DEVELOPMENT OF HIGH-PERFORMANCE CONCRETE FROM METASTABLE CALCINED CLAY AND RICE HUSK ASH WITH SUPERABSORBENT POLYMERS

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17PCB01679

MARCH, 2022

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY (Ph.D) IN BUILDING TECHNOLOGY (BUILDING STRUCTURES) IN THE DEPARTMENT OF BUILDING TECHNOLOGY, COLLEGE OF SCIENCE AND TECHNOLOGY, COVENANT UNIVERSITY, OTA, OGUN STATE, NIGERIA

MARCH, 2022

ACCEPTANCE

This is to attest that this thesis is accepted in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Building Technology (Building Structures) in the Department of Building Technology, College of Science and Technology, Covenant University, Ota, Nigeria

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Prof. Akan B. Williams
(Dean, School of Postgraduate Studies) **Signature and Date**

DECLARATION

I, **NDUKA, DAVID OBINNA (17PCB01679),** declare that this research was carried out by me under the supervision of Prof. Olabosipo I. Fagbenle and Dr. Babatunde J. Olawuyi of the Department of Building Technology, College of Science and Technology, Covenant University, Ota, Nigeria and Department of Building, School of Environmental Technology, Federal University of Technology, Minna, Niger State, Nigeria, respectively. I attest that the thesis has not been presented either wholly or partially for the award of any degree elsewhere. All sources of data and scholarly information used in this thesis are duly acknowledged.

NDUKA, DAVID OBINNA

Signature and Date

CERTIFICATION

We certify that this thesis titled **"DEVELOPMENT OF HIGH-PERFORMANCE CONCRETE FROM METASTABLE CALCINED CLAY AND RICE HUSK ASH WITH SUPERABSORBENT POLYMERS"** is an original research work carried out by **NDUKA, DAVID OBINNA (17PCB01679)** in the Department of Building Technology, College of Science and Technology, Covenant University, Ota, Ogun State, Nigeria under the supervision of Prof. Olabosipo I. Fagbenle and Dr. Babatunde J. Olawuyi. We have examined and found this work acceptable as part of the requirements for the award of Doctor of Philosophy (Ph.D) degree in Building Technology (Building Structures).

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DEDICATION

I wholeheartedly dedicate this thesis to the Almighty Jehovah for his manifold wisdom, sound mind, guidance, strength, and healthy life bestowed on me throughout this study and beyond according to His eternal purpose.

ACKNOWLEDGEMENTS

To faithful God alone be all glory, adoration, praise and honour, the author and finisher of my life, who has endowed me to accomplish this great feat in life and career. The journey of this research began with divine inspiration. He guided me and shaped my understanding of how natural and industrial by-products have been wasted and created environmental hazards with ideas for recycling for sustainable product development. I am sincerely grateful to Him.

I most reverentially acknowledge our dear father, the Chancellor and Chairman of the Board of Regents, Covenant University, Dr. David O. Oyedepo, whose vision and values provided a blossoming platform to fulfil my career. I also sincerely acknowledge the Covenant University management team led by our amiable Vice-Chancellor, Prof. Abiodun H. Adebayo, for his drives toward the actualisation of the 1-of-10-in-10 mandate and for putting policies and strategies in place which gave birth to this research. I equally express my profound gratitude to the Registrar, Dr. Oluwasegun P. Omidiora, for his support and contribution to the drive of the University's **CORE VALUES** and the vision 10-2022 mandate. I truly appreciate the Dean, School of Postgraduate Studies (SPS), Prof. Akan B. Williams, and the Sub-Dean SPS, Dr. Emmanuel O. Amoo, for their unalloyed support and contribution at various levels of this research. I would like to appreciate the Dean, College of Science and Technology, Prof. Temidayo V. Omotosho and the Head of Department, Building Technology, Prof. Olabosipo I. Fagbenle, who also doubles as my main supervisor. Words are inadequate to expatiate how grateful I am to you, Sir. Your unwavering work, quality mentorship, unceasing encouragement, germane ideas and unflagging follow-up in the course of this research was apposite in birthing this output.

My unfathomed gratitude goes to the indefatigable co-supervisor, Dr. Babatunde J. Olawuyi, for his detailed inputs in this study. Cognisant of note is the sacrifices made at travelling down from Minna, Niger State, to guide the laboratory works and at the various stages of oral presentations. I recognise the help of Prof. Timothy O. Mosaku, the first appointed main supervisor, who bowed out of the teaching and research service of the University with joy after he meritoriously reached the age criteria for a professor. Sir, you helped me find my footing as I started this process. May God continue to renew your strength and pour His unstoppable blessings on you. Many thanks to Covenant University Centre for Research, Innovation, and Development (CUCRID), headed by Prof. Emeka E. J. Iwela for the Seed Grant offered me to complete the advanced quantitative analyses of the study samples. Finally, my sincere gratitude goes to Dr. Belén G. Fonteboa, who accepted me as a visiting researcher to undertake my benchwork at the University of A Coruña, Spain. Although the trip was aborted due to the Covid-19 pandemic yet, your interest in my research and willingness to cooperate to achieve a measure of success is commendable.

I am grateful for the vital input and contribution to this research by the former Heads of Building Technology Department, Dr. James D. Owolabi and Asso. Prof. Lekan M. Amusan. In the same vein, I cannot but express my sincere appreciation to the members of the Postgraduate Committee in the Building Technology Department for their timely response and action at various stages of this research. My inestimable thanks go to the College of Science and Technology Postgraduate Coordinator, Prof. Oluwatayo A. Adedapo and the past and present Building Technology Department Postgraduate Coordinators, Dr. Ignatius O. Omuh and Dr. Patience F. Tunji-Olayeni and all other Faculty and Staff of the Building Technology Department for their innumerable support and painstaking contribution to this research. I especially want to thank Dr. Opeyemi O. Joshua, who provided invaluable contact for the co-supervisor. Your encouragement to write this thesis made me confident that the topic was worthy of investigation. Also of note are the suppliers of the superplasticiser- Masterglenium Sky 504 by BASF Limited, West Africa facilitated by Mr. Adesola Mofikoya; superabsorbent polymers by SNF Floerger-ZAC de Milieux, France and Dr. Charles C. Osadebe of Nigerian Building and Road Research Institute (NBRRI), Ota who expediated the release of 100 mm metal concrete cubes. The technical assistance of the laboratory staff at the Departments of Building Technology, Civil Engineering, Chemical Engineering, Petroleum Engineering and Chemistry, Covenant University is highly appreciated.

Furthermore, I wish to express my profound gratitude to my precious late parents, Mr. & Mrs. Philemon and Martina Nduka; your fathomless love and desire for me to succeed in life, particularly in education, yielded this accomplishment. Continue to rest in the Lord until we meet to part no more, Papa and Mama. My heartfelt gratitude goes to my siblings, especially my only brother, Mr. Levi Nduka. He had unconditionally supported and protected me in every decision I made in life since I was young. My other siblings and their husbands, Mr. & Mrs. late Maurice and Chinyere Philip, Mr. & Mrs. Paschal and Oluchi Onyekachi, Mr. and Mrs. Julius and Ifeoma Raphael, Mr. & Mrs. Anslem and Ngozi Nyeaka, Mr. & Mrs. Chigozie and Chinenye Alaegbu, Rev. & Dr. (Mrs.) Kingsely and Onyinyechi Onuoha and Ms Osinachi Nduka, your enormous sacrifices to see me climb the ladder of life successfully are worthy of thanks. I am proud of you all at all times of my life. Finally, thankfulness goes to my wife - Ezinne and children - Darrel, Donald, and Davina, for your understanding when I had to share the attention I ought to give to you all with my research work. Without your support, love, and prayers, this thesis would not have been accomplished. God bless you all richly. To God alone be all the glory here on earth and beyond forever and ever. Amen.

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LIST OF SYMBOLS

$\propto_c$	Degree of hydration of binder
$\propto_{max}$	Ultimate degree of hydration
$f_{c,cube}$	Cube compressive strength (N/mm^2)
$f_{c,cube28}$	28th day cube compressive strength (also known as f_c28)
f_c,cyl	Cylinder compressive strength (N/mm^2)
$K_{Bolomey}$	Material constant given by the Bolomey's formula (A)
Rc_{28}	Compressive strength of standard mortar after 28 days of curing (N/mm^2)
V_m	Total surface area of the solid phases is related to the computed cement composition
X_{pc}	Gel-space ratio of the HPC mortar paste
$dmax$	Maximum size of aggregate
f_c	Characteristic strength obtained (also known as fck) - (N/mm^2)
f_{cm}	Mean cylinder compressive strength (N/mm^2)
f_{cr}	Target strength at maturity (often 28 days) - (N/mm^2)
$f_{ct.fl}$	Flexural tensile strength
$f_{ct.sp}$	Splitting tensile strength
f_{ctk}	Characteristic tensile strength
f_{ctm}	Mean value of tensile strength (N/mm^2)
vc	**S**pecific volume of anhydrous binder (i.e., binary or ternary)
wn	Non-evaporable water
ρ_c	Relative density of the cementitious material
B	Second material constants by Bolomey
σ	Standard deviation
n	Porosity

ABBREVIATIONS

ACI	American Concrete Institute
ACV	Aggregate crushing value
AEC	Architecture, Engineering, and Construction
AFS	Acetone formaldehyde sulphide
AGS	Autogenous shrinkage
AIV	Aggregate impact value
Al-MAS-NMR	Nuclear magnetic resonance spectroscopy
ASTM	American Society for Testing and Materials
BET	Brunauer–Emmett–Teller
b_{wob}	by weight of binder
b_{woc}	by weight of cement
BSI	British Standard Institute
$Ca(OH)_2$	Calcium hydroxide
$CaCl_2$	Calcium chloride
Cc	Coefficient of gradation
CEM I	Cement type I
CEM II	Cement type II
CO_2	Carbon dioxide
CS	Chemical shrinkage
C-S-H	Calcium-silicate-hydrate
Cu	Coefficient of uniformity
D_{10}	Cumulative 10% passing

D_{50}	Cumulative 10% passing
D_{90}	Cumulative 90% passing
EDX	Energy Dispersive X-ray
FA	Fly ash
FHWA	Federal Highway Administration of United States Department of Transport
FM	Fineness modulus
FTIR	Fourier Transmission Infra-red Spectroscopy
GGBS	Ground granulated blast-furnace slag
GHG	Greenhouse gases
HCL	Hydrochloric acid
HDC	High-durability concrete
HES	High early strength
HESC	High-early strength concrete
HPC	High-performance concrete
HPM	High performance mortar
HSC	High strength concrete
HVFA	High-volume fly ash concrete
IC	Internal curing
IC-agent	IC agent
ICP-MS	Inductive coupled plasma spectrometry
LOI	Loss on ignition
LWA	Lightweight aggregates
MCC	Metastable calcined clay

MIP Mercury Intrusion porosimetry

MK Metakaolin

Na_2SO_4 Sodium sulphate

NBRRI Nigerian Building and Road Research Institute

NSC Normal strength concrete

PC Portland cement

PCE Polycarboxylate Ether

pH Power of hydrogen (it has a numeric value defined as a negative base 10 logarithm of the molar concentration of hydrogen ions). This is a measure of acidity (< 7) and alkalinity (> 7).

PMS Melamine sulfonate

PNS Poly (naphthalene sulfonate)

PR penetration resistance

PSD Particle size distribution

RH Relative humidity

RH_7 Factor Rate of hydration based on 7th-day degree of hydration for reference mixtures

RHA Rice husk ash

RPC Reactive powder concrete

SAP Superabsorbent Polymers

SCC Self-consolidating concrete

SCM Supplementary cementitious materials

SCMs Supplementary cementitious materials

SDGs Sustainable Development Goals

SEM	Scanning Electron Microscopy
SF	Silica fume
SFRHPC	Self-compacting Fibre Reinforced High-Performance Concrete
SHRP	Strategic Highway Research Programme
SPSS	Statistical Package for Social Sciences
t_1	Early age at the time of one-day curing
t_d	Early age duration of curing after casting taken as greater than 1 and up to day 10
UHPC	Ultra-high-performance concrete
VES	Very early strength
VHS	Very high strength
W	Mixing water
W/B	Water: binder ratio
W/C	Water: cement ratio
WA	Water absorption capacity
XRD	X-ray diffraction
XRF	X-ray fluorescence

ABSTRACT

The research was conducted to determine the potential use of metastable calcined clay (MCC) as a supplementary cementitious material (SCM) in a binary binder for high-performance concrete (HPC) production. The attractive properties of calcined clay based on literature have influenced an SCM choice in concrete production. Therefore, to improve the performance of the structural elements regarding increasing height, span length, and load, a thermally activated MCC of Nigerian origin gave a point of view to more investigation and compared with rice husk ash (RHA). Different HPC mixtures at 5-30% with MCC or RHA content of cement replacements of five steps intervals were produced with superabsorbent polymers (SAP) introduced as an internal curing agent. The water-binder ratio (W/B) of all the mixes was kept constant at 0.3 while Masterglenium Sky 504, a polycarboxylate ether-based superplasticiser (PCE), was used to improve the HPCs workability. To obtain the properties of the cementitious materials, the chemical composition, mineral phases, morphology, calcination efficiency, and physical properties were quantitatively analysed using the advanced techniques of X-ray fluorescence (XRF), scanning electron microscopy/energy dispersive x-ray (SEM/EDX), X-ray diffraction (XRD), Fourier transform infrared/Attenuated total reflection (FTIR/ATR), Thermogravimetric analysis (TGA), laser particle sizing and Brunauer–Emmett–Teller (BET) nitrogen absorption method. The MCC's effect on the workability, early-age degree of hydration, early-age compressive strength, hardened mechanical properties (compressive, splitting tensile and flexural strengths), durability (water absorption, sorptivity, and chemical attack), and microstructure (morphology and crystalline phases) of hardened MCC based HPCs samples were determined. The determined early-age compressive strength of HPC mortar was further curve-fitted into Powers' model to assess the relationship between compressive strength and gel/space ratio. All the properties of HPCs containing MCC were compared to those of PC mixes. The XRF result shows that the chemical oxide composition of MCC confirmed the pozzolanic material requirements with recorded high useful oxides content. At the same time, the SEM image presents particles of broad, solid masses with a wider surface area of irregular shape. The XRD results show that the MCC was a major illite-based clay mineral calcined at a maximum temperature of 650 ℃, as revealed by the TGA. The MCC addition increases the slump flow of HPCs at certain cement replacement with a comparative early-age compressive strength with the control. The MCC incorporation at 10% cement replacement best improved the porosity of HPCs at a later age resulting in increased mechanical, durability, and microstructural properties of tested samples. A simulation of MCC and RHA contents into the Powers' model signalled compatibility for predicting strength development trends in the HPC with SAP. The study has shown that MCC and RHA, which are locally sourced, can be used to produce Class I (50 – 75 MPa) HPC with enhanced mechanical, durability and microstructural properties. Therefore, it is recommended that MCC addition within 10% binder content be adopted for low W/B Class I HPC at no deleterious results on mechanical and microstructural properties of the concrete.

Keywords: High-performance concrete, metastable calcined clay, rice husk ash, superabsorbent polymers, supplementary cementitious materials, Sustainable Development Goals 9,12 and 13