INDUSTRIAL AND GEOLOGICAL STUDY OF PROTOZOIC METACARBONATE ROCKS FROM SOUTHERN AND CENTRAL NIGERIA

by

JIMOH ABDULLATEEF ONIMISI

Thesis submitted in fulfilment of the
requirements for the degree
of Doctor of Philosophy

November 2017

ACKNOWLEDGEMENTS

Special thanks to my family: my late mother, Salamat Oyiza Momohjimoh, my father, Momohjimoh Audu Onipe, for their continual and unwavering support throughout my academic journey. I humbly thank my beloved wife, Mariam Abdullahi and my son, Amir Ohinoyi Abdullateef and my daughter, Salma Oyiza Abdullateef for their patience, understanding, sacrifice, support and prayers throughout my programme.

I would like to express my sincere thanks to my main supervisor, Prof Madya Dr. Kamar Shah Ariffin for his help, advise, guidance constructive criticism and valuable suggestion during my research, and also my co-supervisor, Prof Madya Dr Hashim Hussin for his generous assistance and kind support.

Also, my sincere appreciation to Prof Zuhailawati Hussain (the Dean), management and the entire staff in the School of Materials and Mineral Resources Engineering for their support and assistance. Gratitude is also expressed to Okoye Ugochukwu Patrick for his assistance in the research work.

Furthermore, a special acknowledgement is given to Federal University Lokoja for giving me study leave with full pay.

Lastly, I would like to thank all my friends who helped me directly or indirectly in making my stay in USM an exciting and memorable experience.

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LIST OF ABBREVIATIONS

ACC	Amorphous calcium carbonate
ASTM	American Society of Testing and Materials
BET	Brunauer, Emmet, Teller
CMCS	Carboxymethyl chitosan
CTAB	Cetyl trimethylammonium bromide
DDS	Dodecyl sulfonate
DDTAB	Dodecyltrimethylamonium bromide
DTA/TGA	Differential/Thermogravimetric Analysis
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive X-ray
FGCC	Fine grounded calcium carbonate
FTIR	Fourier Transform Infrared Spectroscopy
GCC	Grounded calcium carbonate
GTE	Green Tea Extract
HCL	Hydrochloric acid
HDPE	High-density polyethylene
IR	Infra-red
KBr	Potassium Bromide
LOI	Loss on Ignition
MOL	Milk of Lime
PAA	Poly acrylic acid
PAAM	Polyacrylamide
PCC	Precipitated Calcium Carbonate
PDDA	Poly-diallyldimethylammonium –chloride
PEO	Polyethylene oxide

PIPAAM	Poly-N-isopropyl acrylamide
PP	Polypropylene
PSA	Particle Size Analysis
P-SA	Poly-2-acrylamido-2-methyl-propane sulfonic acid
PVA	Polyvinyl alcohol
PVP	Poly (N-vinyl-pyrrolidone)
SDS	Sodium dodecyl Sulfate
SEM	Scanning Electron Microscopes
SLS	Sodium lignosulfonate
SMI	Speciality Mineral Inc.
TMA	Thermomechanical analyzer
XRD	X-Ray diffraction
XRF	X-Ray fluorescence
ZnCl	Zinc chloride

LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
CO_2	Carbon dioxide
$CaCO_3$	Calcium Carbonate
$MgCO_3$	Magnesium carbonate
$Ca(OH)_2$	Calcium hydroxide
$Mg(OH)_2$	Magnesium hydroxide
H_2O	Water
D_{10}	10% volume of particles with size value lower than or equal to D_{10}
D_{50}	50% volume of particles with size value lower than or equal to D_{50}
D_{90}	90% volume of particles with size value lower than or equal to D_{90}
L	Litre
Wt%	Weight percentage
ml	millilitres
M	Mole
aq	Aqua solution
s	Solid
g	gas

KAJIAN INDUSTRI DAN GEOLOGI UNTUK BATUAN METAKARBONAT PROTOZOIK DI SELATAN DAN TENGAH NIGERIA

ABSTRAK

Mendapan metakarbonat di selatan Nigeria terbentuk berselang lapis dengan batuan gneiss kalk-silikat dan gneis magmatit berusia Proterozoik. Kajian ini memberi tumpuan kepada penilaian kesesuaian mendapan metakarbonat Okpella dan Emiworo bagi aplikasi industri dengan merujuk kepada pencirian dan proses pensintesisan bahan. Kajian ini dilaksana menggunakan teknik Pembelauan Sinar-X (XRD), Mikroskop Pengimbas Elektron (SEM), Mikroskop cahaya biasan, terkutub, analisa kimia, pembezaan terma/ analisis terma gravimetrik (DTA/TGA) dan juga sifat-sifat fizikal dan kimia dari sampel-sampel batuan metakarbonat berkenaan. Kalsit adalah fasa mineral utama manakala silika adalah komponen sampingan dalam batuan kapur Okpella ini. Batuan kapur Okpella ini mempunyai cirian seperti serapan air yang rendah, kekuatan mampatan, kadar kehilangan pembakaran dan nilai graviti tentu yang baik. Kapur tohor yang dikalsin pada suhu 900 °C, 1100 °C adalah tidak reaktif selepas masa rendaman 60, 90 dan 120 minit. Kapur tohor yang dikalsin pada suhu 1000 °C mempamerkan kereaktifan yang tinggi. Sebaliknya, kajian fasa mineral untuk batuan Emiworo menunjukkan dolomit adalah fasa mineral utama bersama mineral silikat sebagai fasa sampingan. Kapur tohor yang diukur selepas pengkalsinan pada suhu-suhu berbeza, menunjukkan kapur tohor yang dihasil pada suhu 950 °C dan 1000 °C selama 1 jam adalah lebih reaktif. Perbandingan data menunjukkan Emiworo mempunyai kadar serapan air, kekuatan mampatan, kadar kehilangan pembakaran dan graviti tentu pukal yang lagi rendah berbanding batuan metakarbonat Okpella. Batu kapur ini mempunyai ciri-ciri yang dapat memenuhi permintaan industri bertepatan disebabkan oleh mikrostruktur, komposisi kimia dan perguraian yang baik dari batu tersebut. Ekstrak Lidah buaya (*Aloe vera*) telah diguna dalam penghasilan kalsium karbonat melalui kaedah mendakan, dan didapati boleh menpengaruhi ciri-ciri Morfologi,

saiz partikel, struktur hablur dan ciri-ciri terma partikal PCC yang disentisis dalam kajian ini. Dengan menggunakan reaktor berbentuk tubular secara aliran berterusan pada suhu bilik (*ambient*) dan kadar aliran gas karbon dioksid 1 liter/minit, polimorf kalsit rombohedron dan komposit polimorf aragonit dengan struktur polikristakin seakan bentuk loceng, dengan hujung bercabang telah dihasilkan daripada Batu marmar Okpella. Selain itu, PCC aragonit " hierarchical" bertingkat bersaiz nano telah dihasilkan menggunakan dolomit Emiworo semulajadi. Pengaruh negatif Mg terhadap ketulenan PCC yang dihasilkan telah diatasi dengan penyingkiran unsur kalsium dolomit menggunakan ekstrak D-glukos.

INDUSTRIAL AND GEOLOGICAL STUDY OF PROTOZOIC METACARBONATE ROCKS FROM SOUTHERN AND CENTRAL NIGERIA

ABSTRACT

The metacarbonate deposits in the southern Nigeria intercalated with calc-silicate gneiss, intrusive granite and migmatite gneiss rocks are of Proterozoic age. The study focused on examining the suitability of the Okpella and Emiworo metacarbonate via characterization and synthesis for industrial applications. This study is based on X-ray Diffractometry (XRD), Scanning electron microscopy (SEM), polarizing and refracted light microscopy; chemical and differential thermal analysis/thermal gravimetric analysis (DTA/TGA) and also the physical properties of the raw marble resources and derived product. Calcite is the dominant phase while silica is the subordinating component of Okpella marble. The Okpella metacarbonate characterized by minimal water absorption, appreciable compressive strength, high loss of ignition (LOI) and bulk specific gravity (SG). The quicklime calcined at 900°C and 1100°C for 60, 90 and 120 minutes of soaking time were unreactive. However, the quicklime calcined at 1000°C exhibited high reactivity. On the other hand, the phase characteristics of the Emiworo marble show that dolomite is the dominant mineral with low silicates. Reactivity of the quicklime measured after calcination at different temperatures revealed that only the quicklime produced in 1 hour at 950°C and 1000°C was found to be more reactive. Physical properties and comparative data show that the Emiworo marble displays lower water absorption, lower compressive strength, and higher loss on ignition compared to the Okpella marble. The marble has affluent industrial applications characteristics attributed to its established microstructure, chemical composition and thermal decomposition behavior. Aloe-Vera extract was found to have an effect on the precipitated calcium carbonate (PCC) morphology, particle sizes, and thermal characteristics of the synthesized PCC. Utilizing a continuous unique tubular reactor under ambient temperature and 1 L/min CO_2 flowrate, rhombohedral calcite

polymorph and aragonite polymorph composite with polycrystalline dumb bell-like structure, having radiating ends was produced from Okpella marble. However, uniform hierarchical aragonite precipitated calcium carbonate stacked from nanoparticles was synthesized using a natural occurring Emiworo dolomite. The tainted Mg influence on resultant PCC purity was averted via D-glucose extraction of dolomite constituent.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

The chemical composition and purity of Proterozoic metacarbonate rocks (marble), require adequate consideration to know its quality. This will determine its commercial application in terms of construction, plastics paints, cosmetics, rubber and pharmaceutical items among others. Marbles are generally considered as metamorphosed limestone or dolostone depending on the recrystallization settings (Max, et al., 2017; Zsolt et al., 2016), they are from the aggregate of calcite minerals, and/or aragonite and quartz crystal grains. Precipitated calcium carbonate (PCC) are normally derived from metacarbonate and carbonate-rich rocks.

PCC is a bright white synthetic calcium carbonate in its purest form characterized by unique crystal morphology, shape, and size (texture). They are utilized mostly as functional fillers in plastics, papers, adhesives, inks, pharmaceuticals, rubber, nutritional supplements, and cosmetics. PCC find widespread application as additives in many industries that depends mostly on their purity or chemical content. Therefore, prior concise chemical characterizations are necessary before any industrial application. PCC is a value added product (in high demand), due to its wide applications in industries such as paper, paint, textile, detergents, adhesives, rubber, plastics, magnetic recordings, electronics, ceramics, polymer composites, foods, cosmetics, detergent, biomaterials etc. (Zhang et al., 2012).

1.2 Global Consumption of Precipitated Calcium Carbonate (PCC)

There are different types of PCC morphology and particle sizes, each of which possesses different properties. Thus, PCC can be marketed in more than one grade by varying the particle size, particle size distribution, surface area, and particle morphology. Compared to ground calcium carbonate (GCC), PCC has better physical properties, including high brightness, opacity, and purity (Towler and Sinnott, 2012). PCC has internal porosity and a higher specific area, together with a very good chemical absorption and binding performance. However, PCC has a high degree of aggregation, with several crystals growing together forming a single particle. Particle size distribution is also more uniform than with GCC, providing smoothness and low abrasion (Declet et al., 2016). A high standard of technical knowledge is crucial in being able to produce PCC of consistently high quality. However, PCC finds it difficult to achieve the > 70% solids coating slurries requirements and rheological behaviour of PCC is more difficult to control. This is due to the high amount of PCC ratio required for filler use.

The adhesive and sealant usage incorporate a wide range of products extending from household caulks to joint cement compounds and carpet backings. The use of PCC accounts for about 5% of total coating collective usage (Bajpai, 2015).

Asia is by far the highest regional world consumer of FGCC and PCC. China tops the world in FGCC usage, with about 26% of entire FGCC consumption, trailed closely by the United State of America, with about 25%. Asia is also the world's major consumer of PCC, China accounts for over half of global PCC consumption. The United States is also the second-largest PCC consumer, with 16%, with just a little beneath 13% Western Europe (the largest consumer). However, in 2013, PCC demand

by papermaking industries in Western Europe accounted for roughly 85% of overall demand (Bajpai, 2015). The paper industry has remained the driving force behind the growth of PCC market, as shown in Figure 1.1. The impending growth of PCC in Europe rest on the capacity of new PCC on-site plants, which can be cost-competitive with fine ground calcium carbonate producers**.** In Malaysia, PCC production is limited to Schaefer Kalk (M) Sdn Bhd and Specialty Minerals Malaysia Sdn. Bhd. They produce a capacity equivalent of 50,000 and 25,000 to 35,000 tons of PCC manufactured annually respectively. This is estimated to be at 0.08% of the global PCC consumption (Thenepalli, 2015)

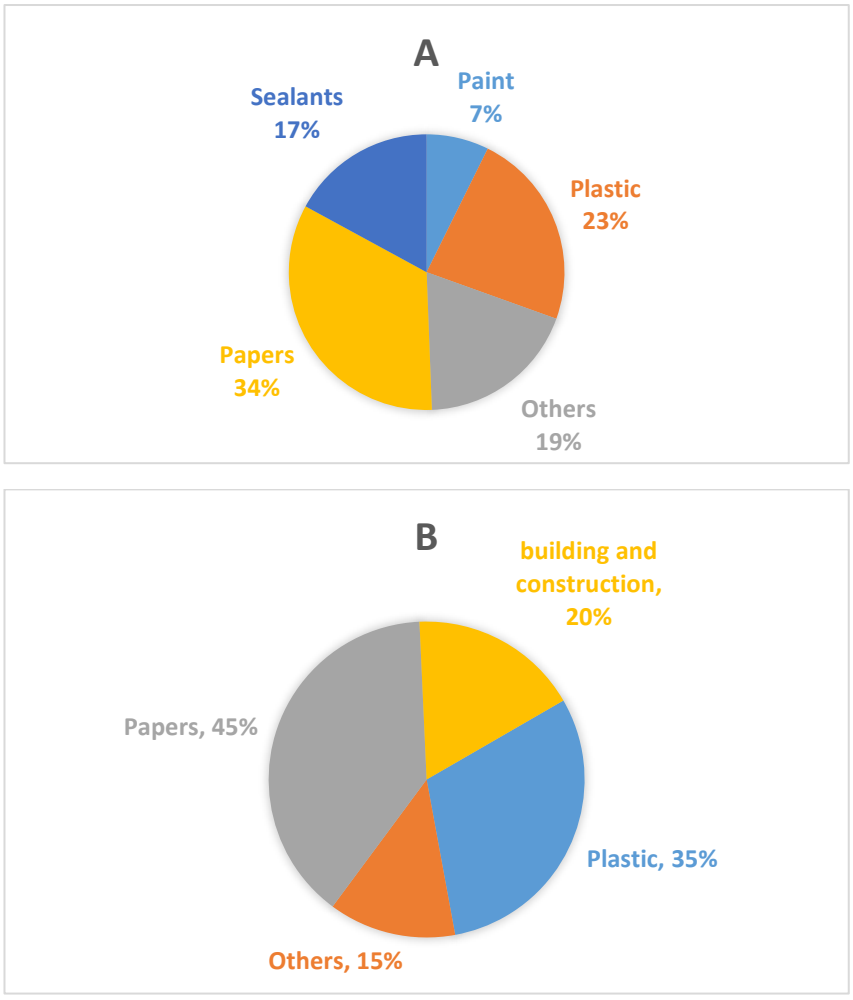

Figure 1.1: Global consumption of GCC and PCC by market (a) 2011 (b) 2012 (adapted from Stratton, 2012).