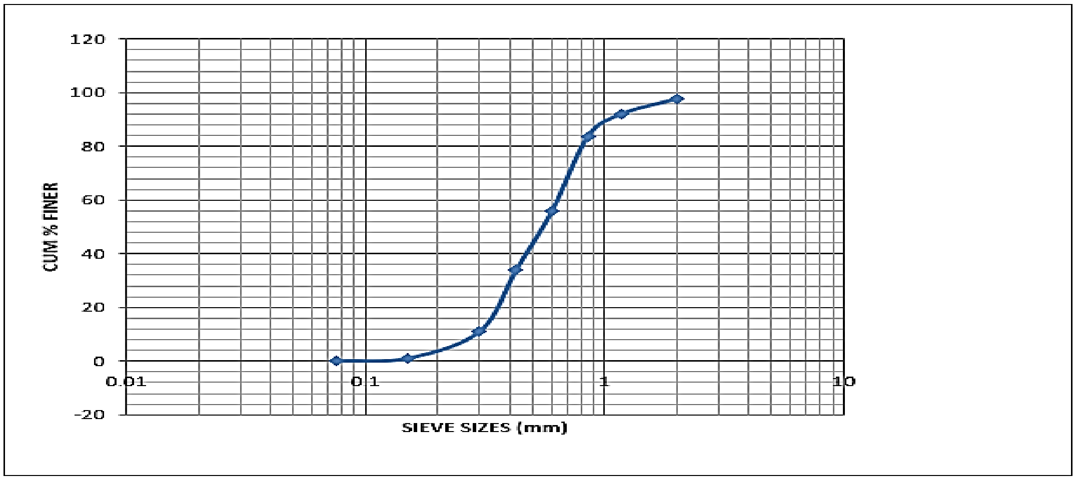

Figure 1 Gradation curve for fine aggregate

Figure 2 Gradation curve for Coarse aggregate

***Workability Test Result*:** Good workability in concrete mix shows that the concrete is easier to handle. All the concrete mix had a moderate slump value. A close investigation and analysis of the results revealed that sample B and sample C gave higher workability values than sample A. This may be due to the low percentage composition of Silicon Dioxide of Sample A compared to that of Samples B and C. It is believed that Silicon Dioxide impacts the workability, setting time and durability of concrete. The slump values for Sample A, Sample B and Sample C are; 46mm, 63mm and 59mm respectively and presented on Figure 3.

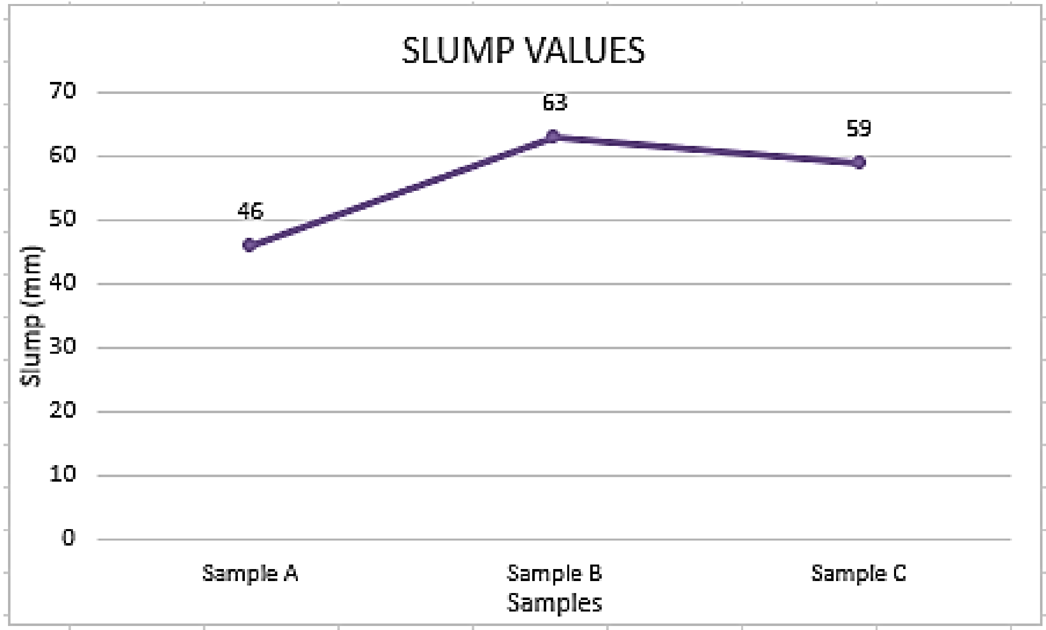

Figure 3 Slump Value Against Samples A, B and C.

***Compressive Strength Test*:** Compressive strength tests were conducted on the concrete cubes in conformity with the specifications of BS EN 12390-2 (2019). Three cubes were crushed for each sample at each curing age and the average taken as the compressive strength. Sample A gave 13.40N/mm^2, 23.03N/mm^2, 28.33N/mm^2 and 32.33N/mm^2 for 7, 14, 21 and 28days. Sample B gave 15.17N/mm^2, 24.40N/mm^2, 29.43N/mm^2 and 34.07N/mm^2 for strength at 7, 14, 21 and 28days. Sample C gave 14.67N/mm^2, 22.57N/mm^2, 26.93N/mm^2 and 31.3N/mm^2 for 7, 14, 21 and 28days. The test results are presented on Table 2. From the compressive strength result on Figure 4, it was observed that the compressive strength increases with an increase in curing age. This is as a result of the ongoing hydration process of cement which results to strength development. Again, the effects of the percentage composition of essential chemicals in Portland limestone cement can be seen in the strength of the concrete. All the concrete gave good compressive strength, which is due to their chemical composition. The differences between the compressive strength for the samples are negligible.

Table 2 Compressive Strength at 7, 14, 21 and 28 Days Curing Age

Samples	Fine Aggregate From River Niger Onitsha (Sample 1) Average Compressive Strength (N/mm^2)			
	7Days	14Days	21Days	28Days
A	13.40	23.03	28.33	32.33
B	15.17	24.40	29.43	34.07
C	14.67	22.57	26.93	31.30

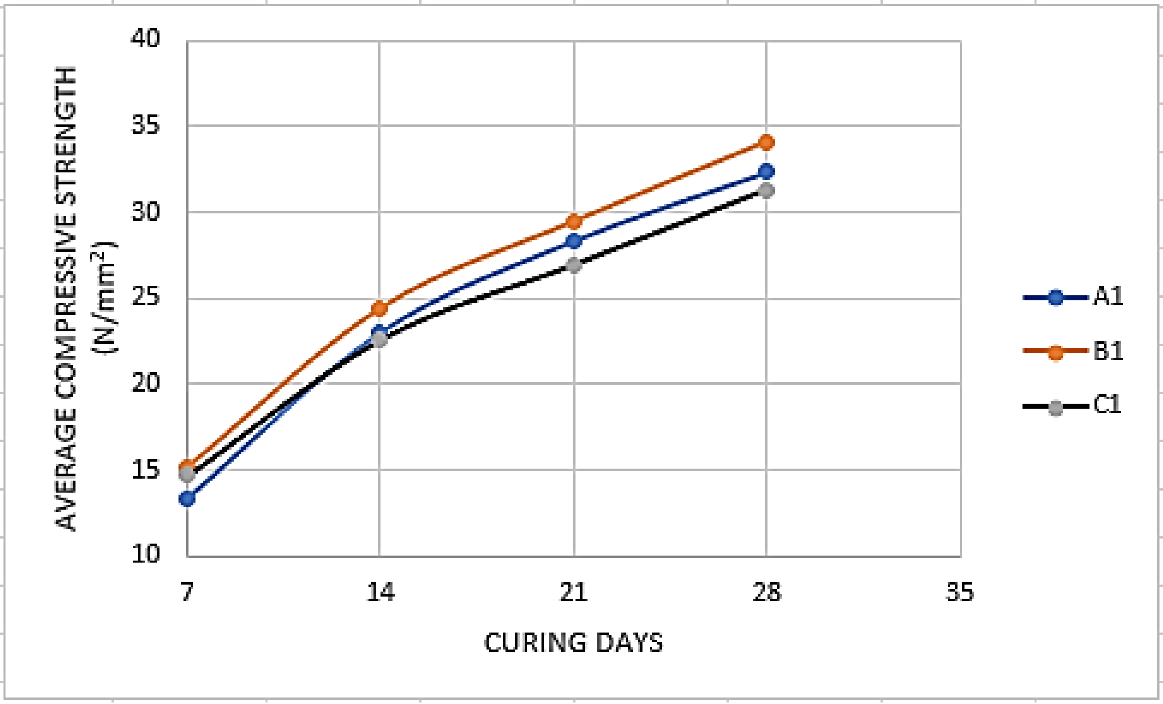

Figure 4 Average Compressive Strength against Curing Days

5.0. Conclusion

The effects of percentage composition of essential chemicals in Portland limestone cement on the strength and workability of concrete in this research can be concluded as follows;

1. CaO, SiO_2, Al_2O_3, Fe_2O_3 and SO_3 are the main chemical components of Portland limestone cement. They made up an average of 95.62% of the compositions. This is in conformity with the specifications of BS EN 197-1(2011).
2. The compressive strength of concrete is increased with an increase in the Silicon Dioxide (SiO_2) content (7% to 15%), Alumina Oxide (Al_2O_3) content, (4% to 7%) and Calcium Oxide (CaO) content (70% to 75%).
3. The three samples of Portland limestone cements due to their different percentage of chemical compositions, have different effects on the properties of concrete.
4. The strength of concrete cubes increases with an increase in the curing age.
5. Very fine Portland limestone cement increases the rate of hydration in concrete. Sample B has a finer particles compared to sample A and C. Though their difference in fineness is negligible.
6. The setting time of concrete is increase with an increase in the aluminium oxide (Al_2O_3) content and sulphur trioxide (SO_3) content.
7. The workability of concrete is also impacted by the chemical composition of Portland limestone cement.

In general, the differences in the chemical composition, fineness, workability and strength of the three samples of Portland limestone cement are negligible. This implies that one cannot necessary say a particular brand is better than another. This research has enlightened Engineers and professionals in the industry on the compositions and qualities to look out for when making their choice of Portland limestone cement depending on the type of construction. It has also pointed out the importance of continuous and frequent assessment of the qualities of Portland limestone cement used for construction.

6.0 Recommendation

In line with the findings and objectives of this research work, the researchers recommends the following to improve the quality and safety of construction materials and practices:

1. A strict and quality control system for construction materials, including Portland limestone cement and fine aggregates should be implemented to monitor and test these materials to ensure they meet established standards for chemical composition, physical properties and performance characteristics. Relevant regulatory bodies should ensure certification of construction materials to meet specified standard for use.
2. Engineers should consistently source their construction materials from reputable suppliers or specific locations with proven and known quality, to reduce the risk of variability in material quality.

References

Abdulhakeem, S. 2023. *Physicochemical and strength assessment of Portland limestone cement in Nigeria*. A Preprint on *Resaerch Square*. ISSN 2693-5015. Available: https://doi.org/10.21203/rs.3.rs-3195665/v1

Araromi, D.O. Odewale, S.A. and Hamed, J.O. 2015. *Neuro-fuzzy modelling of blending process in cement plant. Advances in Science and Technology Research Journal* 9 (28), 27–33. Available: http://doi.org/10.12913/22998624/60779

ASTM C117(2017. *Standard test methods for materials finer than 75-μm (No. 200) Sieve in mineral aggregates* by Washing. *American Society for Testing and Materials*

ASTM C150/C150M. 2019. *Standard specification for Portland cement. American Society for Testing and Materials.*

ASTM C33/C33M 2018. *Standard specification for concrete aggregates. American Society for Testing and Materials.*

Awadh, S. M. and Al-Owaidi, M. 2021. *Designing raw mix for manufacturing Portland cement using Euphrates Formation Marl Instead of Clays. Iraqi Geological Journal*, 54 (2D), 87-97, 2021 https://www.igj-iraq.org

Bamigboye, G. O., Ede, A. N., Egwuatu, C., Jolayemi, J. Olowu, O. and Odewumi, T. 2015. *Assessment of compressive strength of concrete produced from different brands of Portland cement. Journal of Civil and Environmental Research*, 7(8), 21-27.

BS EN 12390-2 2019. *Testing hardened concrete compressive strength of test specimens. European Standards*.

BS EN 12620 2002 *Aggregates for concrete. British Standard Institute*.

BS EN 12620 2013 *Aggregates for concrete. British Standard Institute*.

BS EN 17075 2018. *Water quality -general requirements and performance test procedures for water monitoring equipment – measuring devices. British Standard Institute*.

BS EN 197-1 2011. *Composition, specifications and conformity criteria for common cement. British Standard Institute.*

BS 8110 Part 1 1985. *Structural use of concrete. British Standard Institute*.

Chaves, J.F.N., Junior, F.E., Rego, J.H.S., and Vasques, L.P. 2023 *Dataset construction and data science analysis of physicochemical characterization of ordinary Portland cement. IBRACON Structures and Materials Journal*, vol. 16, no. 6 el6609 2023. https://doi.org/10.1590/S1983-41952023000600009

Dinh, N. D., and Truong, P. V. 2022. *Effects of limestone content on properties of Portland limestone cement produced by inter grinding. Journal of Materials and Construction*, 12(01). https://doi.org/10.54772/jomc.v12i01.333

Ikumapayi, C. M. & Alamu, O. F. (2022). *Compressive strength and thermogravimetric analysis of Metakaolin Blended Cement. FUOYE Journal of Engineering and Technology*, 7(2), 2579-0627. ISSN: 2579-0617, https://doi.org/10.46792/fuoyejet.v7i2.835

Marvillet, C., and Benboudjema, F. (2019). *Literature review on Portland limestone cement. Performance and Sustainability Materials.* 12(4), 575-583

Obi, K.O. and Adinna O.B. (2023). *Strength and workability of concrete with inclusion of flyash, quarry dust and a generic naphthalene-based superplasticizer. Fuoye Journal of Engineering and Technology*. 8(1) 115 – 119. https://doi.org/10.46792/fuoyejet.v8i1.984 30th March, 2023.

Tyopine, A.A. (2014). *Lyses of some cement brands in the Nigeria market and optimization of limestone content of limestone composite Portland Cement. PhD Dissertation, Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka.*